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Arindam Sinharoy
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Renewable Energy Technologies for Energy Efficient Sustainable Development

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Contents

Part I Process Fundamentals

Part II Pretreatment

Part III AD of Specific Waste-Streams

Part IV Downstream Processing for Resource Recovery

Part V Integration of AD in Biorefineries

Part VI Life Cycle Analysis

Part I
Process Fundamentals

Chapter 1
Fundamentals of Biofuel Production Using Anaerobic Digestion: Metabolic Pathways and Factors Affecting the Process

Adriana Ferreira Maluf Braga and Marcelo Zaiat

Abstract The need for a change in the global energy matrix from a fossil fuel based to a renewable energy one is critical for sustainable development. In this context, biofuels from anaerobic digestion of agro-industrial waste and wastewater, i.e., biohydrogen and biomethane, represent an attractive option. The dark fermentation process for biohydrogen production involves several possible microbial pathways that are dynamics and need to be understood to overcome limitations and process optimization. Methanogenesis for biomethane production occurs close to thermodynamic limitations. Thus, the system needs to be balanced to achieve stability and satisfactory biofuel production. Several operational parameters interfere with the process, and the knowledge about them allows to maximize the methane yield. Besides problems with gas supersaturation, the role of micronutrients and adequate removal of toxic compounds released during the biomass decay represent themes that still must be solved to achieve the full potential of biofuels generation. This chapter provides fundamental knowledge to overcome the technological limitation and advance towards a wide production of biofuels from organic waste using anaerobic digestion.

Keywords Biohydrogen · Biomethane · Dark fermentation · Methanogenesis · Renewable energy

1.1 Introduction

The growing concern on climate change has driven attention to alternative energy supplies to convert the current energy matrix based on fossil fuels to renewable ones. The world's energy consumption from fossil fuels, i.e., oil, gas, and coal, represented

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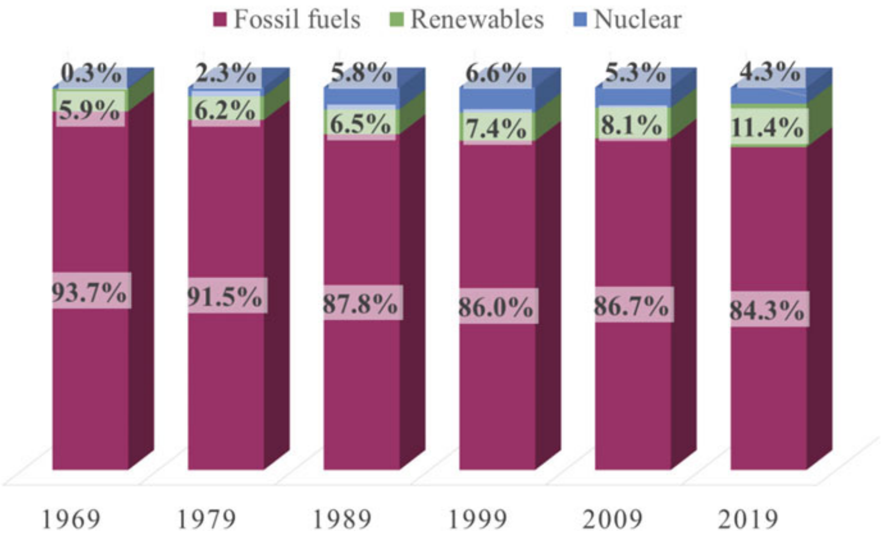

Fig. 1.1 Global consumption by source in the last 50 years (Data source: Ritchie and Roser 2020)

84.3% in 2019 (Ritchie and Roser 2020), compared with 4.3% from nuclear and 11.4% from renewable sources. A decrease of only 9.4% in the last 50 years (Fig. 1.1) demonstrating the urge to improve the sustainable energy grid.

Among the renewable sources, i.e., wind, solar, and hydropower, biofuels have received increasing attention in the last decades. Biofuels can be produced by microbial fermentation of biomass and presented as solid, liquid, and gaseous fuels, such as ethanol produced by yeast from sugarcane and corn, biodiesel from microalgae, and biomethane upgraded biogas from anaerobic fermentation of waste and wastewater by syntrophic interaction between bacteria and archaea.

CH_4 produced from organic matter degradation through anaerobic digestion (AD) can be upgraded to biomethane ($BioCH_4$) by removing CO_2, achieving >96% purity of CH_4 and an energy density of 50–55 kJ g^{-1} (Beil and Beyrich 2013). The AD process occurs in a closed reactor in the absence of oxygen. It is divided into (1) hydrolysis of macromolecules, (2) fermentation of monomers into organic acids, hydrogen (H_2), CO_2 and alcohols, (3) conversion of previous intermediate products into acetate, and (4) final conversion of acetate and hydrogen to biogas (mixture of CH_4 and CO_2).

Hydrogen thus produced, also called $BioH_2$, can also be considered a biofuel, as it is a clean energy carrier with an energy density of 122 kJ g^{-1}, 2.75-fold higher than that of fossil fuels and generating only water when converted to electricity in fuel cells. The $BioH_2$ production through anaerobic fermentation of organic matter is a process called dark fermentation. $BioH_2$ is generated to balance the cell redox potential during fermentation by using the electrons eliminated in the process for reducing protons and then excreted from the cells as dissolved gas (Cabrol et al. 2017; Schwartz and Friedrich 2006).

As the dark fermentation process corresponds to the acidogenic step of AD, it can be followed by acetogenesis and methanogenesis. The latter results in the formation of biogas, from which the CH_4 can be enriched to BioCH_4. Arreola-Vargas et al. (2016) demonstrated that the overall energy recovery from bagasse is higher in a system performing BioH_2 followed by BioCH_4 production (two-phase) than a system producing only BioCH_4 (single-phase). Therefore, coupling both processes can improve the biofuel production, representing advances towards renewable and sustainable energy production. Therefore, its fundamentals and process interferences will be addressed in this chapter.

1.2 Metabolic Pathways

1.2.1 BioH_2 Production Via Dark Fermentation

The organic fraction of waste and wastewater provided to microorganisms for biofuel production through anaerobic digestion is composed of a combination of carbohydrates, proteins, and lipids. Carbohydrates and amino acids are the most common carbon source utilized by fermentative microorganisms, and glucose is considered a model substrate (Cabrol et al. 2017). After hydrolysis, the monomers entering the microbial cell follow a series of chemical reactions to provide energy and components for the microorganisms' metabolism.

The breakdown of 1 mol of glucose through the Embden-Meyerhof-Parnas (EMP) glycolysis results in 2 moles of pyruvate, 2 moles of ATP, and 2 moles of NADH (Fig. 1.2). The pyruvate can be metabolized through pyruvate-formate-lyase (PFL), resulting in formate and Acetyl-CoA production. The former is secreted out of the cell, and Acetyl-CoA can be used for ATP generation. This pathway is associated with facultative microorganisms, such as Enterobacteria, and BioH_2 generation is triggered by extracellular formate ($pKa = 3.75$) excess and pH dropping of the medium (Pinske and Sargent 2016). After a formate threshold level is reached, it is transported back into the cell to be oxidized by formate hydrogen lyase (FHL), catalysed by a molybdenum-dependent selenoenzyme (McDowall et al. 2014). The electrons are used for a reduction of H^+, with the participation of a [NiFe] Ech (*Escherichia coli* hydrogenase 3) hydrogenase or a formate-dependent (COO^-) [FeFe] hydrogenase (Cabrol et al. 2017; McDowall et al. 2014).

Strict anaerobes, such as Clostridia, break down pyruvate through the ferredoxin oxidoreductase (PFOR) pathway. In these microorganisms, PFOR catalyzes the oxidative pyruvate decarboxylation, and the electron acceptor is a ferredoxin, which can be re-oxidized by a ferredoxin-dependent hydrogenase (Fd[FeFe]), releasing BioH_2 (Cabrol et al. 2017; Chabrière et al. 1999). The regeneration of NADH produced during the glycolysis, coupled with reduced ferredoxin via ferredoxin oxidoreductase (NFOR), can yield 4 moles of BioH_2 per mol of glucose, whether the acetyl CoA is driven to acetate production (Eq. 1.1) (Cai et al. 2011).

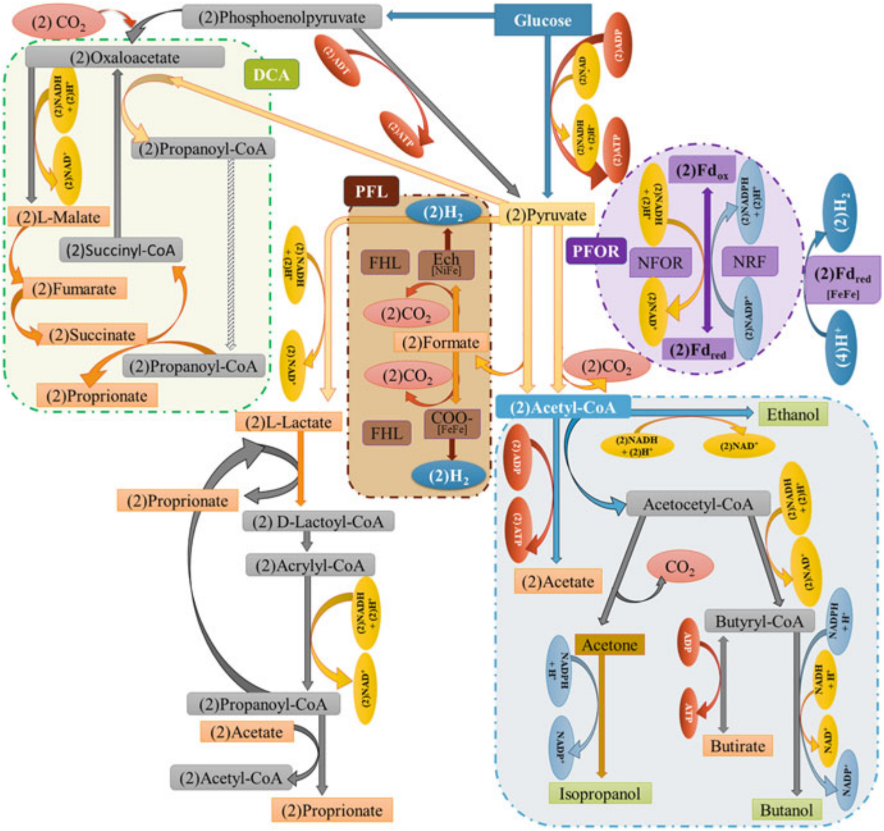

Fig. 1.2 Main metabolic pathways and products associated with dark fermentation from glucose, considering the Embden–Meyerhof–Parnas (EMP) glycolysis. Pyruvate can be converted into Acetyl-CoA either through the pyruvate-formate-lyase (PFL) or pyruvate ferredoxin oxydoreductase (PFOR) pathway depending if the microorganisms are facultative or strict anaerobes. In the PFL pathway, the BioH_2 and CO_2 production from formate might follow a reaction catalyzed by formate hydrogen lyase (FHL) along with either a [NiFe] Ech (*Escherichia coli* hydrogenase 3) hydrogenase or a formate-dependent (COO^-) [FeFe] hydrogenase. In the PFOR pathway, a ferredoxin-dependent (Fd-[FeFe]) hydrogenase is involved in the production of BioH_2 via NADH: ferredoxin oxidoreductase (NFOR) or $NADP^+$ reducing factor (NRF). The acetyl CoA branch generates organic acids and alcohol. Pyruvate can directly generate L-lactate, which might lead to propionate for reducing NADH. Propionate can also be formed through the dicarboxylic acid (DCA) cycle. Numbers between parentheses represent stoichiometry for 1 mol of glucose. Adapted from Cabrol et al. (2017) and Hoelzle et al. (2014)

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2\ CH_3COOH + 4H_2 + 2CO_2\ \Delta G^{\circ} - 206.0\ \text{kJ mol}^{-1} \qquad (1.1)$$

Acetate and butyrate are the primary pathways in the acetyl Co-A branch, as these products result in the highest ATP production (Hoelzle et al. 2014). Butyrate is favoured over acetate when an alternative electron sink is necessary. Ethanol, butanol, and acetone are other alternatives to sink electrons onto and avoid the increase of the hydrogen partial pressure and pH drop (Hoelzle et al. 2014). Isopropanol might be produced by reducing acetone and sinking more electrons. Although the alcohol production decreases the $BioH_2$ production yield, the solventogenic pathway described can be explored for liquid biofuel production.

Microorganisms without PFOR are unable to oxidize NADH with $BioH_2$ production via NFOR, and the NAD^+ release occurs during the production of reduced organic acids and alcohols. Additionally, dark fermentation is affected by $BioH_2$ accumulation at different levels depending on the electron carriers. $BioH_2$ continues at a hydrogen partial pressure lower than 0.3 atm, while NADH activity can be hindered at a hydrogen partial pressure higher than $0.6x10^{-4}$ atm (Angenent et al. 2004).

Lactate is produced directly via pyruvate and does not act as an electron sink. Nevertheless, it is the preferred pathway for propionate producers resulting in the re-oxidation of 2 moles of NADH (Eq. 1.2) (Saady 2013).

$$\begin{gathered} CH_3COCOOH + 2NADH + 2H^+ \rightarrow CH_3CH_2COOH + 2NAD^+ + H_2O \\ \Delta G^{\circ} - 186.2\ \mathrm{kJ\ mol^{-1}} \end{gathered} \tag{1.2}$$

Propionate can also be generated by the dicarboxylic acid (DCA) cycle carried out by *Propionibacterium* species. The cycle begins when the oxaloacetate is reduced to L-malate, followed by fumarate and succinate production, which generates propionate when succinate receives the CoA from the propanoyl-CoA (Hoelzle et al. 2014). The succinyl-CoA leads to the regeneration of oxaloacetate by transferring CoA to pyruvate to form propanoyl-CoA (Hoelzle et al. 2014).

1.2.2 BioCH$_4$ Via Methanogenesis

Methanogenesis is a series of biochemical reactions composing the last step in AD and promoting organic matter degradation into CH_4 and CO_2. Methanogens can metabolize three classes of substrates: CO_2-type substrate, methyl substrates, and acetotrophic substrate (Madigan et al. 2010).

Methanogenesis from acetate cleavage requires ATP consumption and results in acetyl-CoA formation. Acetyl-CoA decarbonylase/synthase (ACS) catalyses the breaking down of the acetyl-CoA into CoA, CO, and a methyl group, generating a methylated corrinoid (Can et al. 2014; Mulrooney and Hausinger 2003). The oxidation of CO catalysed by CO-dehydrogenase (CODH) forms CO_2, whereas the CH_4 is produced from the reduction of the corrinoid-bound methyl group with the participation of methyl-coenzyme M reductase, coenzyme B, and the cofactor F_{430} (Mulrooney and Hausinger 2003). The autotrophic pathway to produce acetate, the Wood-Ljungdahl pathway, is energy conservative, and methanogens use it in the reductive direction for CO_2 fixation (Ragsdale and Pierce 2008). This pathway is known as the homoacetogenic pathway and responsible for depletion in BioH_2 production, and it is also spread among *Clostridium* genus (Castelló et al. 2020).

The CH_4 production can occur in a single-phase reactor using raw waste or wastewater or using a two-phase system that receives the effluent of the dark fermentation reactor. In two-phase systems, the methanogenic reactor is fed with a substrate formed by a mixture of organic acids and alcohols. Therefore, it is necessary to convert these compounds into the substrates required by methanogenic archaea, mainly acetate, CO_2 and H_2.

Generally, the acetogenic reactions are thermodynamically not favourable, as no energy is released (Table 1.1). Nevertheless, the consumption of the dissolved hydrogen and acetate by methanogenic archaea allows a syntrophic relationship that alters the energetic balance, allowing sufficient energy production to allow the growth of the acetogenic microorganisms (Madigan et al. 2010).

The global reaction (Eq. 1.13) demonstrates that the propionate yields 56.6 kJ per mol converted, divided among the groups involved (acetoclastic bacteria, hydrogenotrophic and acetoclastic methanogens), hence explaining their low growth rate and biomass yield.

$\underset{\text{propionate}}{CH_3CH_2COO^-} + 3H_2O \rightarrow \underset{\text{acetate}}{CH_3COO^-} + HCO_3^- + H^+ + 3H_2$	+76.1 kJ	(1.3)
$\underset{\text{acetate}}{CH_3COO^-} + H_2O \rightarrow \underset{\text{methane}}{CH_4} + HCO_3^-$	−31 kJ	(1.9)
$\underset{\text{hydrogen}}{3H_2} + 0.75\ HCO_3^- + 0.75\ H^+ \rightarrow \underset{\text{methane}}{0.75\ CH_4} + 2.25\ H_2O$	−101.7 kJ	(1.10)
$\underset{\text{propionate}}{CH_3CH_2COO^-} + 1.75\ H_2O \rightarrow \underset{\text{methane}}{1.75\ CH_4} + 1.25\ HCO_3^- + 0.25\ H^+$	−56.6 kJ	(1.13)

Harper and Pohland (1986) used the results from thermodynamic calculations of main anaerobic reactions versus hydrogen partial pressure (Fig. 1.3) to establish a methanogenic niche, in which the hydrogen partial pressure ranges from 10^{-6} to 10^{-4} atm. This range is thermodynamically favourable for the syntrophism between organic acid producers and consumers, consequently, for CH_4 production.

Operational failures, such as shock loads, biomass wash-out, changes in temperature and pH, might lead to BioH_2 and acetate accumulation and inhibiting the degradation of reduced organic acids, as acetogenic reactions occur close to the thermodynamic equilibrium. Proprionate concentrations exceeding 900 mg L^{-1} decrease the acetogenic bacterial activity, hampering other organic acids degradation and leading to more accumulation in the system (Wang et al. 2009). The organic acids accumulation causes the drop of the system pH, as the alkalinity of the medium is consumed, hindering methanogenic archaea growth and activity, which causes acetate accumulation until the CH_4 is completely ceased (Wang et al. 2009). Therefore, methanogenic systems are more sensitive to variations and susceptible to failures.

Table 1.1 Main reactions involved in acetate and methane production from organic waste and wastewater (Harper and Pohland 1986; Thauer et al. 1977)

Stage	Reaction	ΔG° (kJ)	Eq.
Acetogenesis	$\underbrace{CH_3CH_2COO^- + 3H_2O}_{\text{propionate}} \rightarrow \underbrace{CH_3COO^- + HCO_3^- + H^+ + 3H_2}_{\text{acetate}}$	+76.1	(1.3)
	$\underbrace{CH_3CH_2COO^- + 2HCO_3^-}_{\text{propionate}} \rightarrow \underbrace{CH_3COO^- + H^+ + 3HCOO^-}_{\text{acetate}}$	+72.2	(1.4)
	$\underbrace{CH_3CH_2CH_2COO^- + 2H_2O}_{\text{butyrate}} \rightarrow \underbrace{2CH_3COO^- + H^+ + 2H_2}_{\text{acetate}}$	+48.1	(1.5)
	$\underbrace{CH_3CH_2OH + H_2O}_{\text{ethanol}} \rightarrow \underbrace{CH_3COO^- + H^+ + 2H_2}_{\text{acetate}}$	+9.6	(1.6)
	$\underbrace{CH_3CHOHCOO^- + 2H_2O}_{\text{lactate}} \rightarrow \underbrace{CH_3COO^- + HCO_3^- + H^+ + 2H_2}_{\text{acetate}}$	−4.2	(1.7)
	$\underbrace{2HCO_3^- + 4H_2 + H^+}_{\text{bicarbonate}} \rightarrow \underbrace{CH_3COO^- + 4H_2O}_{\text{acetate}}$	−104.6	(1.8)
Methanogenesis	$\underbrace{CH_3COO^- + H_2O}_{\text{acetate}} \rightarrow \underbrace{CH_4 + HCO_3^-}_{\text{methane}}$	−31	(1.9)
	$\underbrace{4H_2 + CO_2}_{\text{hydrogen}} \rightarrow \underbrace{CH_4 + 2\,H_2O}_{\text{methane}}$	−131	(1.10)
	$\underbrace{HCOO^- + \frac{1}{4}\,H_2O + \frac{1}{4}\,H^+}_{\text{formate}} \rightarrow \underbrace{\frac{1}{4}\,CH_4 + \frac{3}{4}\,HCO_3^-}_{\text{methane}}$	−32.6	(1.11)
	$\underbrace{HCO_3^- + 4H_2 + H^+}_{\text{bicarbonate}} \rightarrow \underbrace{CH_4 + 3H_2O}_{\text{methane}}$	−135.6	(1.12)

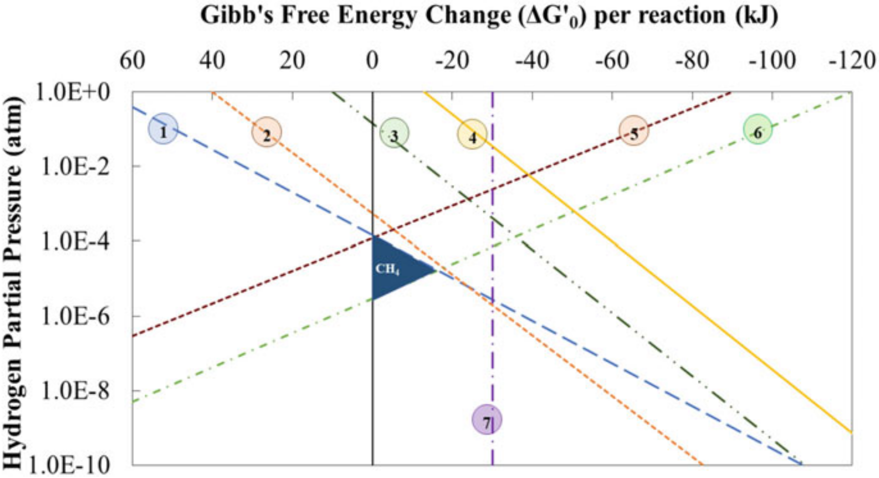

Fig. 1.3 Diagram indicating the favourable niche for BioCH_4 production from anaerobic degradation of organic waste and wastewater, based on the hydrogen-dependent thermodynamics of the main reactions: (1) Propionic acid oxidation to acetic acid. (2) Butyric acid oxidation to acetic acid. (3) Ethanol to acetic acid. (4) Lactic acid to acetic acid. (5) Acetogenic respiration of bicarbonate. (6) Methanogenic respiration of bicarbonate. (7) Methanogenic cleavage of acetic acid. Acetic acid, 25 mM; propionic, butyric, lactic acids, and ethanol, 10 mM; bicarbonate, 20 mM; methane 0.7 atm. (Source: Harper and Pohland 1986)

1.3 Factors Affecting the Process

1.3.1 Inoculum Source

The microorganisms established in the system are the most crucial factor affecting the metabolic pathway, and consequently, the biofuel production and yield of the process. Therefore, the inoculum source plays the primary role.

A pure culture can be selected and used to ensure higher control of a specific step of the biofuel production through the desired pathway. Microorganisms have an optimal condition for growth and metabolic activity. Hence, a pure culture allows product yield maximization during the industrial process. The enhancement of the BioH_2 production rate from monomers, i.e., glucose, by *Thermotoga neapolitana cf. Capnolactica* was demonstrate via heterofermentation pathway (acetate and lactate) varying the inoculum concentration by Dreschke et al. (2018). A co-culture of isolated strains can collaborate to overcome technical aspects of the conversion of substrates in biofuel. The combination of pure cultures strictly anaerobic and facultative can eliminate O_2 in the medium; strains able to hydrolyse cellulose can provided carbohydrate monomers for high BioH_2 producers in dark fermentation; strains able to produce BioH_2 at different pH can maintain the production without require buffering (Elsharnouby et al. 2013). A co-culture of *E. coli CECT432* strain and *Enterobacter spH1* showed a three-fold higher H_2 productivity from pure glycerol compared with pure of *E. coli CECT432* strain (Maru et al. 2016). However, isolated cultures require sterilization before using equipment and feeding the system, turning this option infeasible for real substrates, such as wastewater containing indigenous microorganisms.

Diverse mixed consortia obtained from indigenous/autochthonous substrate and inoculum provide the system with notable robustness regarding operational changes, such as variation in substrate composition and characteristics due the higher microbial diversity without the cost for sterilizing the system and substrate (Cabrol et al. 2017). However, mixed non-isolated consortia for BioH_2 production must avoid the presence of consuming H_2 populations, such as methanogenic archaea and sulfate-reducing bacteria. Therefore, inoculum pre-treatment is an option to select a group of microorganisms. Thermal (temperatures from 90 to 100 °C), acidic (pH lower than 3), and alkaline (pH higher than 11) pre-treatment or a combination of them are widely adopted to select acidogenic bacteria for dark fermentation and to avoid the presence of methanogenic microorganisms in the dark fermentation reactor. Some acidogenic bacteria can form spores under extreme conditions, while archaea typically present in anaerobic sludge are sensitive to the pre-treatment conditions.

Mockaitis et al. (2020) applied acidic, thermal, and acidic-thermal and thermal-acidic pre-treatments to a mixed-culture for BioH_2 production from xylose. The authors obtained better results with acidic pre-treatment, achieving a BioH_2 yield equal to 1.57 mol H_2 mol xylose^{-1}. Rafieenia et al. (2018) evaluated inoculum pre-treatment for BioH_2, followed by BioCH_4. Heat shock, aeration, alkaline and an innovative pre-treatment with saponified frying oil (WFO) were evaluated using synthetic food waste as the substrate. The authors found better results using the WFO for BioH_2 and BioCH_4, respectively, 76.1 mL gVS^{-1} and 598.2 mL gVS^{-1}. Penteado et al. (2013) compared BioH_2 production in packet-bed reactor using pre-treated inoculum from an UASB reactor treating poultry slaughterhouse wastewater, an UASB fed with swine wastewater and natural fermentation of the substrate. These authors found higher BioH_2 yield using the inoculum from natural fermentation (2.1 ± 1.8 molH_2 mol$_{\text{sucrose}}{}^{-1}$) and higher stability using inoculum pre-treated with an acid shock (2.0 ± 1.1 molH_2 mol$_{\text{sucrose}}{}^{-1}$).

Natural fermentation was also applied using sugarcane vinasse from ethanol and sugar mill using packed bed (Ferraz et al. 2014) and structured bed reactor (Fuess et al. 2019) continuous reactors. This inoculation strategy exploits the development of an adapted consortium in the substrate exposed to the ambient conditions, which will be further recirculated in the reactor for microorganism attachment (Leite et al. 2008). Autochthonous mixed consortia developed naturally in the substrate such as mushroom farm waste (Lin et al. 2017) and banana waste (Mazareli et al. 2020) were also used for BioH_2 production in batch experiments and represent a suitable inoculation approach for BioH_2 production from real waste and wastewater.

1.3.2 pH

Microorganisms have an optimal pH growth and are classified into neutrophile ($5.5 < pH < 8$), acidophile ($pH < 5.5$) and alkaliphile ($8 \geq 8$), which is measured externally, as the intracellular pH remains close to neutrality (Madigan et al. 2010). Changes in pH values from the optimal can cause cellular lyase or denaturation of enzymes necessary for microbial activities and affect the speciation of compounds present in the medium. Acetic and butyric acids (HA) equilibrium with their ionic counterparts, acetate and butyrate (A^-), depends on the pH according to Eq. 1.14. The undissociated forms of these acids can cross the cell membrane and release protons, altering the internal pH, reducing or inhibiting the cellular activities (Castelló et al. 2020).

$$pH = pK_a + log\left(\frac{A^-}{HA}\right) \tag{1.14}$$

Dark fermentation is generally performed under acidic conditions. Horiuchi et al. (2002) observed a shift from butyrate and acetate to propionate production when increasing the pH value from 5.0–7.0 to 8.0 in a completely mixed fermenter fed with glucose. Fuess et al. (2019) concluded that an increase in pH value from <5.0 to 5.0–5.5 leads to a shift from lactate production to $BioH_2$ production via butyrate, with a further increase (pH >6.0) associated with propionate and sulfate-reducing activity using sugarcane vinasse as the substrate. Similar results had already been reported by Hwang et al. (2009), who found a decrease in $BioH_2$ production at pH values equal 5.8 and 6.2 compared to a pH value of 5.5, due an increase in the activity of sulfate-reducing bacteria using glucose as the substrate and adding iron sulfate.

Methanogenic archaea are able to live in extreme environments. However, the adequate pH range for the anaerobic process for methane production was found to be around 7.0–7.5, narrower than the range for dark fermentation (Liu and Sung 2002; Sprott et al. 1984). Additionally, a more robust methodology was proposed by Ripley et al. (1986) to monitor the methanogenic system and avoid process failure. According to the authors, the ratio of the intermediate alkalinity (IA): partial alkalinity (PA) at the range 0.1 to 0.35 allowed to ensure adequate bicarbonate buffering and avoid excess of organic acids. Other authors have adopted the IA:total alkalinity (TA) ratio as a stability parameter, although still considering values lower than 0.3 (Garcia et al. 2007).

1.3.3 Temperature

Microorganisms possess an optimal temperature for developing their metabolic functions at the maximum rate, although their activities are still developed within

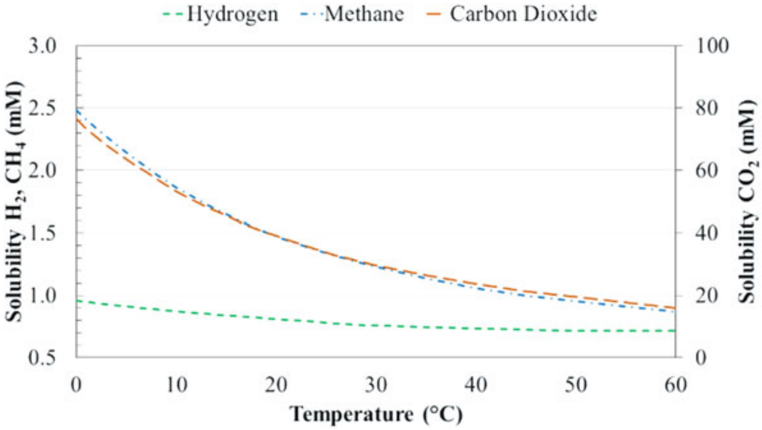

Fig. 1.4 Solubility of H_2, CH_4, and CO_2 in water. The measurements are normalized for standard conditions (0 °C and 1 atm). (Data source: Dean 1999)

at a certain temperature range. At the lower range value, the semifluid cytoplasmic membrane begins a solidification process, hindering the transport in the microbial cell (Madigan et al. 2010). The upper range value indicates the temperature triggers the collapse of the cytoplasmic membrane, with enzyme denaturation, and thermal lysis (Madigan et al. 2010). Psychrophilic microorganisms are adapted to temperatures ranging from 0 to 10 °C; mesophiles possess optimal temperature at 40 °C, but their metabolism is functioning from 10 to 45 °C; thermophiles have an optimal temperature around 60 °C, with activity in the range from 45 to 65 °C; and hyperthermophiles are able to live in environments with temperatures from 90 to 115 °C, with an optimum at 105 °C (Madigan et al. 2010).

The temperature also affects the solubility of the main gases participating in AD. The solubility values decrease with the increase in temperature (Fig. 1.4), indicating that higher operational temperatures might help overcome mass transport and thermodynamic limitations.

Regarding dark fermentation, the lower solubility of H_2 increases the BioH_2 yield by enhancing the mass transfer from the liquid to the gaseous phase and limiting the homoacetogenesis due to the lower CO_2 solubility. In methanogenesis, the lower solubility of CH_4 allows the higher mass transfer of CH_4 to the gaseous phase. However, the lower CO_2 solubility might impact the activity of hydrogenotrophic methanogens. Labatut et al. (2014) found that mesophilic continuously-stirred anaerobic digesters (CSADs) producing CH_4 from cow manure co-digested with dog fod waste was more robust and stable than a thermophilic CSAD, despite a slightly lower CH_4 yield.

Supersaturation of CH_4 in the liquid phase has already been reported by Yeo et al. (2015). Despite the low solubility of H_2 ($<CH_4 << CO_2$), BioH_2 supersaturation was observed in several studies under mesophilic and thermophilic conditions (Beckers et al. 2015; Dreschke et al. 2019a, b; Obazu et al. 2012; Zhang et al.

2012). Values up to seven-fold the values calculated for equilibrium conditions were found by Beckers et al. (2015) during $BioH_2$ production using the pure *Clostridium butyricum* strain, demonstrating that other strategies besides increasing temperature must be applied to promote a higher $BioH_2$ yield.

1.3.4 Nutrients and Potentially Toxic Compounds

An interesting alternative substrate of biofuel production from AD is organic waste and wastewater generated from municipal solid waste, food and beverage industries, and agro-industrial activities. The use of residues as a resource for biofuel production through AD relies on the biorefinery concept and can reduce production costs while enhancing environmental gains. However, the composition of a substrate from agro-industrial activities differs depending on the industrial process, soil and climate conditions and varies seasonally. Consequently, these substrates might contain inhibitory compounds and provide unbalanced macro and micronutrient supply for the microorganisms.

Macro and micronutrients are frequently found in poor concentrations in the substrate, as pointed out by Thanh et al. (2016). Nutritional deficiency in anaerobic reactors might limit microbial growth and metabolic activities, as trace elements often composes the reactive centres of metalloenzymes and cofactors (Vignais and Colbeau 2004). Zhang et al. (2019) observed complete inhibition of methanogenic activity in a semi-continuous reactor fed with food waste and demonstrated that supplementation of Fe, Co, Mo and Ni at concentrations, respectively, 100, 1, 5 and 5 mg L^{-1} eliminated all factors causing failure in the system. Molaey et al. (2019) observed an increase in methane production from chicken manure with a total ammonia nitrogen concentration of 3000 mg L^{-1} by supplementing the system with concentration up to 5 mg L^{-1} Ni, 5 mg L^{-1} Co, 1 mg L^{-1} Mo, 1 mg L^{-1} Se, 1 mg L^{-1} W, and 25 mg L^{-1} Fe. Conversely, concentrations over two-fold caused a decrease in CH_4 production and rate (Molaey et al. 2019).

The presence of sulfate in the substrate might impact biofuels production, as the activity of sulfate-reducing bacteria and the hydrogen sulfide generated might hamper the $BioH_2$ (Fuess et al. 2019) and the CH_4 (Kiyuna et al. 2017) production from sugarcane vinasse. Ammonia has also demonstrated to have an inhibitory effect on CH_4 production at concentrations exceeding 400 mg L^{-1} in a CSTRs fed with soluble non-fat dry milk as organic substrate and operated under thermophilic (55 ± 1 °C) conditions (Liu and Sung 2002).

For the biofuel production from lignocellulosic materials, a physicochemical pre-treatment is necessary to turn the monosaccharides available for AD. The pre-treatments include mechanical (high-pressure homogenizer and bead mills), physical (microwave and ultrasonic), thermal (autoclave and steam explosion) and chemical (catalysis and enzymes) techniques (Onumaegbu et al. 2018). These procedures also release phenols and furans, their concentration depends on the lignocellulosic material type and the pre-treatment technique applied (Monlau et al. 2014).

The $BioH_2$ production can be inhibited by furanic and phenolic compounds with a concentration range of 250–1000 mg L^{-1} (Elbeshbishy et al. 2017). The inhibition by phenolic compounds is related to the damage in the microbial cell membrane, while the furans interfere with enzyme activity (Elbeshbishy et al. 2017). Fang et al. (2006) demonstrated 70% phenol degradation at a concentration of 630 mg L^{-1} in a thermophilic UASB at HRT of 28 h. A specific methanogenic activity (SMA) test demonstrated that the sludge was able to degrade the phenols at a range concentration of 600–1000 mg L^{-1} and produce CH_4; however, no phenol degradation was achieved at 2000 mg L^{-1} (Fang et al. 2006).

1.3.5 Reactor Configuration

Ideally, the liquid flow pattern in continuous reactors can be classified in plug-flow and mixed flow, determined by models such as tank-in-series and dispersion (Levenspiel 1999). It directly impacts the kinetics of the process. Some reactor configurations applied to biofuels production are presented in Table 1.2. The mixed flow present in the continuous stirred tank reactor (CSTR) allows a homogenous composition throughout the reactor and favours the mass transfer of the products excreted by the microorganisms (Bailey and Ollis 1986). The plug-flow pattern allows a longitudinal microorganism separation, and consequently, the composition of the medium changes throughout the reactor, and it is suitable for substrates with potentially toxic compounds (Parkin and Speece 1983). Plug-flow reactors can be used in large-scale for CH_4 production from cattle manure in long term operation (Dong et al. 2019). However, most of the reactors possess a non-ideal flow pattern, standing in between mixed and plug-flow.

Important reactors characteristics are the presence or absence of a support material for microbial attachment, recirculation of liquid or gas, and up or downflow velocity. Reactor modifications that promote sludge settling and aggregation of biomass, e.g. three-phase separator in UASB reactors, disconnect the hydraulic retention time (HRT) from the sludge retention time (SRT), allowing a high-rate reactor (Lettinga et al. 1980). This also occurs when adding support material such as in packed and structured bed reactors. Liquid recirculation can be used to increase the upflow velocities as in expanded granular sludge blanket (EGSB) reactors, increasing the contact between substrate and microorganisms (Verstraete et al. 1996). It can also improve the alkalinity in methanogenic reactors and dilute toxic compounds present in the system. Gas recirculation can be applied to overcome H_2 supersaturation (Beckers et al. 2015; Dreschke et al. 2019a).

Table 1.2 Reactors used for biofuels production through anaerobic digestion

Stage	Reactor	Substrate	Inoculum	ORL (gCOD L^{-1} d^{-1})	Temperature (°C)	pH initial	Biofuel yield	Biofuel production	Reference
Dark fermentation	Continuous stirred tank reactor (CSTR)	Glucose	*Thermotoga neapolitana cf. capnolactica*	–	80	7	3.5 ± 0.2 molH_2 mol^{-1}	850 ± 71 mLH_2 L^{-1} h^{-1}	Dreschke et al. (2019b)
Dark fermentation	Internal circulation (IC) reactor	Glucose	Mixed culture (thermal pre-treatment)	–	35 ± 1	6.5	1.4 ± 0.21 molH_2 mol^{-1}	10.78 ± 0.84 L^{-1} d^{-1}	Su et al. (2020)
Dark fermentation	CSTR	Tequila Vinasse	Mixed culture (thermal pre-treatment)	32.8	37	7.5	1.68 molH_2 mol^{-1}	0.42 ± 0.02 NL H_2 L^{-1} d^{-1}	García-Becerra et al. (2019)
Dark fermentation	Up-flow packed bed reactor (UPBR)	Glucose	Mixed culture (thermal pre-treatment)	64	48 ± 2	6.0 ± 0.5	0.89 molH_2 mol^{-1}	4.73 LH_2 L^{-1} d^{-1}	Karapinar et al. (2020)
Dark fermentation	Anaerobic structured bed reactor (AnSTBR)	Sugarcane vinasse	Natural fermentation	56	70	6.5	2.6 ± 0.5 molH_2 mol^{-1}	630 ± 47 mLH_2 L^{-1} d^{-1}	Niz et al. (2019)
Methanogenesis	Plug-flow reactor	Cattle manure	Mixed culture	3.6	37–40	7.85 ± 0.05	–	0.43–0.75m^3 m^{-3} d^{-1}	Dong et al. (2019)
Methanogenesis	Fixed-bed digester (two-phase system)	Municipal organic waste percolate	Mixed culture	0.7	37–40	7–8	–	335 N-LCH_4 $kgVS^{-1}$ [a]	Knoop et al. (2018)
Methanogenesis	Horizontal-flow reactors with	Cassava processing wastewater CPWW	Mixed culture	2.3–8.5	28.5 ± 1.5	7-8[b]	0.3–0.15 LCH_4 $gCOD_{removed}^{-1}$	0.5–4.5 LCH_4 d^{-1}	Palma et al. (2016)

	dolomite rocks								
Methanogenesis	CSTR	Sugarcane trash untreated (ST) and treated (TT) sugarcane bagasse untreated (SB) and treated (TB)	Mixed culture	2.5 (gVS L^{-1} d^{-1})[c]	37 ± 1	7.3–7.8[b]	121 (ST), 226 (TT), 148 (SB), and 236 (TB) (mLCH_4 gVSfed^{-1})	303 (ST), 565 (TT), 370 (SB) and 590 (TB) (mLCH_4 L^{-1} d^{-1})	Paulose and Kaparaju (2021)
Methanogenesis	CSTR and Covered lagoon biodigester (CLB) lab and full scale	Swine manure solid (CSTR) and liquid (CLB) phase	Mixed culture	0.165 lab and 0.356 full CLB; 1.340 lab and 1.618 full CSTR	23–24 BLC 34–37 CSTR	7.4 BLC and 7.8 CSTR	0.9 lab and 0.56 full CLB, 0.46 lab and 0.38 full CSTR (NL_{biogas} $gVS_{add}{}^{-1}$	0.2 lab and 0.18 full CLB, 0.61 lab and 0.65 full CSTR (NL_{biogas} L^{-1} d^{-1})	Tápparo et al. (2021)

[a] Value from biochemical potential assay

[b] Effluent pH

[c] Best OLR

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Chapter 2
Engineering Direct Interspecies Electron Transfer for Enhanced Methanogenic Performance

Changsoo Lee

Abstract Producing biogas from organic waste streams through anaerobic digestion (AD) is a well-established bioenergy technology. Efficient electron transfer between syntrophic bacteria and methanogens is critical for balancing acidogenesis and methanogenesis, which is necessary for stable digester operation. The recently discovered direct interspecies electron transfer (DIET) links syntrophic partners via cell-to-cell electrical connections without using diffusive electron carriers such as H_2. Promoting DIET by adding conductive materials has been suggested as a possible method to accelerate syntrophic degradation of organic compounds, and many studies have demonstrated the enhancement of methanogenesis by the addition of conductive materials. Although further research is needed for practical applications, accumulated evidence indicates that engineering DIET is a promising strategy to enhance the performance and stability of AD processes. A few recent studies have also demonstrated the scale-up potential of DIET-aided AD.

Keywords Anaerobic digestion · Conductive material · Direct interspecies electron transfer · Electric syntrophy · Electrotrophic methanogens · Exoelectrogenic bacteria · Methanogenesis

2.1 Introduction

Anaerobic digestion (AD) is a multi-step process involving biochemical reactions mediated by taxonomically and metabolically very diverse microorganisms, and their concerted activity is necessary for methanogenic degradation of organic matter under anaerobic conditions. Various microorganisms with different ecophysiological characteristics coexist in AD processes even if a single substrate is utilized

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(Fernandez et al. 2000). The microbial community structure and interspecies interactions will be even more complicated in anaerobic digesters treating complex organic wastes. Therefore, facilitating and harmonizing the activities of individual community members is the key to stable and robust AD.

Methanogenesis, the last step of AD, is performed by a unique group of strictly anaerobic microorganisms belonging to the domain *Archaea*, known as methanogens. All methanogens identified so far are classified into one phylum, *Euryarchaeota*, while the existence of putative methanogens in uncultured phyla *Bathyarchaeota* (Evans et al. 2015) and *Verstraetearchaeota* (Vanwonterghem et al. 2016) was suggested in recent metagenomic studies. Methanogens use a narrow range of substrates such as H_2/CO_2, formate, acetate, methylated compounds and CO, and acetoclastic and hydrogenotrophic pathways are often the main routes of methanogenesis in anaerobic digesters (Enzmann et al. 2018). Therefore, methanogens at the end of the trophic chain of AD need other microorganisms that hydrolyze and ferment organic macromolecules into substrates for methanogenesis. Methanogenesis is usually considered the rate-limiting step of the overall AD process because of the slow growth rate and high sensitivity to environmental conditions of methanogens (Lee et al. 2018). However, hydrolysis can be the rate-limiting step when digesting organic substances with low bioavailability, such as waste activated sludge and lignocellulosic biomass. Furthermore, the degradation of C_3 or higher volatile fatty acids (VFAs) to acetate and H_2/CO_2 (i.e., acetogenesis) also becomes rate-limiting if the syntrophic association between VFA oxidizers and methanogens is not well developed (Baek et al. 2018). In this case, an imbalance between the production and consumption of VFAs (and H_2) can occur and result in a buildup of VFAs (and H_2 partial pressure) and even in a digester failure. Therefore, efficient electron transfer between syntrophic microorganisms involved in anaerobic VFA degradation is critical in maintaining the balance between acidogenesis and methanogenesis for stable AD.

The interspecies electron transfer (IET) between VFA oxidizers and methanogens has been thought to be mediated exclusively by microbially produced H_2 or formate as electron carriers. It was recently revealed that there exists an alternative IET route where electrons are transferred directly from exoelectrogenic VFA oxidizers to electrotrophic methanogens through a cell-to-cell electrical connection. This direct IET (DIET) is energetically and kinetically advantageous over the H_2/formate-mediated indirect IET (IIET), because complex reactions for synthesizing and consuming H_2 or formate are not required (Lovley 2011). This suggests the possibility that thermodynamically more favorable conditions for rapid methanogenic degradation of organic matter can be achieved by promoting DIET (Barua and Dhar 2017). In support of such a possibility, a mathematical modeling study estimated that the cell-to-cell electron transfer rate can be more than eight-fold higher for DIET than for IIET via H_2 (Storck et al. 2016).

The potential for DIET in methanogenic systems was experimentally observed for the first time only a decade ago by Morita et al. (2011) in a study of electron transfer mechanisms within methanogenic granular sludge treating brewery waste. In the next year, Kato et al. (2012) reported a significant acceleration of methanogenesis by the addition of (semi)conductive materials (i.e., hematite (Fe_2O_3) and magnetite (Fe_3O_4)) in methanogenic soil enrichment cultures, and suggested that conductive materials promote DIET between electro-syntrophic partners by serving as conduits for electron flow. Since this work, increasing attention has been paid to whether the addition of conductive materials effectively promotes DIET, thereby enhancing methanogenesis. Many studies have been made to explore this interesting possibility in recent years, using different conductive materials, mostly carbon- or iron-based (Liu et al. 2012; Chen et al. 2014a, b; Baek et al. 2015, 2016; Zhao et al. 2015; Dang et al. 2016; Lee et al. 2016), and it is now apparent that DIET and methanogenic activities are enhanced in the presence of conductive materials.

Engineering DIET with conductive additives has recently emerged as a promising strategy for enhancing the methanogenic performance and stability of AD systems, and an increasing number of studies are looking into its potential for practical applications. This chapter reviews the fundamentals of DIET-based electric syntrophy and recent advances in engineering DIET in AD, and discusses challenges and directions for future research.

2.2 Interspecies Electron Transfer in Anaerobic Digestion

The anaerobic degradation of C_3 or higher VFAs is endergonic under standard conditions and can only be achieved by syntrophic associations between VFA oxidizers and methanogens via IET (Table 2.1). Therefore, the IET-based syntrophy is critical for complete mineralization of organic matter in the AD process. The slow rate of syntrophic VFA oxidation, particularly of propionate, the accumulation of which is toxic to methanogens, often causes an imbalance between acidogenesis and methanogenesis and limits the overall reaction rate in AD (Stams and Plugge 2009). IET in AD can be divided into IIET and DIET, according to whether or not extracellular electron carriers (i.e., H_2 and formate) are required to mediate the redox reactions between the syntrophic partners. Electrons released from the syntrophic oxidation of VFAs are transferred via H_2 or formate (electron donor for CO_2 reduction to CH_4) to hydrogenotrophic methanogens in IIET, and via direct electrical connections between cells to electrotrophic methanogens in DIET (Baek et al. 2018). In this section, the roles, mechanisms, and biochemical characteristics of IIET and DIET in AD are described.

2.2.1 Indirect Interspecies Electron Transfer

IIET between VFA oxidizers and methanogens via H_2 or formate has been considered the major route for syntrophic electron exchange necessary for methanogenic degradation of C_3 or higher VFAs (Fig. 2.1). This syntrophic relationship is very sensitive to the accumulation of oxidation products of VFAs (i.e., H_2 and formate)

Table 2.1 Reactions involved in syntropic oxidation of propionate and butyrate by interspecies electron transfer via hydrogen or formate (adapted from Baek et al. 2018)

Reaction	$\Delta G^{\circ\prime a}$ (kJ/mol)
Methanogenic degradation of propionate via H_2 as electron carrier	
$4CH_3CH_2COO^- + 12H_2O \rightarrow 4CH_3COO^- + 4HCO_3^- + 4H^+ + 12H_2$	+76.5
$3HCO_3^- + 3H^+ + 12H_2 \rightarrow 3CH_4 + 9H_2O$	−101.7
(*overall*) $4CH_3CH_2COO^- + 3H_2O \rightarrow 4CH_3COO^- + HCO_3^- + H^+ + 3CH_4$	−25.2
Methanogenic degradation of propionate via formate as electron carrier	
$4CH_3CH_2COO^- + 8H_2O + 8CO_2 \rightarrow 4CH_3COO^- + 12HCOO^- + 4H^+$	+65.3
$12HCOO^- + 12H^+ \rightarrow 3CH_4 + 9CO_2 + 6H_2O$	−144.5
(*overall*) $4CH_3CH_2COO^- + 8H^+ + 2H_2O \rightarrow 4CH_3COO^- + CO_2 + 3CH_4$	−79.2
Methanogenic degradation of butyrate via H_2 as electron carrier	
$2CH_3CH_2CH_2COO^- + 4H_2O \rightarrow 4CH_3COO^- + 2H^+ + 4H_2$	+48.3
$HCO_3^- + H^+ + 4H_2 \rightarrow CH_4 + 3H_2O$	−67.8
(*overall*) $2CH_3CH_2CH_2COO^- + H_2O + HCO_3^- \rightarrow 4CH_3COO^- + H^+ + CH_4$	−19.5
Methanogenic degradation of butyrate via formate as electron carrier	
$2CH_3CH_2CH_2COO^- + 4H_2O + 4CO_2 \rightarrow 4CH_3COO^- + 4HCOO^- + 4H^+$	+38.5
$4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O$	−96.3
(*overall*) $2CH_3CH_2CH_2COO^- + 2H_2O + CO_2 \rightarrow 4CH_3COO^- + CH_4$	−57.8

[a] $\Delta G^{\circ\prime}$, Standard Gibbs free energy change of reaction at pH 7

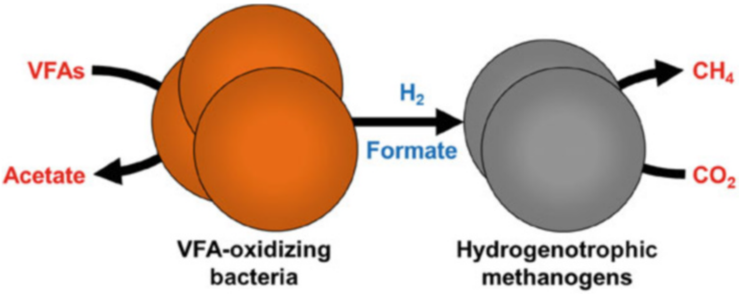

Fig. 2.1 Indirect interspecies electron transfer (IIET) between syntrophic VFA-oxidizing bacteria and hydrogenotrophic methanogens via H_2 and formate

because of the unfavorable thermodynamics of anaerobic VFA degradation (Table 2.1). High H_2 partial pressure inhibits the regeneration of the cytoplasmic pool of oxidized coenzymes in acetogenic bacteria (Thiele and Zeikus 1988), and needs to be kept below approximately 10^{-4} and 10^{-3} atm for degradation of propionate and butyrate, respectively, through IIET in methanogenic environments (Schmidt and Ahring 1993). Therefore, H_2 (and formate) should be rapidly consumed by hydrogenotrophic methanogens for stable AD. When the balanced production and degradation of VFAs is disturbed, acidogenic products, such as H_2, formate, and acetate, rapidly accumulate, leading to further inhibition of syntrophic VFA oxidation through IIET. The vicious cycle of process imbalance and acidification can result in significant deterioration or even total failure of the AD process.

Methanogenesis is a major terminal electron-accepting process in anaerobic environments, and H_2 serves as a primary electron donor for different microbial reduction reactions occurring in AD processes, including the methanogenic reduction of CO_2 (Stams and Plugge 2009). The key enzyme in the synthesis and utilization of H_2 is hydrogenase, a family of iron-containing metalloenzymes (Fe, Fe-Fe, and Fe-Ni) that catalyze the reversible oxidation of H_2 (Lubitz et al. 2014). Bacteria containing H_2-producing hydrogenase reduce protons through the oxidation of reduced intracellular redox mediators, such as ferredoxin, NADH, and $FADH_2$ (Stams et al. 2006). The oxidation of reduced ferredoxin or NADH is thermodynamically feasible when the H_2 partial pressure is kept low by H_2-consuming microorganisms, preferably hydrogenotrophic methanogens, while ATP is required for the oxidation of $FADH_2$ (Schink 1997). Metabolic H_2 produced by the oxidation of VFAs (and other organic matter) is taken up by hydrogenotrophic methanogens and oxidized by H_2-uptake hydrogenase for the reduction of oxidized ferredoxin and coenzyme F_{420} that provide electrons to convert CO_2 into CH_4 (Kim and Geoffrey 2008).

Another important diffusive electron carrier mediating IIET between VFA oxidizers and hydrogenotrophic methanogens is formate. Many syntrophic VFA oxidizers produce both H_2 and formate, and most hydrogenotrophic methanogens can use both of them as electron donors to reduce CO_2 to CH_4 (de Bok et al. 2004; Schink et al. 2017). In addition, many H_2/formate-metabolizing microorganisms, such as hydrogenotrophic methanogens and acetogenic bacteria, are able to interconvert H_2/CO_2 and formate (Lemaire et al. 2020; Nielsen et al. 2019). This complexity makes it difficult to determine whether H_2 or formate is a more important electron carrier for IIET. H_2 has a much lower solubility in water (0.8 mM at 1 atm, 20 °C) than formate, and therefore the concentration gradient between the producers and consumers (>1000-fold) can be much larger with formate than with H_2 (de Bok et al. 2004; Felchner-Zwirello et al. 2013). Meanwhile, the diffusion coefficient in water (25 °C) is more than four times higher for H_2 (5.11×10^{-3} mm^2/s) than for formate (0.96×10^{-3} mm^2/s) (Lide 1995; Prüsse et al. 2000). Given that the diffusive flux of interspecies electron carriers is proportional to their diffusion coefficients and concentration gradients between the syntrophic partners (Fig. 2.2), it is likely that H_2 and formate are primarily involved in short- and long-distance IIET, respectively (de Bok et al. 2004).

Thiele and Zeikus (1988) found that formate-mediated IIET was the main IET mechanism during the syntrophic conversion of ethanol to methane in cultures of methanogenic flocs from a lab-scale digester treating whey. Boone et al. (1989) calculated that H_2 diffusion alone could not support the syntrophic degradation of propionate and butyrate in suspended cultures (i.e., IIET between dispersed cells) and that formate diffusion contributed 98 times more to IET than did H_2 diffusion. In contrast, Goodwin et al. (1991) reported that the H_2 diffusion rate was fast enough to account for the methanogenesis rate in anaerobic microbial aggregates degrading lactate. Schmidt and Ahring (1995) also suggested that H_2 was the dominant electron carrier in methanogenic granular sludge degrading propionate and butyrate. Since the diffusion distance between syntrophic partners is mainly determined by cell

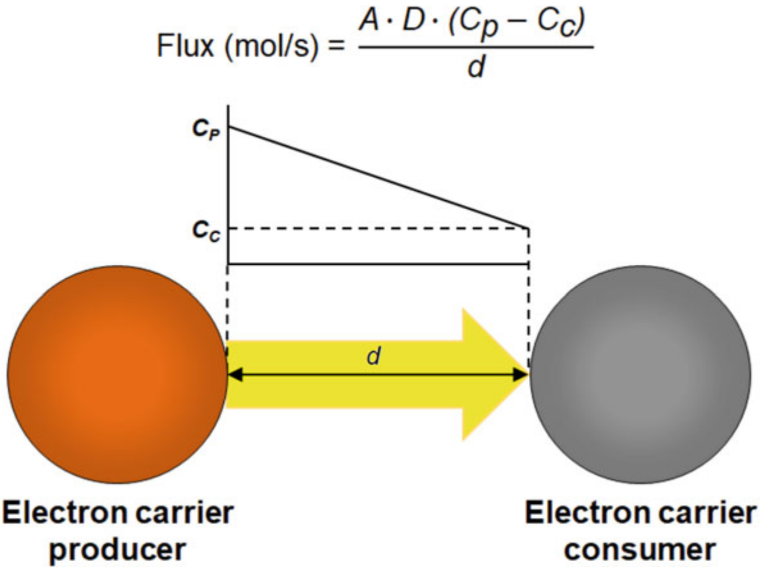

Fig. 2.2 Diffusive flux of interspecies electron carriers between a producing and a consuming microorganism (adapted from de Bok et al. 2004). *A*, the surface area of the electron carrier producer; *D*, the diffusion coefficient of the electron carrier; *Cp*, the concentration of the electron carrier at the surface of the producer; *Cc*, the concentration of the electron carrier at the surface of the consumer; and *d*, the distance between the producer and consumer

density, it is understandable that IIET via formate may be preferred in planktonic cultures, whereas H_2 diffusion may dominate IIET in methanogenic aggregates or biofilms. Recent measurements in different anaerobic digesters suggest that the pool sizes of H_2 and formate are energetically nearly equivalent, and both H_2- and formate-mediated IIET likely occur at the same time in a methanogenic system (Schink et al. 2017). Therefore, the electron transfer efficiency can be expected to increase with increasing cell density (i.e., reducing intercellular distance). Accordingly, previous studies have reported that the syntrophic degradation rate of VFAs could be enhanced by forming compact microbial aggregates/granules, reducing the mixing level, or adding H_2/formate-utilizing microorganisms (Schmidt and Ahring 1995; Stroot et al. 2001; Kim et al. 2002; Kaparaju et al. 2008).

2.2.2 Direct Interspecies Electron Transfer

2.2.2.1 Introduction

Recent discoveries revealed that DIET is an important alternative IET route for the use of electrons derived from the oxidation of acidogenic metabolites, such as VFAs and ethanol, for the methanogenic reduction of CO_2 in AD environments (Morita et al. 2011; Kato et al. 2012; Rotaru et al. 2014a, b). In contrast to IIET, DIET excludes the involvement of electron carriers (i.e., H_2 and formate) because electrons released by exoelectrogenic bacteria flow directly via intercellular electrical connections to electrotrophic methanogens. Therefore, electrically coupled syntrophic partners by DIET can avoid complex reactions for the synthesis, diffusion, and utilization of interspecies electron carriers, which makes DIET energetically and kinetically advantageous over IIET (Lovley 2011). An imbalance between the production and consumption of VFAs often occurs in AD processes due to the large difference in growth rate between acidogens and methanogens, especially under high organic loading conditions. In such cases, VFAs (and H_2 partial pressure) build up to levels that cannot be effectively stabilized by IIET-driven hydrogenotrophic methanogenesis, resulting in severe inhibition of methanogenic activity. DIET-driven electrotrophic methanogenesis can accelerate the stabilization of VFA accumulation and help to maintain a stable methanogenic system because of the higher electron transfer efficiency and smaller intermediate loss in DIET compared to IIET (Kato et al. 2012; Leng et al. 2018). For example, the Gibbs free energy change at pH 7 ($\Delta G^{\circ\prime}$) of the propionate oxidation through DIET (Eq. 2.1) is significantly lower than that of the propionate oxidation through IIET via H_2 (Eq. 2.2), with the former being negative (i.e., spontaneous reaction) and the latter being positive (i.e., non-spontaneous reaction) (Jing et al. 2017).

The concentration gradient of electron carriers between syntrophic partners is the main limiting factor for IIET, while that for DIET is considered to be the activation loss (or overpotential) during the flow of electrons through cellular components comprising cell-to-cell electrical connections (Storck et al. 2016). Activation loss is the energy lost to overcome the energy barrier and initiate electron transfer, for example, between terminal membrane-bound redox proteins and e-pili in DIET. It takes place as a result of slow charge transfer in an electrochemical redox reaction, and a certain portion of the electron energy is consumed to drive the reaction at a certain rate (Petrovic 2021).

$$\begin{gathered} C_2H_5COO^- + 0.75H_2O \rightarrow CH_3COO^- + 0.25HCO_3^- + 0.25H^+ + 0.75CH_4 \\ \Delta G^{\circ\prime} = -26.4\ \mathrm{kJ/mol}\ \left(37^{\circ}\mathrm{C}, \mathrm{pH}\ 7\right) \end{gathered} \tag{2.1}$$

$$\begin{gathered} C_2H_5COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2 \\ \Delta G^{\circ\prime} = 72.7\ \mathrm{kJ/mol}\ \left(37^{\circ}\mathrm{C}, \mathrm{pH}\ 7\right) \end{gathered} \tag{2.2}$$

The possibility of DIET between exoelectrogenic bacteria and electrotrophic methanogens was first raised by Stams et al. (2006) based on the observation that acetogens and methanogens form direct physical contact in some methanogenic environments. Experimental evidence for the electro-syntrophic methanogenesis through DIET was first presented in the early 2010s by Morita et al. (2011) with anaerobic granules treating brewery waste, and subsequently by many others in different methanogenic environments (Kato et al. 2012; Liu et al. 2012; Chen et al.

2014b; Rotaru et al. 2014a, b; Shrestha et al. 2014). Given the compact and dense structure of granular sludge, DIET can explain the efficient degradation of propionate by anaerobic granules even when the Gibbs free energy change calculated from the dissolved H_2 available for the granules was positive (Dubé and Guiot 2015).

DIET mechanisms can be classified into two types: biological DIET (bDIET) and mineral DIET (mDIET). The former involves direct cell-to-cell contact via biotic components, whereas abiotic conductive materials support electrical connections between cells in the latter (Shrestha and Rotaru 2014). Electrons are transferred via electron transport proteins, such as outer surface *c*-type cytochromes, or electrically conductive pili (e-pili), also known as nanowires, in bDIET (Fig. 2.3). Electric syntrophy through bDIET was first described by Summers et al. (2010) in defined co-cultures of *Geobacter metallireducens* and *Geobacter sulfurreducens* with ethanol and fumarate as the sole electron donor and acceptor, respectively. *G. metallireducens*, which can oxidize ethanol to obtain energy for growth but cannot use fumarate as an electron acceptor, and *G. sulfurreducens*, which cannot use ethanol as an electron donor but can reduce fumarate as an electron acceptor, developed dense electrically conductive aggregates and syntrophically metabolize ethanol with the reduction of fumarate in the co-cultures, even when an *hyb*-deleted mutant strain of *G. sulfurreducens,* unable to utilize H_2 or formate, was used. However, deletion of the genes encoding OmcS (a multi-heme *c*-type cytochrome) or PilA (the structural protein for e-pili) prevented the syntrophic metabolism between the *Geobacter* strains and their growth. Studies with different mutant strains and transcriptome assays proved the development of DIET via e-pili networks associated with *c*-type cytochromes in the *Geobacter* co-cultures (Summers et al. 2010; Rotaru et al. 2012; Shrestha et al. 2013; Vargas et al. 2013).

2.2.2.2 Biological Direct Interspecies Electron Transfer (bDIET)

The first example of bDIET involving methanogens was demonstrated in co-cultures of *G. metallireducens* and *Methanothrix* (formerly *Methanoseata*) *harundinacea*, which were isolated from an anaerobic digester treating brewery waste with ethanol as the sole substrate for growth (Rotaru et al. 2014b). The co-cultures converted one mole of ethanol to 1.5 moles of methane, indicating that *M. harundinacea* produced methane not only by splitting acetate derived from the oxidation of ethanol by *G. metallireducens,* but also by using other electron donors produced during the ethanol oxidation. *M. harundinacea*, an acetoclastic methanogen that cannot use H_2 or formate as electron donor for methanogenesis, expressed genes for the reduction of CO_2 to CH_4 at high levels. Radiotracer experiments using ^{14}C-bicarbonate showed that one-third of the methane production was derived from CO_2, according to the stoichiometric reactions involving electrotrophic methanogenesis (Eqs. 2.3–2.6). Additionally, the PilA-deficient mutant strain of *G. metallireducens* failed to develop syntrophic IET with *M. harundinacea* and to metabolize ethanol to methane in the co-culture. The multiple lines of evidence proved that the two species were capable of exchanging electrons through DIET for the electrotrophic

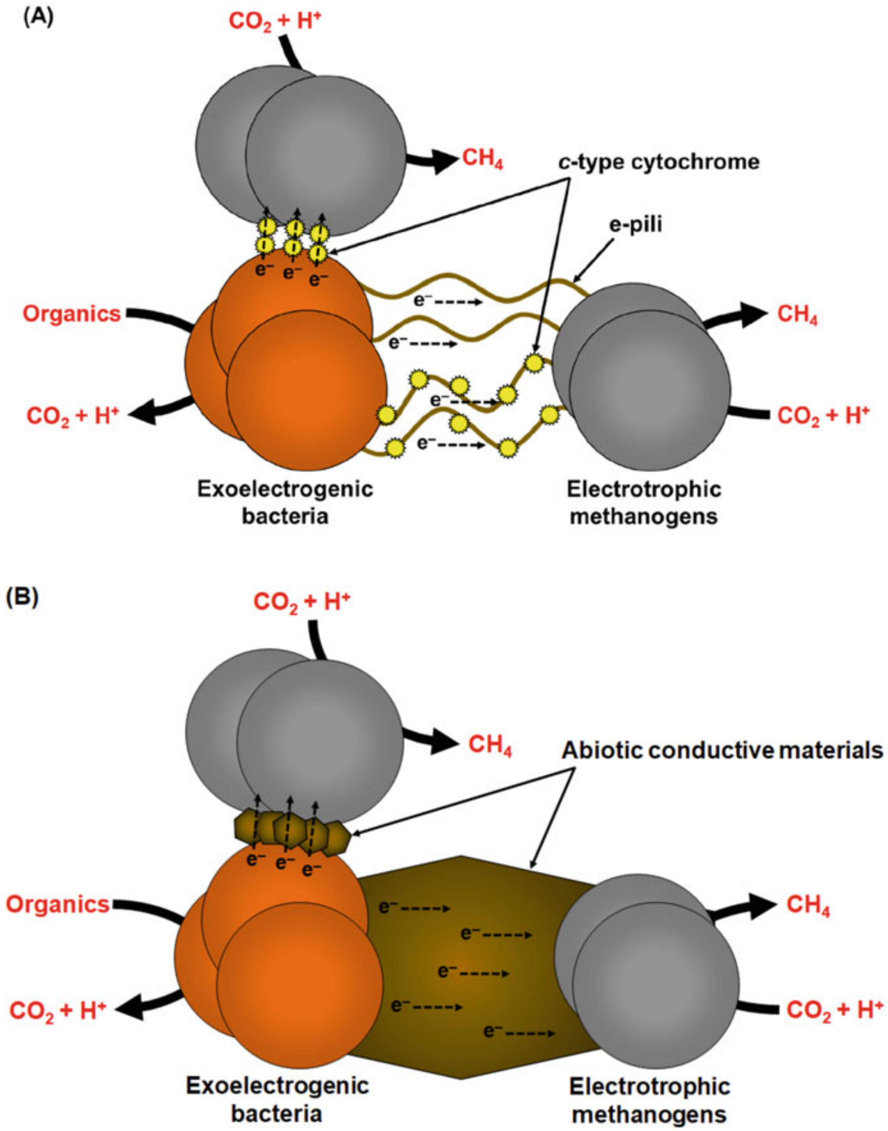

Fig. 2.3 Direct interspecies electron transfer between syntrophic VFA-oxidizing bacteria and hydrogenotrophic methanogens via biotic compounds (A) and abiotic conductive material (B)

methanogenesis of CO_2 and that e-pili played an important role in building their electrical connections. Although the genes for CO_2 reduction were previously found in *Methanothrix* species (Zhu et al. 2012), the electrotrophic conversion of CO_2 to CH_4 by *Methanothrix* was first demonstrated by Rotaru et al. (2014b). This was a surprising finding because *Methanothrix* species were by then known to be strictly acetoclastic and unable to reduce CO_2 (Smith and Ingram-Smith 2007).

$$\textit{Ethanol oxidation}: CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^- \quad (2.3)$$

$$\textit{Acetoclastic methanogenesis}: CH_3COOH \rightarrow CH_4 + CO_2 \quad (2.4)$$

$$\textit{Electrotrophic methanogenesis}: 0.5CO_2 + 4e^- + 4H^+ \rightarrow 0.5CH_4 + H_2O \quad (2.5)$$

$$\textit{Overall reaction}: CH_3CH_2OH \rightarrow 1.5CH_4 + 0.5CO_2 \quad (2.6)$$

A further study by Rotaru et al. (2014a) demonstrated that another acetoclastic methanogen, *Methanosarcina barkeri*, which is metabolically much more diverse than *Methanothrix* species (Boone and Castenholz 2001), could exchange electrons with *G. metallireducens* through DIET via e-pili networks in a similar way, and syntrophically convert ethanol to methane in defined co-cultures. Several other *Methanosarcina* and *Methanothrix* species/strains were additionally shown to be able to accept electrons directly from exoelectrogenic syntrophic partners, and it has been assumed until very recently that only the members of the order *Methanosarcinales*, which have multiheme *c*-type cytochromes, are capable of bDIET among all methanogens (Yee et al. 2019; Yee and Rotaru 2020). However, although the direct electron uptake mechanisms of these methanogens are yet to be fully understood, it was revealed that multiheme *c*-type cytochromes are not necessary in extracellular electron uptake via DIET by *Methanosarcinales* (Yee and Rotaru 2020). Furthermore, the first discovery of DIET involving *Methanobacterium* was very recently reported in defined co-cultures of *Methanobacterium* sp. strain YSL and *G. metallireducens* fed with ethanol (Zheng et al. 2020). This finding contrasts with previous studies that showed the inability of strictly hydrogenotrophic methanogens, *Methanospirillum hungatei*, *Methanoculleus marisnigri* (both belonging to the order *Methanomicrobiales*), and *Methanobacterium formicicum* (belonging to the order *Methanobacteriales*) to grow via DIET in syntrophic associations with exoelectrogenic *Geobacter* species (Rotaru et al. 2014b; Yee et al. 2019; Yee and Rotaru 2020). The results of the iterative defined co-culture studies raise the possibility that much more diverse methanogens are capable of participating in bDIET, which certainly deserves further investigation to better understand (electro-)syntrophic interactions in methanogenic communities. A recent study thermodynamically analyzed the effects of carbon sources and conductive components electrically connecting cells (biotic or abiotic) on DIET in methanogenesis and reported that ethanol may be the most favorable organic carbon source for DIET (Gu et al. 2019).

The bDIET capacity of methanogens has so far only been confirmed in defined co-cultures with exoelectrogenic *Geobacter* species using ethanol as the electron donor. However, Yee and Rotaru (2020) have recently reported that *Rhodoferax ferrireducens* showed significantly higher electron recovery as methane from glucose in co-cultures with electrotrophic methanogens than with strictly hydrogenotrophic methanogens. The use of ethanol that favors the enrichment of

Geobacter species to develop e-pili networks was likely an important factor that facilitated the electro-syntrophic interactions in the DIET co-cultures (Martins et al. 2018). This corresponds to the fact that the existence of bDIET involved in methanogenic systems was first observed in studies of conductive methanogenic aggregates derived from brewery waste digesters (Morita et al. 2011; Rotaru et al. 2014b; Shrestha et al. 2014). Many (putative) exoelectrogenic bacteria other than *Geobacter* species have been suggested (not yet proven) in recent studies to participate in DIET with (putative) electrotrophic methanogens (Barua and Dhar 2017; Park et al. 2018a). Therefore, in order to gain a comprehensive understanding of DIET mechanisms and the involved microorganisms in diverse methanogenic environments, more studies are needed, for example, in defined co-cultures or complex mixed cultures with different electron donors other than ethanol.

2.2.2.3 Mineral Direct Interspecies Electron Transfer (mDIET)

The potential of mDIET in methanogenic environments was first documented by Kato et al. (2012) in enrichment cultures from rice paddy soil. The methane production rates from both acetate and ethanol increased significantly with the addition of (semi)conductive iron oxides, magnetite and hematite (20 mM Fe), in the enrichment cultures. Dissolution of the iron oxides and the use of iron ions as a nutrient or electron shuttle were unlikely to have contributed to the enhancement of methanogenesis, because the ferrous ion concentration was negligible in the cultures. Adding ferrihydrite, an insulative iron oxide, did not accelerate, and even suppressed, methanogenesis. The accelerated methanogenesis was attributed to the stimulation of DIET between *Geobacter* and *Methanosarcina*, based on their predominance in the cultures to which (semi)conductive iron oxides had been added, where the growth of *Geobacter* was suppressed by the addition of 2-bromoethane sulfonate (BES), a methanogenic inhibitor.

Soon after, Liu et al. (2012) demonstrated in defined co-cultures with ethanol as the sole electron donor that granular activated carbon (GAC) could promote DIET between *G. metallireducens* and *M. barkeri* and accelerate the syntrophic conversion of ethanol to methane. The microorganisms were tightly attached to the surface of GAC but did not form direct physical contact as required for bDIET. The DIET-promoting effect of GAC was even more pronounced in the cultures of methanogenic aggregates from a digester treating brewery waste, which was previously reported to be DIET-active (Morita et al. 2011), with the methane production rate from ethanol being 2.5-fold higher with GAC than without. Later, carbon cloth (Chen et al. 2014a) and biochar (Chen et al. 2014b) were also demonstrated in co-cultures of *G. metallireducens* and *M. barkeri* to stimulate the syntrophic metabolism of ethanol through DIET. Conductive materials serve as an electrical conduit for DIET by connecting syntrophic partners, which aggregate to form cell-conductive material complexes (Lovley 2017; Baek et al. 2019). The physical structure of such complexes varies with the particle size of the abiotic conductive materials involved. Microorganisms attach and form biofilms on the surface of

Table 2.2 Electrical conductivity of abiotic conductive materials used for promoting DIET

Conductive materials	Conductivity (mS/cm)	Reference
Granular activated carbon	3–1200	Liu et al. (2012), Cheng et al. (2018)
Carbon cloth	4350	Lei et al. (2016)
Biochar	0.002–220	Chen et al. (2014b), Cheng et al. (2018)
Magnetite	10^5–10^6	Cornell and Schwertmann (2003)
Graphene	8.5×10^5	Lin et al. (2018)
Carbon nanotube	$>10^5$	Yan et al. (2019)
Stainless steel	0.667	Li et al. (2017)
Polyaniline nanorod	~740	Hu et al. (2017)
G. Sulfurreducens e-pili[a]	51	Adhikari et al. (2016)

[a] Pili from wild-type cells were measured in a hydrated state at pH 7

conductive materials that are large enough to serve as supporting media for attached growth, while submicron/nanoparticles agglomerate together with microorganisms to form aggregates such as flocs or granules (Baek et al. 2019).

Conductivity is the key characteristic of abiotic additives for promoting mDIET, bypassing the need for electrical contacts via biological components necessary for bDIET (Shrestha and Rotaru 2014). In support, magnetite nanoparticles were able to compensate for the absence of OmcS, which, together with e-pili, forms electrical conduits for DIET, in co-cultures of a mutant *G. sulfurreducens* strain deficient in OmcS and *G. metallireducens* with ethanol as the electron donor (Liu et al. 2015). In contrast to magnetite, which could only marginally compensate for the lack of PilA (Liu et al. 2015), GAC was able to promote mDIET between the two *Geobacter* species in co-cultures with ethanol, and to effectively compensate for the lack of both PilA and OmcS (Liu et al. 2012). The findings of these studies, although not performed with methanogenic cultures, confirm that abiotic conductive materials can electrically connect DIET partners and stimulate their electric syntrophy, independent of bDIET, and that the DIET mechanisms may differ among different conductive additives with different characteristics, such as conductivity and size (Baek et al. 2019). Biochar (Chen et al. 2014b) was shown to be comparably effective to GAC (Liu et al. 2012) or carbon cloth (Chen et al. 2014a) in promoting DIET, although the conductivity of biochar is approximately 1000-fold lower than that of the others (Table 2.2). Furthermore, semiconductive hematite and conductive magnetite showed similar methanogenesis-accelerating effects in DIET-stimulated soil enrichment cultures with acetate or ethanol (Kato et al. 2012). By contrast, Baek et al. (2015) and Zhuang et al. (2015) reported that the addition of iron oxides with different conductivities (i.e., goethite, hematite, and magnetite) promoted DIET to different extents in methanogenic cultures degrading whey and benzoate, respectively. These results indicate that the DIET-promoting effect of a conductive additive is not determined solely by its conductivity and will thus not continuously increase in proportion to its electrical conductivity (Barua and Dhar 2017).

Following the studies in defined co-cultures, mostly pairing methanogens with *Geobacter* species, which confirmed the existence of DIET in anaerobic environments, many studies have investigated DIET in more environmentally relevant, mixed cultures. In those studies, assessing whether the addition of conductive materials could promote DIET and enhance methanogenesis was of primary interest. Different conductive materials (mostly carbon- or iron-based), such as GAC (Lee et al. 2016; Zhao et al. 2016b; Dang et al. 2017; Yan et al. 2017; Yang et al. 2017; Capson-Tojo et al. 2018; Park et al. 2018b; Chowdhury et al. 2019; Xu et al. 2020; Zhang et al. 2020a), biochar (Luo et al. 2015; Li et al. 2018; Wang et al. 2019b, 2020b; Lü et al. 2020), carbon cloth (Dang et al. 2017; Zhao et al. 2017c), carbon nanotubes (Li et al. 2015b; Zhang and Lu 2016; Yan et al. 2017), graphene (Lin et al. 2017; Tian et al. 2017), magnetite (Cruz Viggi et al. 2014; Baek et al. 2015; Li et al. 2015a; Yamada et al. 2015; Zhuang et al. 2015; Yang et al. 2016; Zhang and Lu 2016; Jing et al. 2017; Yin et al. 2017b; Wang et al. 2018c, 2020a; Zhang et al. 2019a), hematite (Zhuang et al. 2015), and stainless steel (Li et al. 2017) have been tested for their DIET-promoting potential in batch methanogenic cultures with different inocula and substrates. The key observations and culture conditions, such as conductive material dose, inoculum source, and carbon/electron source, of the previous studies are described in detail in recent reviews (Barua and Dhar 2017; Baek et al. 2018; Park et al. 2018a; Gahlot et al. 2020; Zhao et al. 2020a).

Enhancement of methanogenesis by promoting mDIET in mixed-culture studies has been demonstrated on various substrates (or electron donors) besides ethanol, for example, VFAs, glucose, sucrose, benzoate, phenol, whey, waste activated sludge, livestock manure, food waste, and waste cooking oil. Many studies have examined the effect of promoting mDIET on the methanogenesis of VFAs, the main intermediates of AD, and the methanogenic conversion of C_3 or higher VFAs was found to be significantly higher in the presence of conductive materials (Cruz Viggi et al. 2014; Li et al. 2015a, 2017; Yamada et al. 2015; Lee et al. 2016; Yang et al. 2016; Zhang and Lu 2016; Zhao et al. 2016b; Jing et al. 2017). Cruz Viggi et al. (2014) first demonstrated the acceleration of methanogenesis from propionate (up to a 33% increase in the degradation rate) by the addition of submicron magnetite particles in methanogenic cultures derived from a sewage sludge digester. Li et al. (2015a) reported the enhanced methanogenesis from butyrate by supplementation with magnetite nanoparticles in paddy soil enrichments. Yang et al. (2016) showed in a similar study using an equimolar mixture of C_2–C_6 VFAs that the methanogenic degradation rates of the VFAs, particularly higher VFAs, were significantly increased by the addition of magnetite nanoparticles. Furthermore, Lee et al. (2019) demonstrated that the methanogenic conversion rates of C_2–C_4 VFAs could be significantly increased by the addition of magnetite even under high ammonia stress (6.5 g total ammonia N/L). The results of these and other studies suggest that both methanogenic performance and process stability of anaerobic digesters can be improved by promoting DIET with conductive additives. In support, changes in microbial community structure and metabolic properties, accompanied by the DIET-facilitated degradation of VFAs, have been identified by different meta-omic approaches (Li et al. 2015a; Jing et al. 2017; Lee et al. 2019). Besides the accelerated degradation of VFAs, metabolic shifts towards more acetic-type fermentation, which is favorable for methanogenesis in the presence of (semi)conductive iron oxides, were noted in methanogenic reactors treating whey (Baek et al. 2015). The accumulated evidence suggests that promoting mDIET by adding conductive materials can provide a simple and effective means for enhancing methanogenic performance and maintaining stable operation of AD processes.

2.3 Engineering Direct Interspecies Electron Transfer with Conductive Additives

Since the observation by Kato et al. (2012) that methanogenesis was accelerated by adding (semi)conductive iron oxides in anaerobic mixed cultures with acetate or ethanol, the potential of promoting mDIET as a means to improve the performance of anaerobic digesters has gained much attention. As described in the preceding section, many subsequent studies confirmed the widespread occurrence of DIET-active methanogenic consortia in anaerobic environments and demonstrated the DIET-promoting and methanogenesis-boosting effects of various conductive materials in defined co-cultures and mixed cultures. Adding inexpensive conductive materials is currently considered a promising approach to enhance methanogenic performance at a more fundamental level, and significant research efforts have recently been made to investigate this possibility under more realistic conditions for practical applications. This section describes the recent advances in engineering DIET with conductive additives for enhanced methanogenesis in (semi-)continuous anaerobic digesters treating complex organic wastes, including the latest studies at pilot scale. Particular attention is given to the use of different (mostly carbon- or iron-based) conductive additives and their effects on the digester performance.

2.3.1 Carbon-Based Materials

2.3.1.1 Granular Activated Carbon (GAC)

Carbon-based conductive additives, such as activated carbon (both granular and powdered), anthracite, biochar, carbon cloth/felt/fiber, carbon nanotube, graphene, and graphite, have been extensively used to promote mDIET in different types of (semi-)continuous anaerobic digesters (Table 2.3). GAC, which is commonly used as a support medium for biofilm development in attached-growth bioreactors, is among the most used additives to promote mDIET because of its high surface area and electrical conductivity (Table 2.2). Lee et al. (2016) reported in a study using continuously stirred tank reactors (CSTRs) fed with synthetic wastewater containing acetate that the methane production rate was 1.8-fold higher in the digester supplemented with GAC than in the control digester without GAC. Zhao et al. (2017b) operated four two-phase AD systems (i.e., combinations of acidogenic reactors with or without magnetite, and methanogenic reactors with or without

Table 2.3 Studies on engineering DIET in (semi-)continuous anaerobic digesters with conductive additives

Additive[a]	Dose[b]	Inoculum[c]	Substrate[d]	Reactor type[e]	Temp[f] (°C)	Reference
GAC	10 g/L	ADS	SWW (Hac)	CSTR	35	Lee et al. (2016)
	40 g/L	ADS	SWW (glucose + milk powder)	Two-phase SBR	37	Zhao et al. (2017b)
	25 g/L	ADS	SWW (glucose)	UASB	20.0 ± 0.5	Zhang et al. (2020c)
	15 g/L	ADS	SWW (glucose)	UASB	37	Guo et al. (2020a)
	5 g/L	SSS	SWW (ethanol + glucose)	UASB	35 ± 2	Xu et al. (2015)
	100% (v/v)	ADS	SWW (fructose + polyethylene glycol)	UPBR	35	Mei et al. (2018)
	100 g/L	ADS	Commercial dog food	SBR	37	Dang et al. (2016)
	75 g/L	ADS	MSW incineration plant leachate	UASB	33 ± 1	Lei et al. (2019)
	10 g/L	ADS	HTLWW from sewage sludge	SBR	37	Usman et al. (2019)
	80 g/L	ADS	HTLWW from swine manure	UPBR	37	Yang et al. (2020b)
	25 g/L	ADS	Municipal primary effluent	UASB	16.5 ± 2.0	Zhang et al. (2020b)
PAC	5 g/L	SSS	SWW (EtOH + glucose)	UASB	35 ± 2	Xu et al. (2015)
	5–35 g/L	ADS	Food waste	CSTR	35	Zhang et al. (2017)
	7.5–30 g/L	ADS	Food waste	CSTR	37	Zhang et al. (2018)
Biochar	2.5 g/L	ADS	SWW (EtOH)	UASB	37	Zhao et al. (2015)
	5 g/L	ADS	SWW (EtOH + Hpr)	UASB	37	Zhao et al. (2016a)
	5 g/L	ADS	SWW (EtOH + Hbu)	UASB	37	Zhao et al. (2016a)
	4 g/L	–	SWW (sucrose)	UASB	35 ± 2	Wang et al. (2018a)
	4 g/L	–	SWW (sucrose)	UASB	35 ± 2	Wang et al. (2021a)
	5–10 g/L	ADS	Food waste	Two-phase CSTR	35/55[g]	Lim et al. (2020)
Carbon cloth	200 cm^2/L	ADS	SWW (EtOH)	UASB	37	Zhao et al. (2015)
	500 cm^2/L	ADS	SWW (butanol)	SBR	37	Zhao et al. (2017c)
	667 cm^2/L	ADS	SWW (glucose + glycine)	Two-phase CSTR	35 ± 1	Feng et al. (2020)
	977 cm^2/L	ADS	Commercial dog food	SBR	37	Dang et al. (2016)

(continued)

Table 2.3 (continued)

Additive[a]	Dose[b]	Inoculum[c]	Substrate[d]	Reactor type[e]	Temp[f] (°C)	Reference
	833 cm^2/L	ADS	MSW incineration plant leachate	UASB	33 ± 1	Lei et al. (2016)
Graphite	200 cm^2/L	ADS	SWW (EtOH)	UASB	37	Zhao et al. (2015)
	106 cm^2/L	ADS	SWW (EtOH + Hpr)	SBR	37	Zhang et al. (2019b)
	106 cm^2/L	ADS	SWW (EtOH + Hbu)	SBR	37	Zhang et al. (2019b)
	60% (v/v)	MECE	SWW (glucose)	UPBR	25 ± 3	Guo et al. (2018)
	1000 cm^2/L	ADS	Commercial dog food	SBR	37	Dang et al. (2016)
Carbon felt	30 g/L	ADS	SWW (glucose)	Upflow SBR	35 ± 3	Xu et al. (2016)
	977 cm^2/L	ADS	Commercial dog food	SBR	37	Dang et al. (2016)
Anthracite	100% (v/v)	ADS	SWW (fructose + polyethylene glycol)	UPBR	35	Mei et al. (2018)
Carbon fiber	1.583 m^2/L	ADS	SWW (Hpr + Hbu)	Fed-batch	37 ± 1	Barua et al. (2018)
CNT	1.5 g/L	ADS	Beet sugar wastewater	EGSB	36 ± 1	Ambuchi et al. (2017)
Graphene	30–120 mg/L	ADS	SWW (glucose)	UASB	10–20	Tian et al. (2017)
Magnetite	100 g/L	ADS	High-salinity SWW (Hac)	UASB	37	Chen et al. (2020)
	10 g Fe/L	–	SWW (Hac)	UASB	35 ± 2	Wang et al. (2020a)
	10 g Fe/L	–	SWW (Hpr + Hbu)	UASB	35 ± 2	Wang et al. (2020a)
	10 g Fe/L	–	SWW (sucrose)	UASB	35 ± 2	Wang et al. (2020a)
	20 mM Fe	ADS	Sulfate-rich SWW (glucose)	UASB	37 ± 1	Jin et al. (2019)
	10 g/L	ADS	Sulfate-rich SWW (EtOH + Hac + Hpr)	SBR	35 ± 1	Liu et al. (2019)
	10 g Fe/L	–	SWW (sucrose)	UASB	35 ± 2	Wang et al. (2019a)
	10 g/L	ADS	SWW (Hac + starch + tryptone)	SBR	35	Yin et al. (2017b)
	10 g/L	ADS	SWW (tryptone)	SBR	35 ± 1	Yin et al. (2017a)
	10 g/L	SSS	SWW (tryptone)	SBR	35 ± 1	Yin et al. (2018)
	20 mM Fe	ADS	Whey	CSTR	35 ± 2	Baek et al. (2016)
	20 mM Fe	ADS	Whey	CSTR	35	Baek et al. (2017)
	10 g/L	ADS	MSW incineration plant leachate	UASB	35 ± 1	Lei et al. (2018)

	0.1–0.3 g/L	ADS	Fischer-Tropsch wastewater	SBR	37	Wang et al. (2018b)
	2–20 mM Fe	ADS	*Ulva*/whey mixture	CSTR	35 ± 2	Jung et al. (2020)
IONP	0.75 g/L	ADS	Beet sugar wastewater	EGSB	36 ± 1	Ambuchi et al. (2017)

[a] GAC, granular activated carbon; PAC, powdered activated carbon; CNT, carbon nanotube; IONP, iron oxide (Fe_2O_3) nanoparticle

[b] Concentration (mass, molar, or volumetric) or geometric surface aera per reactor working volume

[c] ADS, anaerobic digester sludge; SSS, settled secondary sludge; MECE, microbial electrolysis cell effluent

[d] SWW, synthetic wastewater (main carbon sources); MSW, municipal solid waste; HTLWW, hydrothermal liquefaction wastewater; Hac, acetate; Hpr, propionate; Hbu, butyrate; EtOH, ethanol

[e] CSTR, continuously stirred tank reactor; SBR, sequencing batch reactor; UASB, upflow anaerobic sludge blanket; UPBR, upflow packed bed reactor; EGSB, expanded granular sludge bed

[f] Temp, reactor operation temperature

[g] Temperature-phased (acidogenic reactor/methanogenic reactor)

GAC) with synthetic dairy wastewater in sequencing batch mode. They found that GAC could accelerate the syntrophic methanogenesis of simple organics, such as ethanol and VFAs, when efficient acidogenesis was achieved in the presence of magnetite.

Zhang et al. (2020c) and Guo et al. (2020a) reported significant increases in chemical oxygen demand (COD) removal and methane production in upflow anaerobic sludge blanket (UASB) reactors treating low-strength synthetic wastewater containing glucose (500 mg COD/L) at psychrophilic and mesophilic temperatures, respectively. Xu et al. (2015) compared the effects of GAC (0.84–2.00 mm) and powdered activated carbon (PAC; 75–177 μm) on the anaerobic treatment of synthetic brewery wastewater in UASB reactors. Both GAC and PAC enhanced the methanogenic degradation of ethanol and VFAs and facilitated the enrichment of methanogens, while PAC with more abundant micro-mesoporous structures for the colonization of DIET partners induced a greater increase in methane production, particularly at higher organic loading rates (OLRs). Mei et al. (2018) reported, in a study of the DIET-stimulated methanogenic degradation of synthetic soft drink processing wastewater using upflow packed bed reactors (UPBRs), that the daily methane production relative to the biomass concentration was 43.3% and 31.5% greater in the digesters filled with GAC and anthracite, respectively, than in the control digester with non-conductive ceramic media. They suggested a syntrophic association between a novel *Geobacter* population and *Methanothrix* in the DIET-stimulated digesters based on the metagenomic analysis results.

Additionally, several studies have reported the promotion of mDIET with activated carbon in (semi-)continuous digesters treating real waste/wastewater of different characteristics. Dang et al. (2016) compared four carbon-based conductive materials (GAC, carbon cloth, carbon felt, and graphite rod; with similar geometric surface areas of ~1000 cm^2/L) for their effects on the performance of anaerobic sequencing batch reactors (SBRs) treating commercial dog food (as a proxy for food waste). The digesters supplemented with GAC, carbon cloth, and carbon felt showed better and more stable AD performance than the control digesters with polyester cloth or no material added, particularly at higher OLRs, whereas adding graphite rods was ineffective in promoting or stabilizing methanogenesis.

Usman et al. (2019) and Yang et al. (2020b) studied the effect of adding GAC in anaerobic digesters treating hydrothermal liquefaction wastewaters from sewage sludge (SBR) and swine manure (UPBR), respectively. Both studies claimed that GAC enhanced the methanogenic performance of the digesters by promoting DIET, although the adsorption of inhibitors by GAC also must have contributed to the improved methane yield. Lei et al. (2019) reported that GAC dosing promoted DIET involving electroactive *Geobacter* and *Methanosarcina* and enhanced the methanogenic performance in UASB reactors fed with municipal solid waste incineration leachate. The leachate was effectively treated without a lag period in the GAC-added digester at increasing OLRs from 5.9 to 36.7 g COD/L·d, while the control digester without GAC failed within the first 17 days of operation at the lowest OLR of 5.9 g COD/L·d. Zhang et al. (2020b) compared low-temperature (16.5 ± 2.0 °C) UASB reactors with and without GAC addition for the methanogenic treatment of municipal sewage (primary-treated effluent). Potential electro-syntrophic partners including *Geobacter* were enriched by the addition of GAC, and accordingly the GAC-amended digester showed significantly higher COD removal and methane production.

Zhang et al. (2017) investigated the effects of different doses of PAC (5–35 g/L) in anaerobic CSTRs treating food waste. PAC addition facilitated the colonization of microorganisms, particularly methanogens, and accelerated the degradation of lipids, thereby enhancing the conversion of food waste to methane, with the optimal PAC dose to promote methanogenesis being 15 g/L. Zhang et al. (2018) conducted a similar study of food waste AD in lab-scale CSTRs, with a similar PAC dose range (7.5–30 g/L), and then operated a pilot-scale CSTR (working volume, 700 L) supplemented with the optimal amount of PAC as determined from lab-scale experiments (15 g/L). Enhancements of methane production and operation stability were achieved by the addition of PAC in the lab- and pilot-scale experiments, with the methane yield of the pilot-scale digester being 41% higher with PAC supplementation than without.

2.3.1.2 Biochar

Biochar, particularly when produced from waste biomass, is a low-cost alternative to GAC. Although much less conductive than other carbon-based materials (Table 2.2), biochar is highly porous and rich in electroactive surface functional groups such as quinones (Sun et al. 2017), which is beneficial for enriching electroactive microorganisms and promoting DIET (Chen et al. 2014b; Zhao et al. 2016a). Several studies have demonstrated the enhancement of methane production, mostly from synthetic wastewater, by the addition of biochar in (semi-)continuous experiments (Table 2.3). Zhao et al. (2016a) reported, in a study using UASB reactors fed with ethanol/propionate or ethanol/butyrate mixtures, that biochar effectively enriched electroactive *Geobacter* and *Methanothrix* species and promoted the DIET-based syntrophic degradation of propionate or butyrate. Similar DIET-promoting effects, along with the enrichment of potential electro-syntrophic partners, were also observed with the addition of biochar in UASB reactors treating synthetic wastewater containing sucrose (Wang et al. 2018a, 2021a).

Zhao et al. (2015) compared biochar, carbon cloth, and graphite rod for their effectiveness in enhancing the AD of synthetic wastewater containing ethanol in UASB reactors. The three conductive additives significantly enhanced the syntrophic conversion of ethanol to methane, resulting in greater organic removal and methane production compared to those of the control digester without conductive material. The differences became more pronounced with increasing OLR (4.11–12.33 g COD/L·d), and the enhancement of methanogenic performance disappeared immediately when the conductive additives were removed from the digesters. Lim et al. (2020) examined the effect of biochar at different doses (5 and 10 g/L) on the food waste AD in temperature-phased two-phase CSTRs (i.e., mesophilic acidogenesis and thermophilic methanogenesis). The biochar-supplemented digesters showed comparable methane yields, which were significantly higher than those of the control digester without biochar, and the 5 g/L dose of biochar (representing an 18% increase in methane yield) was found to be optimal for the two-phase AD system. Biochar addition enriched methanogens (i.e., increase in the archaea-to-bacteria ratio) and electroactive bacteria, thereby enhancing the degradation of VFAs by promoting both DIET and acetoclastic methanogenesis.

2.3.1.3 Carbon Cloth, Felt and Fiber

Carbon cloth, felt, and fiber with high electrical conductivity have also been demonstrated to promote syntrophic metabolism and accelerate methanogenesis in several (semi-)continuous digesters fed with synthetic wastewaters with different organic compounds as the main electron donor, such as ethanol (Zhao et al. 2015), butanol (Zhao et al. 2017c), glucose (Xu et al. 2016), a propionate/butyrate mixture (Barua et al. 2018), and a glucose/glycine mixture (Feng et al. 2020). As mentioned above, carbon cloth and felt were tested, together with other conductive additives, in a study using SBRs treating commercial dog food, and their effectiveness in promoting DIET and improving digester performance and stability was demonstrated (Dang et al. 2016). Lei et al. (2016) reported in a study using UASB reactors treating municipal solid waste incineration leachate, that the carbon cloth-added digester maintained stable performance with high organic removal at OLRs up to 49.4 g COD/L·d, where the control digester without carbon cloth failed with an accumulation of VFAs. They found that the addition of carbon cloth enriched potential exoelectrogenic bacteria and electrotrophic methanogens and increased sludge conductivity by approximately two-fold, indicating the development of a DIET-active methanogenic community.

2.3.1.4 Carbo Nanotubes

Ambuchi et al. (2017) assessed the effects of adding multi-well carbon nanotubes or iron oxide (Fe_2O_3) nanoparticles in expanded granular sludge bed reactors treating beet sugar wastewater. The digester supplemented with Fe_2O_3 nanoparticles (0.75-g/L dose) produced more methane than the one with carbon nanotubes (1.5-g/L dose), while both digesters showed significantly higher methane production than the control without conductive additive, although the cumulative methane content in biogas was as low as 32–33% in all three digesters. Both carbon nanotubes and Fe_2O_3 nanoparticles were suggested to provide electrical connections between DIET partners and accelerate methane production. However, the former promoted the enrichment of bacteria rather than methanogens, whereas the latter showed the opposite tendency. Notably, carbon nanotubes have been reported to enhance methanogenesis in pure cultures of methanogens, independently of DIET (Salvador et al. 2017). This effect was attributable to the reduction of the oxidation-reduction potential (only in the presence of reducing agents) and provision of large electroactive surface area for microbial adhesion, both of which are beneficial for the growth of methanogens, by the addition of carbon nanotubes (Martins et al. 2018). The market price of carbon nanotubes is US$100–150/kg (Fan et al. 2020), which is 10–100 times more expensive than activated carbon (Yunus et al. 2020). Hence, its continuous addition to digesters, despite its demonstrated effectiveness, is not economically feasible.

2.3.1.5 Graphite

Graphite is a crystalline form of carbon that is highly conductive and commonly used as electrode material. Promotion of DIET and enhancement of methanogenesis by the addition of graphite in the form of felt, granules, and rods have been demonstrated in SBRs, UPBRs, and UASB reactors fed with synthetic wastewaters containing ethanol, VFAs, and/or glucose as the main electron donors (Zhao et al. 2015; Guo et al. 2018; Zhang et al. 2019b). In contrast, Dang et al. (2016) reported that graphite rods did not have any promoting effect, while the other carbon-based materials tested in parallel (i.e., GAC, carbon cloth, and carbon felt) significantly enhanced methanogenic performance, in anaerobic SBRs treating commercial dog food. This inconsistency was not specifically addressed in the study and requires further investigation for clarification.

Different doses of graphene, or single-layer graphite, were applied to UASBs fed with synthetic wastewater containing glucose in a study on the DIET-promoting effect of graphene during AD (Tian et al. 2017). The low-dose digester (30 mg graphene/L) showed a significantly higher methane production rate compared to the control digester without graphene, whereas the high-dose digester (120 mg graphene/L) showed a slight inhibitory effect on methanogenesis, during the experiments at room temperature (10–20 °C). Although the reasons for this inhibition were not explored, microbial community structure analysis indicated that the long-term exposure to graphene in the high-dose digester may have suppressed the growth of dominant microorganisms, such as *Methanothrix*, *Lactococcus*, and *Anaerolinea*. The addition of graphene helped to maintain a high relative abundance of *Methanothrix* and enriched *Geobacter* in the digesters, reflecting the development of DIET-based electric syntrophy. Although graphene was effective in promoting DIET at a much lower concentration compared to other carbon-based conductive materials described above (Table 2.3), its price is still prohibitive for use in (semi-) continuous applications. The market price of graphene nanoplatelets ranges from several hundred to well over one hundred thousand US dollars per kilogram, depending on the grade (La et al. 2020).

2.3.2 *Iron-Based Materials: Magnetite*

2.3.2.1 Synthetic Wastewater

In contrast to batch studies, use of iron-based conductive additives other than magnetite to promote mDIET during AD has rarely been reported in (semi-) continuous experiments. However, it provides many advantages owing to its low cost (US$0.35–2.7/kg 100-mesh powder at Alibaba.com [accessed 5 Jan 2021]), high abundance in nature, and non-toxicity (He et al. 2017). Yin et al. (2017b) demonstrated in SBRs treating synthetic wastewater containing acetate, soluble starch, and tryptone that the addition of magnetite accelerated methane production. They suggested *Methanosarcina* species as the major methanogens involved in DIET in the digesters, based on high-throughput sequencing data. However, *Methanosarcina* remained as the most abundant methanogen genus throughout the experiment in both the magnetite-added and control digesters. This interpretation may need to be reconsidered and supported by further evidence, particularly given that the operation time of 43 days (cf. sludge retention time of 33 days) would not be sufficient for reshaping microbial community structure. The same group reported similar results in other studies using SBRs fed with synthetic wastewater containing tryptone (Yin et al. 2017a, 2018). Methane production rate and electron transport system activity were significantly enhanced by the addition of magnetite in both studies. The latter study showed that genes involved in the CO_2-reducing methanogenic pathway were assigned mainly to *Methanosarcina,* and the conductivity of sludge increased in the magnetite-added digester, suggesting that magnetite stimulated DIET-driven electrotrophic methanogenesis by *Methanosarcina*.

Wang et al. (2019a) studied the effect of magnetite addition on the start-up and starvation recovery of UASB reactors fed with synthetic wastewater containing sucrose. Both biogas production and organic removal efficiency were enhanced by the addition of magnetite, and the recovery time after a 60-day starvation was shortened by half in the magnetite-supplemented digester compared to that in the control digester without magnetite. Potential DIET partners, such as *Syntrophaceae* and *Methanothrix*, were enriched during the recovery from starvation in the presence of magnetite.

Wang et al. (2020a) compared the AD performance of two UASB reactors added with the same mass of magnetite and silica, respectively, at increasing OLRs from 1 to 10 g COD/L·d while changing the substrate (acetate, propionate/butyrate mixture, and sucrose in order) in synthetic wastewater fed to the digesters. The magnetite supplemented digester showed better COD removal and methane productivity than did the one with silica, for all substrates tested, with the enhancement of biogas production being greatest for sucrose-containing wastewater (23% increase). Magnetite addition also improved the intensity, hydrophobicity, and electroactivity of granular sludge and enriched different potential DIET partners on different substrates. Chen et al. (2020) demonstrated that magnetite addition enhanced the methanogenic treatment of synthetic wastewater containing acetate with high salinity (0.4 M NaCl) in UASB reactors. Significant acceleration of VFA degradation and methanogenesis was observed in the magnetite-supplemented digester compared to the control digester without conductive additive. Microbial community analysis revealed that the addition of magnetite enriched biofilm-forming exoelectrogenic bacteria, especially *Pseudomonas*, and electrotrophic methanogens, especially *Methanosarcina*, which potentially interacted via DIET under the high-salinity experimental conditions.

2.3.2.2 Sulfate Rich Wastewaters

Jin et al. (2019) tested the effect of magnetite addition in UASB reactors treating sulfate-rich synthetic wastewater containing glucose while varying the COD/sulfate ratio from 5.0 to 2.5. They observed simultaneous enhancement of methanogenesis and sulfate removal in the magnetite-supplemented digester and suggested the establishment of electric syntrophy via DIET between Fe(III)/sulfate-reducing bacteria and methanogens. By contrast, Liu et al. (2019) reported that the sulfate-reducing activity was reduced by the addition of magnetite, while VFA degradation and methanogenesis were promoted, in anaerobic SBRs fed with sulfate-rich synthetic wastewater (COD/sulfate ratio = 6.0) containing ethanol, acetate, and propionate.

Furthermore, a more recent study that examined the effect of magnetite in anaerobic CSTRs treating a sulfur-rich organic waste mixture (*Ulva* biomass and cheese whey; 0.8% w/w dry weight) observed no apparent enhancement of methanogenic performance by the addition of magnetite (Jung et al. 2020). It was found instead that the H_2S content in biogas decreased remarkably with magnetite addition through anaerobic oxidation of sulfide to elemental sulfur, which was suggested to be coupled via DIET with electrotrophic methanogenesis. These different observations may be attributed in part to the differences in experimental conditions, such as inoculum source, magnetite dose, substrate/electron donor, and reactor type/operation mode, and at the same time underscore the need for more studies in sulfate/sulfur-rich environments, where sulfate-reducing bacteria can compete strongly with methanogens for common electron donors.

2.3.2.3 Industrial Wastewaters

The DIET-promoting effect of magnetite was also demonstrated with different real waste streams in (semi-)continuous anerobic digesters. Baek et al. (2016) demonstrated the beneficial effect of magnetite on the methanogenic performance and stability of anaerobic CSTRs treating whey in long-term experiments over a one-year period. As an extension study, they investigated the potential of magnetic separation and recycling of magnetite from the digester effluent as a means to maintain enhanced stable digester performance without continuous supplementation with magnetite (Baek et al. 2017). Magnetite recycling effectively maintained promoted DIET and methanogenic activities over a long period of time (>250 days) and helped to maintain high biomass retention by returning active microorganisms associated with magnetite to the digester. In both of the above studies, magnetite addition significantly affected the microbial community structure, and *Methanothrix* was suggested to be responsible for electrotrophic methanogenesis via DIET.

Lei et al. (2018) reported the enhancement of methane production and COD removal with the addition of magnetite in UASB reactors treating municipal solid waste incineration leachate. The microbial community structure was significantly different between the digesters with and without magnetite addition, and exoelectrogenic bacteria and electrotrophic methanogens (*Methanosarcina* and *Methanothrix*), which were potentially involved in DIET, were enriched in the magnetite-supplemented digester. Wang et al. (2018b) compared anaerobic SBRs added with different doses of magnetite (0–0.3 g/L) for the treatment of Fischer-Tropsch wastewater from a coal-to-liquids plant. The digesters supplemented with 0.1 or 0.2 g/L magnetite showed a significantly higher organic removal and methane production compared to the control digester, with 0.2 g/L being the optimal magnetite dose, while the digester dosed with 0.3 g/L magnetite showed the worst performance. Magnetite addition promoted the enrichment of *Geobacter* and *Methanothrix* and their electric syntrophy via DIET, particularly at the optimal magnetite dose.

2.3.3 Other Conductive Additives

New and other conductive materials besides the above-mentioned carbon- and iron-based materials have been evaluated for effectiveness in promoting DIET during AD in recent studies. However, most of the studies have been performed in batch mode with synthetic wastewater, and limited information is available on the practicability of the materials in (semi-)continuous processes. Polyaniline, a conductive polymer, was applied in the form of a hydrogel (Zhou et al. 2021) and nanorod (Hu et al. 2017) to promote DIET in the methanogenic treatment of synthetic wastewater containing sucrose in batch cultures, and proved effective in accelerating methane production. Wang et al. (2021b) prepared magnetite-contained biochar using iron-rich Fenton sludge and demonstrated its promoting effect on DIET and methanogenesis in batch cultures anaerobically treating synthetic dairy wastewater.

Yang et al. (2020a) reported that composite GAC-MnO_2 was significantly more effective than GAC in enhancing electron transfer between syntrophic microorganisms and thus methanogenesis during the batch AD of synthetic wastewater containing starch. Different non-iron transition metal compounds (i.e., WO_2, WC, W_2N, $W_{18}O_{49}$, TaO_x, Nb_2O_5, and HfO_2) were shown to be effective in stimulating DIET and enhancing methane production in anaerobic batch cultures fed with dairy manure (Wang et al. 2020c; Yun et al. 2021). Guo et al. (2020b) examined the effect of nickel foam addition on the batch methanation of synthetic wastewater containing ethanol and reported that nickel foam effectively promoted DIET and accelerated methane production.

Liu et al. (2020) compared the performance of three anaerobic integrated floating fixed-film activated sludge (An-IFFAS) reactors filled with high-density polyethylene (HDPE)-based carriers with 3%, 5%, and 7% (w/w) graphite contents with two control reactors, one anaerobic floc reactor and one An-IFFAS reactor filled with plain HDPE carriers, for the continuous anaerobic treatment of synthetic wastewater containing ethanol. All graphite-modified carrier-filled reactors performed significantly better than the controls, and the reactors filled with the carriers with higher graphite contents showed greater methanogenic performance. The addition of graphite-modified carriers enriched potential DIET partners, *Geobacter* and *Methanothrix*, which could accelerate syntrophic methanogenesis.

2.4 Future Perspectives

VFA oxidizers and methanogens have been conventionally thought to exchange electrons exclusively through IIET via microbially produced H_2 or formate as electron carriers. However, the existence of DIET which transfer electrons through cell-to-cell electrical connections was recently revealed, and it is now clear that different exoelectrogenic bacteria and electrotrophic methanogens involved in AD can exchange electrons through DIET. IIET and DIET coexist in methanogenic environments, and together play an important role in balancing acidogenesis and methanogenesis during the conversion of organic matter into methane. Over the last decade, considerable efforts have been made to enhance the performance and stability of AD processes by promoting DIET, mostly by adding conductive materials (i.e., promoting mDIET), because DIET is energetically and kinetically advantageous over IIET.

The effectiveness of this simple strategy in enriching DIET-active methanogenic consortia and accelerating methanogenesis has been well demonstrated in many recent studies using different conductive additives (mostly carbon- or iron-based) in batch and (semi-)continuous cultures. Our understanding of the role of DIET in methanogenic environments has evolved significantly in recent years, and promoting mDIET using inexpensive conductive additives is considered a promising strategy to accelerate methanogenesis in anaerobic digesters. However, biochemical mechanisms and microbial interactions underlying DIET during AD, particularly in engineered systems treating complex organic wastes, are still poorly understood, and much more work needs to be done to engineer DIET-based electric syntrophy in anaerobic digesters in the field for enhanced methanogenic performance. Outlined below are some points to deliberate in future studies of engineering DIET for practical applications.

2.4.1 Retention of Additives in the Reactor

For field application, preventing or minimizing the loss of conductive additives by washout from (semi-)continuous digesters is important. Continuous addition of conductive materials is not an economical and scalable solution. For example, a pilot-scale food waste digester (1 m^3) added with PAC (15 g/L) lost 0.345 kg PAC daily in the discharged digestate, and the cost of replenishing the loss accounted for up to 81.8% of the income from biogas production (Zhang et al. 2018; Zhao et al. 2020a). Discharge of conductive additives in digestate increases the volume of residual solids that needs further treatment, resulting in an increase in operating costs. Baek et al. (2017) demonstrated that the enhanced methanogenic performance of a CSTR was stably maintained over a long period of time (>250 days) by magnetically separating and recycling magnetite from the digestate. However, this method is not applicable to non-magnetic materials, and the efficiency of magnetic separation (and physical screening) would be low for small-size particles.

Many studies applied upflow reactors (i.e., UASB and EGSB) or SBRs to retain conductive additives, which are heavy enough to settle down and/or aggregate well with biomass, in the digesters with minimum washout loss. Although effective in delaying the loss, this approach cannot prevent the discharge of conductive materials with the excess sludge. Furthermore, UASB/EGSB-type digesters are not suitable for treating suspended solids-rich waste streams, such as food waste, sewage sludge, and manure, which are major feedstocks for biogas production. A promising approach is fixing conductive media in, for example, anaerobic filter or packed bed reactors, although the specific surface area for the attached growth of DIET syntrophic partners will be reduced compared to using small particles. Fabricating and applying non-toxic, non-reactive support media with high conductivity and large specific surface area is a key in this respect. The moving-bed biofilm reactor, which is advantageous in mass transport over fixed-bed reactors, is also a reactor design of choice to apply conductive media for promoting DIET (Liu et al. 2020). However, these biofilm reactors are also not applicable to high-suspended solids waste streams, which can cause biofilm damage and clogging problems. Further research is needed to minimize the consumption of conductive additives while maintaining a desired level of digester performance enhancement for long-term operation.

2.4.2 External Voltage Supply

Several studies applied the addition of conductive materials combined with the application of external voltage as a strategy to further promote DIET and boost syntrophic methanogenesis (Baek et al. 2020, 2021; Vu et al. 2020). Combining AD with a microbial electrolysis cell (AD-MEC) has been suggested as a way to improve AD performance, because the cathodic CO_2 conversion to CH_4 by electrotrophic or hydrogenotrophic methanogens increases methane production. However, it is yet to be clarified whether the main role of the electrodes in an AD-MEC system is providing surfaces for the growth of biofilms (i.e, enhanced biomass retention) or stimulating bioelectrochemical reactions involved in AD (Baek et al. 2021).

External voltage application enhances the activity of microorganisms capable of extracellular electron exchange, and therefore it would be worth investigating whether or not combining AD-MEC and mDIET promotion using conductive additives has a synergistic effect on accelerating methanogenesis. Recent studies using magnetite (Baek et al. 2020) and carbon brush (Baek et al. 2021) reported that adding conductive materials (or providing conductive surface area) was significantly more effective in enhancing AD performance than applying external voltage, which contributed little to methane production. So far, only a few studies have addressed this question, and more results are needed to draw valid conclusions.

2.4.3 Two Stage AD (Ethanol AD)

Another interesting approach which could be applied in combination with adding conductive materials (or applied alone) to promote DIET is ethanol-type fermentation pretreatment. A two-stage process consisting of ethanol-type fermentation and methanogenesis stages has been demonstrated to effectively promote DIET and enhance energy recovery in several recent studies from a research group using synthetic dairy wastewater (Zhao et al. 2017a), waste activated sludge (Zhao et al. 2018), corn straw (Zhu et al. 2019), bagasse wastes (Zhao and Zhang 2019), and food waste (Zhao et al. 2020b). The two-stage approach is reasonable given that ethanol is possibly the most favorable substrate for DIET (Gu et al. 2019) and that DIET syntrophy prevailed in UASB granules treating ethanol-rich brewery wastewater (Morita et al. 2011; Rotaru et al. 2014b; Shrestha et al. 2014). This bDIET-promoting strategy may be combined with the addition of conductive materials for possible synergistic effects on the methanogenic performance and biomass retention (Zhao and Zhang 2019).

2.4.4 Improved Analytical Tools

Although numerous studies have empirically demonstrated the enhancement of syntrophic degradation of fermentation intermediates and methanogenesis by adding conductive materials in anaerobic digesters, to date, the evidence for promoted DIET activity has been indirect and circumstantial. This is due to the lack of techniques to quantitatively trace the flow of electrons released from the degradation of organic matter in complex methanogenic consortia. Although still indirect, a combination of meta-omic, electrochemical (e.g., cyclic voltammetry and sludge conductivity), and metabolic (e.g., stable isotope probing) analyses is currently the best strategy to evaluate the occurrence of DIET. A recent review article discusses different methods that have been used to confirm the occurrence of DIET in methanogenic systems and the need for the development of suitable DIET characterization methods in detail (Van Steendam et al. 2019). Technologies for engineering DIET for enhanced AD are still in the embryonic stage. Quantitative methods to monitor DIET activity will not only help to advance our fundamental understanding of DIET but also to enable better engineering and operation of DIET-aided AD processes. Furthermore, such methods will provide the ability to unravel the conflicting results in the literature.

Although conductive materials have generally been reported to promote DIET and enhance the methanogenic conversion of organic matter, a few studies have demonstrated no or rather inhibitory effects for some carbon- and metal-based conductive materials, such as ferrihydrite, carbon black, magnesium oxide, and silver nanoparticles (Martins et al. 2018; Baek et al. 2019). It is understandable that conductive materials may exert different effects on DIET and thus methanogenesis according to their different physicochemical properties (e.g., electric conductivity, crystallinity, solubility, surface area, porosity, morphology, and point of zero charge) and the digester environmental conditions (e.g., substrate, inoculum, oxidation-reduction potential, pH, temperature, inhibitory substances, and other operational parameters). However, the underlying reasons for the conflicting results, especially for the inhibitory effects, are not well understood, although their understanding is vital for effectively engineering DIET for enhanced methanogenesis.

2.4.5 Other Electro-Syntrophic Interactions

Another point that needs to be addressed is the effect of the addition of conductive materials on electro-syntrophic interactions other than electrotrophic methanogenesis. Many studies have reported enhancement of microbial and enzymatic activities related to hydrolysis, fermentation, and acetoclastic methanogenesis, besides those associated with CO_2-reducing methanogenesis, in methanogenic cultures supplemented with conductive additives. These observations are not surprising given that highly diverse microorganisms, including many (potential) electroactive microorganisms, coexist and interact in mixed-culture methanogenic systems. It is not unlikely that mDIET-promoting approaches may affect other microbial redox processes, either directly or indirectly.

For example, anoxygenic photosynthesis (green sulfur bacteria *Prosthecochloris*) can be coupled to anaerobic respiration (*Geobacter*) via DIET under anoxic conditions (Ha et al. 2017). This syntrophic anaerobic photosynthesis may occur in methanogenic environments, although its effect on the overall AD process would be limited, particularly in field-scale AD plants run under completely dark conditions with no light for photosynthesis. Furthermore, a recent study reported that magnetite addition did not enhance methane production but greatly reduced the H_2S content in biogas during the semi-continuous AD of sulfur-rich organic waste (Jung et al. 2020). The authors found that H_2S was removed by microbial oxidation to S^0 and suggested a novel DIET-based electric-syntrophy coupling the oxidation of sulfide to S^0 to electrotrophic methanogenesis of CO_2. Dissimilatory sulfate reduction is a major electron sink that competes with methanogenesis for electron donors, and the effect of adding conductive materials on the flow of electrons could become even more complex when other electron sinks (i.e., biologically reducible substances in methanogenic environments) are abundant. Various electro-syntrophic associations not directly involved in methane production likely occur in methanogenic systems, and understanding how they function and affect methanogenesis in the presence of conductive materials is important for engineering DIET in practical applications. However, this aspect has been little studied and poorly understood.

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Part II
Pretreatment

Chapter 3
Adsorbents for the Detoxification of Lignocellulosic Wastes Hydrolysates to Improve Fermentative Processes to Bioenergy and Biochemicals Production

Itzel Covarrubias-García and Sonia Arriaga

Abstract The depletion of fossil fuels and their environmental impact has motivated the research on alternative sources of energy. Lignocellulosic wastes are potential substrates for bioenergy and biochemicals production due to the carbohydrate content in the cell wall, which is composed of cellulose (40–80%), hemicellulose (10–40%), and lignin (5–25%). The sugar content of lignocellulosic biomass can be converted into fermentable monomeric sugars by physicochemical or enzymatic process. The hydrolysates produced during those processes have a high content of inhibitory substances such as phenolic and furanic compounds, i.e. syringaldehyde, vanillin, furfural and 5 hydroxymethylfurfural. Thus, the need of a detoxification pretreatment of hydrolysates before the fermentation process should be addressed. There are several detoxification processes reported such as overliming, ion exchange, membranes, use of enzymes or microorganisms and adsorption. Adsorption processes with nanomaterials have emerged as a promising technique for the removal of such inhibitors. This chapter shows the potential methods to detoxify hydrolysates, specifically using the adsorption process with potential adsorbents such as nanomaterials. Furthermore, inhibitors should not be just considered as obstacles for fermentation and hydrolysis, but could also be viewed as valuable chemicals for other industries which is also highlighted in this chapter.

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3.1 Introduction

The price rise, environmental issues and depletion of fossil fuels along with the tremendous increase in the world's energy demand have pushed countries to search for alternative renewable energy options such as biofuel production from lignocellulosic biomass (Onaran et al. 2020). Lignocellulosic biomass is one of the most abundant biopolymers found on earth and includes agricultural residues such as sugarcane bagasse, rice straw, wheat, soy, oats, corn, stump, sawdust, plant and tree branches as well as urban solid residues. The secondary cell wall of plants contains cellulose (40–80%), hemicellulose (10–40%), and lignin (5–25%). Lignocellulosic biomass contain fermentable sugars that have been extensively evaluated for biofuel production. The carbohydrate fraction of the plant cell wall is converted into fermentable monomeric sugars through physical (e.g. milling, ultrasound irradiation and extrusion), chemical (e.g. acid, alkaline, ammonia explosion, organo-solvents and ionic liquids), physicochemical (e.g. steam explosion, microwave and CO_2 explosion) and enzymatic hydrolysis (e.g. cellulose and xylanase) pretreatment or a combination of these methods.

During the pretreatment of lignocellulosic biomass, formation of many inhibitory compounds can take place. These compounds are divided in three main groups based on their origin: weak acids, furan derivatives and phenolic compounds (Palmqvist and Hahn-Hägerdal 2000a). Formation of these inhibitors during pretreatment is a limiting factor in the production of valuable chemicals and bioenergy from lignocellulosic biomass and the selection of an efficient pretreatment method can significantly reduce the production of inhibitory compounds and may lead to enhance in production and yield of the desired product. Presence of inhibitory compounds have adverse effect on the substrate utilization and product yield by fermentative microbes. The unfavourable environment created by the presence of inhibitors increases the length of the lag phase, reduces cell density and lower the growth rates of fermenting microbes (Zabed et al. 2019; Wang et al. 2018; Kumar et al. 2020). Moreover, inhibitors can decrease the activity of several enzymes, break down the DNA, inhibit protein and RNA synthesis in microorganisms (Jung et al. 2014, 2013; Liu et al. 2004; Palmqvist and Hahn-Hägerdal 2000a, 2000b; Taherzadeh et al. 2000).

In order to decrease the amount of toxic compounds, several detoxification methods have emerged such as alkaline detoxification, biological detoxification by microorganisms or enzymes, and adsorption using polymeric sorbents or activated carbon (Grzenia et al. 2010; Ludwig et al. 2013; Myoung et al. 2010; Zhang et al. 2011). Adsorption processes are advantageous to detoxify hydrolysates as they do not modify the chemical composition of the inhibitor which can be desorbed to recover and further utilized as valuable chemical in other industries (Sjulander and Kikas 2020).

This book chapter is focused on examining the fundamentals that govern the function of adsorbents for the detoxification of lignocellulosic wastes hydrolysates to improve fermentative processes to bioenergy and biochemicals production. It also reviews the commonly used adsorbents and discusses the advantages and disadvantages of using each of these methods. Likewise, it will also present the emerging methods used for detoxification and the challenges involved in their application.

3.2 Pretreatment of Lignocellulosic Residues

The main objective of pretreatment of lignocellulosic biomass is to break down the lignin structure and to make the cellulose and hemicellulose more available for bioconversion (Hernández-Beltrán et al. 2019). During the pretreatment, the disruption of the physical barriers such as lignin and hemicellulose take place to depolymerize and to reduce the cellulose crystallinity. The effectiveness of pretreatment depends on the structural and compositional properties of lignocellulosic biomass, such as crystallinity, degree of polymerization, degree of hemicellulose acylation, surface area, pore volume and lignin content (Basak et al. 2020). Pretreatment has been identified as the key step in the bioconversion of lignocellulosic biomass for its use in biorefinery. A large number of pretreatment methods for lignocellulosic biomass have been studied which can be classified into 4 groups: physical, chemical, physicochemical and biological processes. Table 3.1 shows the most common pretreatment methods reported along with their advantages and disadvantages.

3.2.1 Physical Pretreatment

Physical pretreatment includes biomass particle size reduction using grinding, cutting, ball milling among other processes (Table 3.1). The advantage of this process is that it does not produce inhibitory substances. Particle size reduction is necessary prior to most physicochemical pretreatments to improve material handling and enhances the efficiency of physicochemical pretreatments. However, the excessive reduction of size makes the processes economically unfeasible for a potential application, its inability to remove lignin is the main drawback (Taylor et al. 2019). Other physical methods include ultrasonic, extrusion, microwave irradiation, pulsed electric field, freeze pretreatment and pyrolysis.

Table 3.1 Physical, chemical and biological methods to pretreat lignocellulosic biomass (Bajpai 2016; Bhatia et al. 2020; Bhutto et al. 2017; Zabed et al. 2019)

Type of pretreatment		Advantages	Disadvantages
Physical	• Milling • Ultrasound • Gamma irradiation • Extrusion • Microwave radiation • Hydrothermal pyrolysis	• Increases surface area • Decrystallizes cellulose • Removes hemicellulose • No formation of inhibitors • Improves hydrolysis when used in combination with other processes	• Inability to remove lignin • High energy requirement
Chemical	• Acid hydrolysis	• Solubilize hemicellulose • Removes lignin • Improves sugar yield	• Inhibitors formation at high acid concentration • Causes corrosion of equipment • The acid recycling process is expensive • Requires neutralization
	• Alkaline hydrolysis	• Solubilize lignin and hemicellulose • Increase crystallinity of cellulose • Improves glucose yield from biomass	• Reaction time takes days-weeks at room temperature • Harsh chemical conditions
	• Organosolv process	• Efficient lignin removal • Pure lignin obtention • High sugar yield from biomass • Recovery of lignocellulosic components	• Recycling of solvent • Risk in operating at high pressure
	• Ionic liquids (IL)	• Effective in lignin removal • Decrystallize cellulose • As they are non-volatile, biomass is easily treated at high temperature without solvent losses by evaporation • ILs can be recovered and recycled easily	• Extremely viscous solution is formed which limit industrial application • Complex synthesis process • High costs of ILs
	• Ozonolysis	• Selective lignin degradation • Produce biomass with great surface areas • Minimal losses of hemicellulose and cellulose	• High cost of generating ozone
	• Peroxide	• Depolymerize lignin • Mild conditions of temperature and pressure • Reduce inhibitors formation	• Requires to maintain the pH constant to avoid hemicellulose elimination
Combined physical and chemical methods	• Steam explosion	• Solubilize hemicellulose • High removal of lignin • Increase porosity and surface area by disruption of biomass	• Process cost is high • High pressure required • High rate of degradation of sugars

(continued)

Table 3.1 (continued)

Type of pretreatment		Advantages	Disadvantages
		and reduce the crystallinity of cellulose	
	• Thermochemical	• Decrystallize cellulose • Removes hemicellulose • Removes lignin • Alters lignin structure	• Less removal lignin • Yield of sugars is low • Significant consumption of energy
	• Ammonia fiber explosion-AFEX	• Decrease crystallinity of cellulose • Increase surface area and porosity • Break down lignin structure	• Generation of by-products • High initial overhead cost for ammonia reagent
	• Liquid hot water	• Hydrolysis of hemicellulose and lignin content reduction • Cellulose hydration • Low capital costs • Operates under lower pressure • No requires chemicals and corrosion resistant materials	• Formation of inhibitors like furfural and hydroxymethylfurfural (HMF)
	• Wet oxidation	• Increase the solubilisation of hemicellulose and breakdown lignin • High cellulose yields	• Yield of sugar is low • Not yet established at pilot scale
	• Microwave chemical pretreatment	• Decrease crystallinity of cellulose • Depolymerize lignin components • Increase available surface area	• Not economically viable
	• CO_2 explosion	• Increase the surface area • Significant hydrolysis of sugars • Green technology as the CO_2 is recycled	• High pressures of operation • High initial costs and maintenance costs
Biological	• Microbial • Fungi	• Removes hemicellulose • Removes lignin • Alters lignin structure • Environmentally friendly • Low inputs such as energy and chemicals • Low outputs like inhibitors and wastes	• Long process time • Large space requirement • Loss of carbohydrates
	• Enzymes (Cellulases and Xylanases)	• Short residence time • Low nutrition requirements • Cheap process equipment	• High enzyme cost

3.2.2 Chemical Pretreatment

Chemical pretreatment enhances the biodegradability of cellulose by removing lignin and hemicellulose, thus the polymerization and crystallinity of the cellulose is changed. This pretreatment is highly selective for the biomass constituents and requires harsh operational conditions (Peral 2016). These methods include acid hydrolysis, alkaline hydrolysis, organosolv, peroxide and ozonolysis (Table 3.1). The most known acids used are H_2SO_4, HNO_4, HCl, H_3PO_4, HNO_3 and organic acids.

Acid hydrolysis is considered one of the most common lignocellulosic biomass pretreatments and can be performed by using dilute or concentrated acids (4% to 40%). They are flexible in feedstock choice, high monomeric sugar yield, and mild temperature operation conditions. The formation of toxic compounds such as 5 hydroxymethylfurfural (5-HMF), furfural, levulinic and formic acid occurs under acid hydrolysis. A neutralization step is required which adds cost to the overall process.

During alkaline treatment, little degradation of sugars to furfural, HMF and organic acids occurs (Peral 2016). Organic solvent pretreatment involves the use of an organic or aqueous organic solvent mixed with inorganic acid catalysts (HCl or H_2SO_4). Oxalic, acetylsalicylic and salicylic acid can also be used as catalysts. Solvents commonly used are methanol, ethanol, acetone and ethylene glycol (Peral 2016). Organosolv pretreatment hydrolyses lignin bonds as well as lignin-carbohydrate bonds. Lignin is extensively removed and hemicellulose is almost completely solubilized, while cellulose remains in solid form (Peral 2016). This pretreatment is very selective to lignin which can be recovered and utilized for a range of applications such as precursors for various chemicals or fuels in a biorefinery. The challenge with this pretreatment is the recovery of the organic solvents. The high cost involved in the organosolv pretreatment method due to involvement of expensive chemicals and catalyst is the only drawback of this method which make its application less desirable than the other commonly used technologies (Peral 2016). Moreover, in many cases, high temperature (up to 200 °C) is also applied in organosolv pretreatment which can increase the cost of operation.

3.2.3 *Physicochemical Pretreatment*

Physicochemical treatment technology is nothing but combined methods involving both physical and chemical pretreatment techniques (Table 3.1). The lignocellulosic biomass is subjected to chemical modification and the cell wall structure is physically broken (Aslanzadeh et al. 2014). The high pressure and temperatures used in these types of processes increase the costs of applying them in a biorefinery type system. Steam pretreatment is the most common method applied to biomass due to their wide ranging application on various types of biomass, however in case of recalcitrant biomass sources, it may necessitates additional treatment using acid or SO_2 (Aslanzadeh et al. 2014). During steam explosion, fermentation inhibitors are generated such as HMF, weak acids and phenolic compounds. This method requires a high amount of energy and involves elevated operation costs (Peral 2016). Ionic liquids are effective in decrystallizing the cellulose, fractionating lignin and polysaccharide contents into separate streams, making the following hydrolysis step much easier (Aslanzadeh et al. 2014).

3.2.4 Biological Pretreatment

Biological pretreatment is performed by using wood-degrading microorganisms, which includes white-rot fungi, brown-rot fungi, soft-rot fungi, and bacteria (Table 3.1). These microorganism changes the chemical composition and/or structure of the lignocellulosic biomass so as to make the biomass less resistant during the subsequent enzymatic hydrolysis step (Aslanzadeh et al. 2014). They operate under standard conditions of pressure and temperature but long periods of operation are needed (10–14 days).

Enzymatic hydrolysis form sugar monomers by depolymerisation reaction of cellulose and hemicelluloses prior to fermentation (Aslanzadeh et al. 2014). In contrast to the physicochemical treatment, enzymatic hydrolysis is generally performed under milder conditions and does not generate any corrosive compounds. This method can attain nearly complete cellulose conversion without forming any inhibitory by-products (Mussatto et al. 2008; Aslanzadeh et al. 2014). On the other hand, the main drawback is that this method may take longer time (1–4 d) for the completion of the reaction. The commonly used enzymes for this method are cellulases and hemicellulases with very high selectivity to the substrates (Aslanzadeh et al. 2014).

3.3 Fermentation Inhibitors Formed during Pretreatment of Lignocellulosic Biomass

As mentioned in Sect. 3.1, during the pretreatment of lignocellulosic biomass inhibiting compounds are formed. Inhibitors can be divided into five major groups (i) organic acids (acetic, formic and levulinic acids), (ii) furan derivatives (furfural and 5-HMF), (iii) phenolic compounds, (iv) raw materials extractives (acidic resins, tannic and terpene acids) and (v) heavy metal ions (iron, chromium, nickel and copper) (Llano et al. 2017). Figure 3.1 shows the inhibiting compounds profile derived from lignocellulosic materials after pretreatment.

The amount and nature of the formed degradation products depends directly on the type of lignocellulosic biomass, pretreatment method and conditions used (Jönsson and Martín 2016). The degradation products include acetic acid (34–180 mg/L), formic acid (43–250 mg/L), levulinic acid (0.48–41 mg/L), vanillin (1.7–6.7 mg/L), hydroxybenzaldehyde (1.5–4.4 mg/L), furfural (0.40–220 mg/L), and 5-hydroxymethyl-furfural (0.89–44 mg/L) (Bonturi et al. 2017; Poontawee

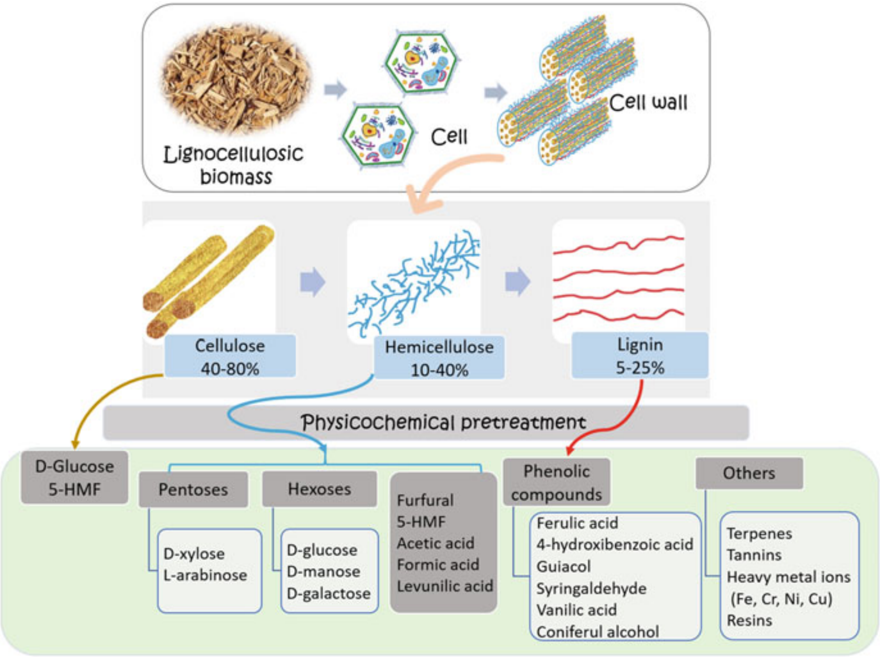

Fig. 3.1 Inhibitory compounds profile derived from lignocellulosic materials during pretreatment

et al. 2017; Yu et al. 2011). Table 3.2 shows the common inhibitors that can be formed from pretreatment of lignocellulosic biomass and their principal effects on fermentative microorganisms.

Table 3.2 and Fig. 3.1 show that inhibitors come from the degradation of each component of the biomass. Cellulose can degrade to hexoses to different extent. Such hexoses could further be dehydrated to 5-HMF, and 5-HMF can be further dehydrated to form levulinic acid and formic acid (Kumar et al. 2018). On the other hand, hemicellulose after pretreatment can degrade into sugar acids, aliphatic acids, and furan aldehydes, where furfural is an abundant and potent inhibitor (Osorio-González et al. 2019; Kumar et al. 2020). Formic acid, acrylic acid and levulinic acid are other carboxylic acids found in hemicellulose hydrolysates (Zabed et al. 2019; Kumar et al. 2020).

Regarding the degradation products from lignin, 4-hydroxybenzoic acid, 4-hydroxybenzaldehyde, vanillin, dihydroconiferyl alcohol, coniferyl aldehyde, syringaldehyde and syringic acid are the most common phenols formed from lignin degradation (Hodge et al. 2009; Kumar et al. 2020). There are different effects associated with each inhibitor. For instance, weak acids in undissociated form can permeate through and inside the cells to release the anion and proton disrupting the intracellular pH (Wang et al. 2018). On the other hand, phenolics are more toxic than aliphatic and furans with the same functional groups and have shown antibiofouling

Table 3.2 Common inhibitors formed during pretreatment of lignocellulosic biomass

Origin	Inhibitors (mg/L)	Effects	References
Cellulose	• 5-HMF (0.89–44) • Levulinic acid (0.48–41) • Formic acid (43–250)	• 5-HMF toxic to the growth of ethanolegens. • Furans enter the cytosol and inhibit NADH-dependent enzymes. • Furfural and 5-HMF bind to nitrogenous bases of DNA and induce strand break, damaging the structure. • Furfural inhibits the synthesis of TTP which lead to the cessation of DNA replication.	Basak et al. (2020); Kumar et al. (2018)
Hemicellulose	• Furfural (0.40–220) • Acetic acid (34–180) • Formic acid (43–250) • Levulinic acid (0.48–41)	• Furfural is the most abundant and potent inhibitor.	Kumar et al. (2020); Zabed et al. (2019)
Lignin	• Hydroxybenzaldehyde (1.5–4.4) • Vanillin (1.7–6.7) • Syringaldehyde (0.6–1.2) • Syringic acid (0.026–1.4)	• Phenols are able to penetrate the cell membrane easily altering cell membrane structure, permeability and integrity. • Phenolic compounds and furans generate reactive oxygen species (ROS) which inactivate enzymes, damaging DNA and cellular proteins.	Basak et al. (2020); Kumar et al. (2018, 2020); Lin et al. (2015)

effects on *Gram* negative bacteria (Pattrick et al. 2019). Likewise, furans present negative effects on glycolytic and fermentative enzymes and can inhibit the synthesis of ATP, which lead to the cessation of DNA replication (Basak et al. 2020). Furfural and 5-HMF bind to nitrogenous bases of DNA and induce strand break, damaging the structure (Liu et al. 2019). Both phenolic compounds and furans generate Reactive Oxygen Species (ROS), which inactivate enzymes, damaging DNA and cellular proteins (Basak et al. 2020; Lin et al. 2015).

In general, the effect of each inhibitor and the degree of inhibition will depend on the fermenting microorganisms and its tolerance to the inhibitor. Additionally, the toxicity of each inhibitor depends on its concentration, chemical structure and reactivity, molecular weight and chemical polarity, which determines their inherent capacity to penetrate the cell membrane and cause cellular damage (Jung et al. 2013; Taherzadeh et al. 2000).

In general if there is more than one inhibitory compounds are present in the lignocellulosic hydrolysates that can have a more severe recalcitrant effect on the microorganisms and enzymatic activity (Almeida et al. 2007; Jayakody et al. 2017;

Wikandari et al. 2019; Sjulander and Kikas 2020). For instance, the effects of inhibitor combinations (i.e. acetate, furfural, 5-HMF, vanillin, p-hydroxybenzaldehyde and syringaldehyde) on *R. toruloides*-Y4 at different concentrations have been analysed. The combinations of the different inhibitors gave a much more complex inhibition effect on the fermentation process (Hu et al. 2009; Zhao et al. 2012).

Currently, different strategies have been employed to tackle problems with inhibition after pretreatment of lignocellulose. Some of the different approaches used are: (i) feedstock selection, that is using less recalcitrant feedstocks in order to generate less inhibitors during pretreatment (Chiaramonti et al. 2012; Larsen et al. 2012); (ii) selection of microorganisms, i.e. the selection of microorganisms that produce less amount of inhibitors, should be done mainly based on specific productivity and product yields (Wimalasena et al. 2014); (iii) adaptive evolution, where microorganism adapt to specific inhibitors (Almario et al. 2013; Koppram et al. 2012); (iv) genetic or metabolic engineering, based on creating tolerance to fermentation inhibitors (Sanda et al. 2011; Wang et al. 2013); (v) culturing schemes such as the use of a large inoculum size (Hoyer et al. 2010; Pienkos and Zhang 2009); (vi) conditioning which consists of addition of chemicals that can improve the fermentability of the substrates (e.g. NH_4OH and NaOH), these agents can be added during fermentation (Alriksson et al. 2011, 2006); and (vii) detoxification of hydrolysate (e.g. distillation, solvent extraction and adsorption) (Mussatto and Roberto 2001; Myoung et al. 2010; Palmqvist and Hahn-Hägerdal 2000a).

3.4 Strategies for the Detoxification of Lignocellulosic Wastes Hydrolysates

So far, there is no single pretreatment method that can perform delignification without sugar degradation. Therefore, the tendency is to apply successive treatment to remove the generated by-products other than sugars (i.e. detoxification). The main concern of detoxification processes is the simultaneous removal of fermentable sugars which results in a reduction of final products (Almeida et al. 2009; Deng and Aita 2018; Li et al. 2013; Myoung et al. 2010). All the different methods using biological, chemical and physical means are employed for detoxification of lignocellulosic hydrolysate (Kumar et al. 2020; Singh et al. 2017).

Physical methods mainly include distillation, solvent extraction and adsorption (Cantarella et al. 2004). The main disadvantage of distillation is that only inhibitors with high boiling point can be removed. On the other hand, solvent extraction presents a low efficiency with a large consumption of solvent. Regarding chemical methods, alkaline detoxification, adsorption and ion exchange have been reported. The used alkali solutions control the pH (9–12) (Alriksson et al. 2006; Nilvebrant et al. 2003) and remove the inhibitors by precipitation, these include $Ca(OH)_2$, NaOH, and NH_4OH solutions. Likewise, sodium borohydride has been reported to be able to effectively remove coniferyl aldehyde, *p*-benzoquinone, 2,6-dimethoxybenzoquinone, and furfural under mild reaction conditions (pH 6 and 20 °C) (Cavka and Jönsson 2013).

Concerning biological detoxification, inhibitors are removed by microorganisms and enzymes. Inhibitors such as furfural (100%), HMF (94%) and acetic acid (82%) have been removed with *Bordetella* spp. without affecting the sugar concentration (Singh et al. 2017). Otherwise, the laccase enzyme of *Trametes maxima* IIPLC-32 has been used to detoxify phenolics from sugarcane bagasse removing 66% of lignin-derived phenolics inhibitors in 55 h (Suman et al. 2018). The main difficulty of the enzymatic and microbial method is their production cost and the fact that the process need to be performed under sterile conditions.

Apart from the conventional methods, there are also few emerging technologies used. The main objective for these processes are the use of simultaneous detoxification and product production which may further improve the process economics and avoid an additional treatment step (Ahmaruzzaman 2008; Bhatia et al. 2020). For example, the addition of chemicals such as ozone is investigated on a Norway spruce hydrolysate and has been found that it effectively reduced the aromatic compounds, furfural and HMF in the hydrolysate. However, the reactive ozone treatment caused increase in the formic acid concentration in the hydrolysate, which made the detoxified hydrolysate unsuited for subsequent fermentation (Cavka et al. 2015).

Other approaches consists of the combination of nanomaterials to immobilize enzymes for detoxification. Yin et al. (2020) developed a novel detoxification strategy of rice straw hydrolysate using immobilized laccase on magnetic Fe_3O_4 nanoparticles for improving lipid production by *Rhodotorula glutinis*. Notably, the immobilized laccase exhibited good reusability in repeated batch detoxification. 78.2% phenols, 43.8% furfural, 30.4% HMF and 16.5% formic acid in the hydrolysate were removed after the fourth batch (Yin et al. 2020). However, it is important to take into account the toxicological issues associated with application of nanomaterials and their fate in the environment.

In comparison to other methods, adsorption has advantages in terms of low energy consumption, environmental friendliness and low cost, hence creating its wider application in removal of fermentation inhibitors from hydrolysates (Chen et al. 2020). Furthermore, use of adsorption as detoxification method compared to other processes can provide the recovery of such inhibitory compounds by desorption, which further can be utilized as valuable chemical in other industries, as during adsorption the inhibitor is not chemically altered (Sjulander and Kikas 2020). Thus, the recovered adsorbed inhibitor has an added economic value. Worth mentioning that the different detoxification methods cannot be strictly compared as the removal efficiency of every method depends on the properties of the inhibitor, such as size, polarity, chemical reactivity, and concentration (Cavka and Jönsson 2013; Qi et al. 2011; Sjulander and Kikas 2020). The adsorption process for detoxification of lignocellulosic biomass is discussed in the following section.

3.5 Detoxification of Hydrolysate Using Adsorption

3.5.1 Adsorbent Materials

Section 3.4 described that removal of inhibitors from hydrolysate is an essential step before performing microbial fermentation. Table 3.3 overviews different adsorption materials that have been tested for their ability to remove inhibitors from lignocellulosic hydrolysates. The types of adsorbents include activated carbons, minerals, resins, industrial and agricultural wastes. The adsorption efficiency of the inhibitors depends on the adsorbent surface area, pore size and chemical properties, and is also influenced by environmental conditions (i.e. temperature, pH, and contact time between inhibitor and adsorbent) (Deng et al. 2018; Sjulander and Kikas 2020).

Activated carbon (AC) either stand-alone or in combination with other chemicals (i.e. alkali and ion exchange resins) is the most common adsorbent used for detoxification. Activated carbons are usually produced from low-cost materials which is one of its main advantage. Apart from that, reliability and consistency of the resource supply, ease of activation, adsorption capacity, and selectivity are notable qualities of AC. Literature has reported several studies where different inhibitors have been removed with activated carbons, such as furfural, 5-HMF, acetic acid and phenolic compounds (Chen et al. 2019; Myoung et al. 2010; Santana et al. 2018; Zhang et al. 2011). It has been suggested that removal of inhibitors is related to the strong hydrophobic nature of the activated carbons (Lee and Park 2016). The main drawbacks in the use of AC are its regenerability and cost, where there is 10% loss during each regeneration cycle. In addition, it can retain up 30% of the fermentable sugars which is not good from the economic point of view (Carvalho et al. 2006; Ranjan et al. 2009). Therefore, the exploration and study of other adsorbents is of interest.

Alternatively, mineral adsorbents including siliceous materials, clay and natural zeolites have been used (Wang and Peng 2010). Ranjan et al. (2009) demonstrated the potential recovery of HMF, furfural and vanillin using hydrophobic zeolites. Removal of model compounds using mineral adsorbents has been also reported (Ahmaruzzaman 2008). On the other hand, different types of resins have been reported to remove inhibitors such as fumaric acid, acetic acid, formic acid, 5-HMF and soluble lignin (Chen et al. 2019; Choi et al. 2017; Zheng et al. 2018). The main advantages in the use of polymeric resins is that they are durable, chemically inert and stable, and possess a high adsorption capacity, efficiency, selectivity and ease of regeneration, with relatively low cost and limited toxicity (Soto et al. 2011).

In addition, the implementation of nanoscale materials has emerged as an attractive alternative in several applications. Their size and their relatively large surface area to volume ratio when compared to larger particles can result in a high adsorption capacity (Alsaba et al. 2020). Few studies have reported the use of nanomaterials for detoxification of hydrolysates. Covarrubias-García et al. (2021) used reduced graphene oxide adorned with magnetite nanoparticles for the removal of fermentation inhibitors such as furfural, 5-HMF, levulinic acid, vanillic acid and vanillin from

Table 3.3 Summary of adsorbents used for detoxification of hydrolysates. “x” means the studies where fermentation step is not performed to produce any product

Type	Adsorbent	Removal of inhibitors (%)	Products	Reference
Activated carbons	Activated carbon	HMF (96) Furfural (93) Formic acid (42) Acetic acid (14)	x	Myoung et al. (2010)
	Activated carbon	Furfural (97)	Ethanol	Zhang et al. (2011)
	Activated charcoal	Phenolic compounds (78) Furfural (99) 5-HMF (99)	Xylitol	Santana et al. (2018)
	Activated carbon	HMF (50–60) Furfural (50–60) Phenolic compounds (50)	Acetone, butanol and ethanol	Wang et al. (2019)
Membranes	Adsorptive membrane (Sartobind Q)	Acetic acid (99)	x	Wickramasinghe and Grzenia (2008)
	Hollow-structured porous aromatic polymer	5-HMF (94)	x	Zhang et al. (2019)
Resins	Amberchrom-CG71C resin	Fumaric acid (99) Acetic acid (99)	x	Choi et al. (2017)
	Microporous polymeric SY-01 resin	Levulinic acid (99)	x	Lin et al. (2017)
	Microporous resin (SY-01)	Formic acid (80) Levulinic acid (16) 5-HMF (63)	x	Zheng et al. (2018)
	Resin CS-6	Soluble lignin (70)	Lipid	Chen et al. (2019)
Nanostructures	Fe^0 nanoparticles on activated carbon	Furfural (99) Acid soluble lignin (81)	x	Sajab et al. (2019)

(continued)

Table 3.3 (continued)

Type	Adsorbent	Removal of inhibitors (%)	Products	Reference
	Laccase on magnetic nanoparticles	Phenols (78) Furfural (44) HMF (30) Formic acid (16)	Lipids	Yin et al. (2020)
	Reduced graphene oxide adorned with magnetite nanoparticles	Furfural 5-HMF (72–76) Levulinic acid (60–63) Vanillic acid (54–57) Vanillin (39–45)	x	Covarrubias-García et al. (2021)
Others	Zeolite	5-HMF (100) Furfural (100) Vanillin (100)	Ethanol	Ranjan et al. (2009)
	Sugarcane bagasse fly ash	Phenolic compounds (80)	x	Freitas and Farinas (2017)

wood hydrolysates with a minimal sugar loss of 5.9, 6.2 and 7.6%, for 10, 20 and 50 mg of the adsorbent, respectively. There are other studies where nanomaterials are immobilized on the AC surface (Sajab et al. 2019) and nanomaterials as a support for enzyme immobilization (Yin et al. 2020) have been reported for removal of toxicants from hydrolysate.

Other types of adsorbents such as sugarcane bagasse derived fly ash has been successfully used to adsorb aromatic compounds, such as tannic acid and vanillin from a lignocellulosic hydrolysate (Freitas and Farinas 2017).

3.5.2 Challenges of Adsorption

The main challenge related to the adsorbent based technology for detoxification of lignocellulosic hydrolysates is related to the desorption and reusability of the adsorbents. Desorbing eluents may not be effective for all the adsorbents and need to be optimized on a case to case basis. Requirement of large amounts of chemicals as desorbing agent, cost associated with them and their disposal may again put a question mark on the sustainability of adsorption. Another issue is the loss of adsorption capacity due to repeated adsorption-desorption cycles: compounds that can be used multiple times without significant loss in adsorption property are more suited economically. It is also somewhat difficult to design a continuous system as even the simplest setup will require at least two continuous columns, one in operation and another in regeneration to avoid any time delay in operation. There are also issues with the effectiveness of adsorption as in some cases an additional step may be required for complete removal of toxic substances from hydrolysate. This type of issues are more prevalent in hydrolysate where different inhibitory compounds are present.

Regarding the emerging adsorbents such as the use of nanoadsorbents, additional challenges are the release and fate of the nanoadsorbent in the environment as well as the toxicity that could be caused. From the process point of view, the challenges are related with the loss of the material in the downstream process. The strategy to avoid its loss would be the immobilization of the nanomaterial in a granular support.

3.6 Recuperation of Commodities from Detoxification

The production of biofuels and value-added biochemicals from evenly-distributed non-food lignocellulosic biomass would decrease net greenhouse gas emissions by replacing the use of fossil fuels and would bring benefits of trade (Lynd et al. 2002; Zhang 2011). Recovery of these compounds is an interesting option for biorefineries because in addition to increasing the suitability of hydrolysates as substrates, it can result in economic benefits. Therefore, it is of great interest to study the recovery of such compounds. The promising products like ethanol, xylitol, organic acids and 2,3-butanediol may play a pivotal role in this direction (Kumar et al. 2020).

The alleviation of the inhibition of fermentation in hydrolysates decreases production costs, however, it is very difficult to separate them from the biomass hydrolysate when they are present in low concentrations ($<5\%$ by weight) (Travália et al. 2019). Thus, it is of interest to understand the separation of fermentation inhibitors from the hydrolysate. Fermentation inhibitors such as acetic acid, furfural, HFM and formic acid can be valuable commodities in the industrial manufacture of pharmaceuticals, dyes, solvents, adhesives, polymers, plastics, resins, lubricants and fuels (Travália et al. 2019). Alternately, bio-oil can be obtained from lignin depolymerisation and lignins can be transformed into other value-added products such as carbon fibers, polyurethanes, biocomposites and nanomaterials for many applications ranging from biomedicine to automobiles (Zevallos Torres et al. 2020).

Among the different approaches to extract the inhibitors, liquid–liquid extraction has been extensively investigated as a recovery method. The major drawback of liquid-liquid extraction is the biological toxicity of the extraction agents, usually organic solvents (Tomek et al. 2015). Likewise, the use of surfactants-based cloud point extraction (CPE) has also been explored. Surfactants, which are soluble in water at low temperatures but insoluble at high temperatures, are used in this approach, allowing for a two-phase extraction. The main advantage of the method is that the surfactants are non-toxic to microorganisms and no sugar loss has been observed (Dhamole et al. 2013). Other studies have reported the extraction of inhibitors with common solvents like deionized water and ethanol. Ranjan et al. (2009) demonstrated the potential recovery of HMF, furfural and vanillin using hydrophobic zeolites. They desorbed with deionized water and indicated that desorption isotherms almost overlapped with the adsorption isotherms. Lin et al. (2017) found that the use of an ethanol solution as an eluent was easy and effective to recover levulinic acid from a SY-01 resin with a 99.4% efficiency and the SY-01 resin was successfully regenerated.

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Chapter 4
Pretreatment of Lignocellulosic Materials to Enhance their Methane Potential

A. Oliva, S. Papirio, G. Esposito, and P. N. L. Lens

Abstract Lignocellulosic materials (LMs) are the most abundant residues on the planet and have a huge potential for methane production. Several strategies have been tested to enhance the methane potential of LMs, with a particular emphasis on environmentally friendly and economically convenient pretreatments. This chapter revisits the potential of two chemical, i.e. organosolv and N-methylmorpholine N-oxide (NMMO)-driven, and one physical, i.e. ultrasounds, pretreatments. Organosolv pretreatment enables to obtain a pure lignin fraction from LMs, leaving most of the fermentable sugars in the solid matrix. The result is a lignin-poor material with an increased porosity and a higher bioavailability of the sugar fraction. Another advantage is the cost-effectiveness and the easy recovery of the chemicals involved. NMMO pretreatment focuses on the cellulosic component of the biomass, aiming to reduce its crystallinity and to increase the porosity of the substrate. The main advantage of NMMO lies in its high recovery percentage, which reaches up to 99%. Ultrasound pretreatment involves ultrasonic waves that allow fractionating LMs, breaking the linkages between lignin, cellulose and hemicellulose, generally leaving cellulose and most of the hemicellulose in the solid fraction and dissolving the lignin in the liquor. Ultrasound pretreatment does not require chemicals and can be easily combined with other pretreatment methods to enhance its effectiveness.

Keywords Lignocellulosic materials · Pretreatment · Organosolv · NMMO · Ultrasound · Anaerobic digestion · Methane

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4.1 Introduction

The interest in renewable energy started when the world experienced an energy crisis in the ‘70s and realised that fossil fuels are not an unlimitedly available resource. More recently, the interest in renewable energy sources is related to global environmental quality (Sen and Ganguly 2017) and geographic independence of the fossil fuels reservoirs (Martins et al. 2019). The first emerging problem regarded the emission of toxic compounds and oxides of nitrogen and sulfur upon combustion of fossil fuels, which contributes to acid rain formation (Singh and Agrawal 2008). At the moment, the main concern relates to global warming caused by the increase in carbon dioxide concentration and other upper atmospheric pollutants deriving from anthropogenic activities (Kweku et al. 2018; Qazi et al. 2019).

The preservation of the environment and the necessity of renewable energy to replace fossil fuels has led to the development of a strong anaerobic digestion (AD) infrastructure worldwide (Vasco-Correa et al. 2018). AD allows for recovering energy (i.e. biogas, a CH_4/CO_2 mixture) from wastes while stabilizing the residual solid/liquid organic fraction (Bharathiraja et al. 2018). AD involves different communities of microorganisms in four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Chen et al. 2008; Zhang et al. 2014). During the first stage, hydrolytic bacteria secrete enzymes able to hydrolise the organic matter and decompose the complex organic polymers (i.e. lipids, carbohydrates, and proteins) into soluble monomers (i.e. monomeric sugars, long-chain fatty acids, and amino acids) and hydrogen. Acidogenesis is the second stage, wherein the soluble monomers are fermented into volatile fatty acids and other products, which, during the subsequent acetogenesis stage, are converted to acetate, carbon dioxide and hydrogen by acetogenic bacteria. In the final phase, methanogenesis, acetic acid, and hydrogen are converted into methane by methanogenic archaea (Bianco et al. 2021a; Luo et al. 2019).

Many waste materials from several activities are lignocellulosic materials (LMs). The disposal of these LMs is often difficult due to the enormous volumes produced, especially during the harvesting season (Barbu et al. 2020; Oh et al. 2018). AD is a viable and green alternative to landfill disposal or combustion for these LMs (Alonso-Fariñas et al. 2020). The use of LMs for AD is, however, still limited by their resistance to biological and chemical degradation. The main issue of AD of LMs is the complex and resistant structure, mainly consisting of cellulose, hemicellulose, and lignin (Bhatia et al. 2020). Various strategies have been explored to increase the biodegradability of LMs (Bianco et al. 2021b; Kohli et al. 2020; Mancini et al. 2018c; Papirio 2020; Yao et al. 2018). Pretreatments of LMs aim to increase the efficacy of lignocellulose hydrolysis by improving the accessibility of microorganisms to the sugar fraction (cellulose and hemicellulose) of LMs. This can be achieved by removing lignin and/or hemicellulose or by decreasing the degree of polymerization and crystallinity of the cellulosic component of the biomass (Kumar and Sharma 2017).

LMs may be converted to various forms of energy, including heat (via burning), steam, electricity, hydrogen, ethanol, methanol, or methane. The choice depends on multiple factors, such as conversion efficiencies, transport of energy, need for heat or steam, economies of scale, and environmental impact. Under most circumstances, methane is an ideal fuel. Firstly, compared to other fossil fuels, methane produces few atmospheric pollutants and generates less carbon dioxide per unit of energy. Therefore, its use for appliances, vehicles, industrial applications, and power generation is increasing. Furthermore, methane can be used at various stages of purity, and its transport cost and energy conversion efficiency are comparable to those of electricity (Chynoweth et al. 2000; Gür 2016). Besides, an extensive pipeline distribution system is already in place worldwide for methane use. In contrast, other fuels such as methanol and hydrogen are not well developed commercially for production, distribution and usage (Chynoweth et al. 2000).

This chapter aims to overview the characteristics and potential of LMs for AD, with a specific focus on three emerging pretreatment technologies to enhance the conversion of LMs into methane: organosolv, N-methylmorpholine N-oxide (NMMO), and ultrasound pretreatment. The principles of each pretreatment will be thoroughly discussed, pointing out advantages and drawbacks. Particular attention will be given to the effect of the three pretreatments on the physical characteristics and chemical composition of LMs, focusing on the subsequent valorisation of the pretreated solid residues through the AD process.

4.2 Lignocellulosic Materials: Structure and Potential

Biomass is one of the most abundant resources on the planet, with a global production of 2×10^{11} tons per year (Reddy and Yang 2005). Biomass can be converted into fuels and provide renewable materials at the same time, offering a viable alternative to fossil fuels. Biomass is produced via photosynthesis, by fixing atmospheric carbon dioxide and converting solar energy to chemical energy to build up the carbon backbone of plant cells (Zhang 2008). LMs represent more than 60% of the global biomass and serve as a cheap and abundant feedstock (Bilal et al. 2017). Agricultural, municipal, and industrial activities generate LMs as waste, generally at low cost (Table 4.1). Also, the use of LMs for biofuel production does not create conflicts between land use for food and energy production (Kucharska et al. 2018). Depending on the origin, LMs are classified as forest residues, municipal solid waste, waste paper, or crop residue resources (Balat 2011).

The structural and chemical composition of LMs is extremely variable (Table 4.1) due to various genetic and environmental factors. The chemical composition of LMs includes mainly cellulose, hemicellulose, and lignin, arranged in a three-dimensional and complex structure (Fig. 4.1) (Zhang et al. 2019). Depending on the specific substrate, a significant part of LMs may consist of non-structural compounds. The most common extractives present in LMs are free sugars (sucrose, glucose, and

Table 4.1 Chemical composition (in terms of cellulose, hemicellulose, and lignin content) of the most employed lignocellulosic materials for methane production

Biomass origin	Substrate	Cellulose[a] (%)	Hemicellulose[b] (%)	Lignin[c] (%)	Reference
Agricultural residues	Maize straw	38.3	29.8	3.8	Khatri et al. (2015)
	Wheat straw	31.0	18.4	18.3	Mancini et al. (2018a)
	Rice straw	28.6	19.5	17.3	Mancini et al. (2018b)
	Barley straw	39.1	25.7	15.2	Duque et al. (2013)
	Sweet sorghum straw	37.7	28.1	21.5	Dong et al. (2019)
	Oat straw	35.0	28.2	4.1	Gomez-Tovar et al. (2012)
	Rye straw	42.1	23.8	19.5	Ingram et al. (2011)
	Triticale straw	33.0	23.0	29.0	Teghammar et al. (2012)
	Sugarcane bagasse	47.6	22.6	27.6	Hashemi et al. (2019a)
	Sunflower stalks	34.1	26.2	26.8	Hesami et al. (2015)
Nuts residues	Peanut shell	23.6	12.2	40.0	Shen et al. (2018)
	Almond shell	23.4	21.9	30.6	Oliva et al. (2021)
	Walnut shell	25.6	23.0	46.7	Şenol (2021)
	Pistachio shell	20.1	23.2	24.3	Shen et al. (2018)
	Chestnut shell	26.8	24.5	36.8	Bianco et al. (2021b)
	Hazelnut shell	18.0	17.2	39.1	Shen et al. (2018)
	Hazelnut skin	10.2	3.6	39.7	Oliva et al. (2021)
Industrial wastes	Spent coffee grounds	8.8	33.6	20.3	Oliva et al. (2021)
	Brewery spent grain	19.2	26.9	30.5	Ravindran et al. (2018)
	Cocoa bean shell	13.5	7.0	29.9	Mancini et al. (2018b)
	Rubber wood waste	43.6	8.3	31.0	Tongbuekeaw et al. (2020)
	Oil palm empty fruit bunch	36.1	22.4	26.4	Tang et al. (2018)
	Olive pomace	12.3	8.9	34.0	Elalami et al. (2020)
	Grape pomace	15.8	8.6	35.4	Bordiga et al. (2019)
Forest residues	Switch grass	42.0	19.0	24.0	Larnaudie et al. (2019)
	Spruce wood	42.0	20.0	27.0	Teghammar et al. (2012)
	Poplar wood	49.0	23.0	27.0	Rego et al. (2019)
	Birch wood	40.1	26.8	24.5	Goshadrou et al. (2013)

(continued)

Table 4.1 (continued)

Biomass origin	Substrate	Cellulose[a] (%)	Hemicellulose[b] (%)	Lignin[c] (%)	Reference
	Pine wood	44.5	28.0	26.8	Mirmohamadsadeghi et al. (2014)
	Elm wood	46.4	26.3	26.2	Mirmohamadsadeghi et al. (2014)

[a] Cellulose content (g/g dry matter) was considered equal to the glucan content (Mussatto et al. 2011)

[b] Hemicellulose content (g/g dry matter) is reported as the sum of xylan, mannan, galactan, arabinan, galactan, and rhamnan (Mussatto et al. 2011)

[c] Lignin content (g/g dry matter) is reported as the sum of acid soluble and acid-insoluble lignin (Sluiter et al. 2008)

fructose), phenolic compounds, proteins, lipids, waxes, chlorophyll, essential oils, starches, and fatty acids (Tajmirriahi et al. 2021a, b).

The complex structure of lignocelluloses results in its resistance to biological and chemical degradation, with hydrolysis being the limiting step (Kainthola et al. 2019a). Hydrolysis of lignocellulose biodegradation requires several enzymes to work together, including cellulases, hemicellulases, and lignin-degrading enzymes (Xu et al. 2019). The main reason for biomass recalcitrance is the low accessibility of crystalline cellulose fibers, which prevents cellulases from working efficiently. Equally, the presence of lignin and hemicellulose prevents cellulase from accessing the substrate efficiently (Mancini et al. 2016a; Xu et al. 2019; Zoghlami and Paës 2019).

4.2.1 Cellulose

Cellulose is a linear polysaccharide consisting of a repeated unit called cellobiose consisting of D-glucose subunits linked to one another by β-(1,4)-glycosidic bonds (Su et al. 2018). The cellobiose units are composed of long-chain cellulose polymers, linked together by van der Waals and hydrogen bonds. Cellulose is packed into microfibrils, which reduce the access of the enzymes and complicate cellulose degradation (Kumar et al. 2009; Zhang et al. 2019). Cellulose alternates crystalline and amorphous regions, with the latter being the weakness for chemical and biological attack. Cellulose degradation aims to decompose the polysaccharide into free sugar molecules. The resulting product is glucose, a six-carbon sugar (Singhvi and Gokhale 2019).

Cellulose crystallinity presents several structures (i.e. I_α, I_β, II, III, and IV), depending on the crystallites disposition (Blanco et al. 2018). Native cellulose has a parallel chain disposition and exists in nature as cellulose I_α and I_β. Cellulose I_α shows one-chain triclinic cells and abounds in bacterial cellulose and algae (Nishiyama 2009). Cellulose I_β is present in cotton and wood materials and reveals

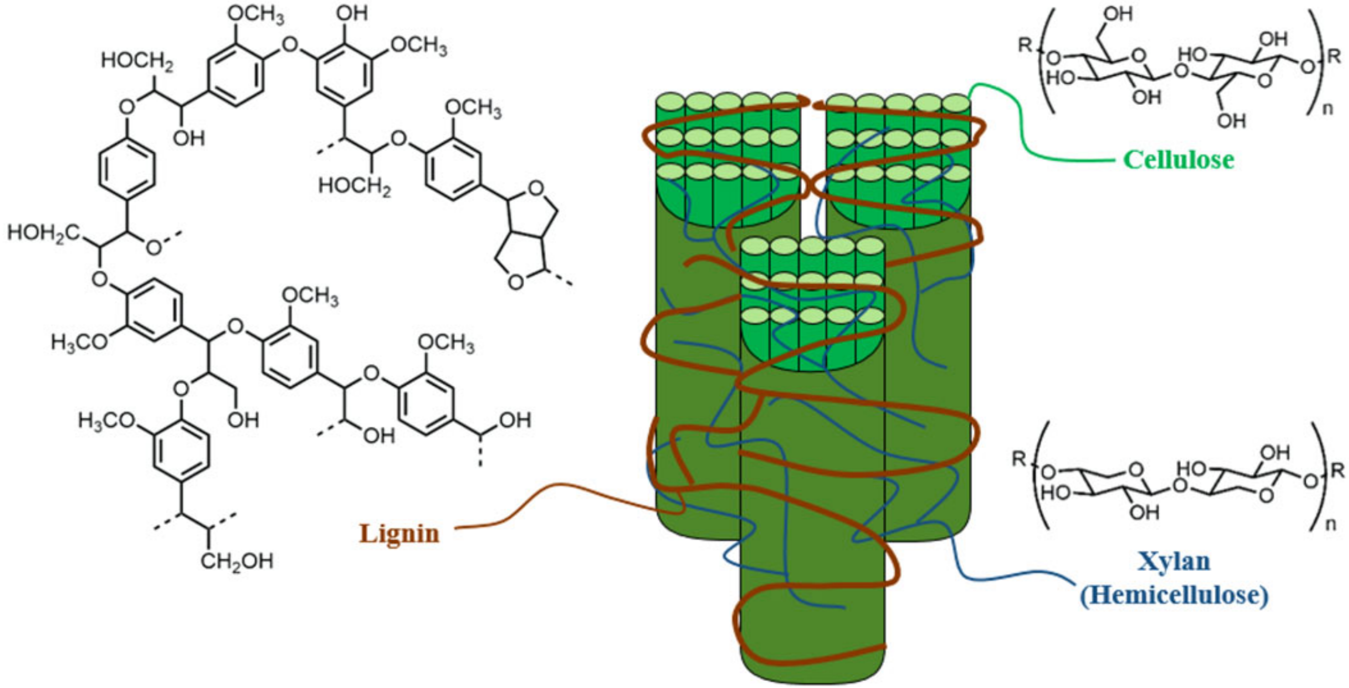

Fig. 4.1 Schematic representation of the structure of lignocellulosic materials containing cellulose, hemicellulose, and lignin

two-chain monoclinic cells (Blanco et al. 2018). Cellulose I_α conversion to cellulose I_β is a non-reversible process requiring high temperatures (260–280 °C) (Matthews et al. 2012). Cellulose II is obtained by maceration or dissolution and subsequent regeneration of cellulose I using solvent-based processes (Corrêa et al. 2010). Cellulose II presents an antiparallel chain disposition, making it more appreciated for textile applications and easily accessible for enzymes and microorganisms (Wikandari et al. 2016). Only very low or high pH allows cellulose solubilisation in water, whereas solvents like NMMO or ionic liquids dissolve cellulose at neutral pH (Baruah et al. 2018). Cellulose III is obtained by treating cellulose I and II with an ammonia solution, whereas cellulose IV derives from cellulose III treatment in glycerol over 260 °C (Corrêa et al. 2010). The transformation to cellulose III and IV can be reverted using thermal or chemical processes (Isogai et al. 1989; Wada et al. 2006). In contrast, cellulose II is non-reversible to cellulose I (Nagarajan et al. 2017).

4.2.2 Hemicellulose

Hemicellulose does not have a fixed structure. Its backbone can be either a homopolymer or a hetero-polymer with short branches linked by β-1,4-glucan bonds and, occasionally, by β-1,3-glucan bonds (Zhang et al. 2019). These branches consist of five-carbon sugars (i.e. xylose, rhamnose, and arabinose), six-carbon sugars (i.e. glucose, mannose, and galactose), and uronic acids. Generally, xylose is the dominant sugar for hardwoods and agricultural residues, while mannose prevails in softwoods (Baruah et al. 2018; Singhvi and Gokhale 2019). Contrary to cellulose, the polymers present in hemicelluloses are easily degradable, due to the amorphous (non-crystalline) structure and the lower degree of polymerisation. Hemicellulose, together with lignin, represents a barrier around the cellulose (Fig. 4.1), reducing the access of cellulases enzymes (Baruah et al. 2018; Zoghlami and Paës 2019). The most common pretreatments for hemicellulose hydrolysis are dilute acid or alkaline compounds, steam explosion or enzymes (Zoghlami and Paës 2019).

4.2.3 Lignin

Lignin is the third most abundant polymer in nature, after cellulose and hemicelluloses, and generally represents 10–25% of the total feedstock dry matter (Balat 2011). Lignin is an aromatic, complex, three-dimensional cross-linked polymer synthesized from phenylpropanoid precursors (Fig. 4.1). The lignin structure consists of phenyl propane structural units, liked by aryl ether linkages. The structural variableness is given by the substitution of the methoxyl groups present in the aromatic rings (Baruah et al. 2018). The lignin content ranges from 10 to 20% in various LMs, such as straws, hulls, bagasse, and stalks, and can increase to 30–40% for nut shells and pinewood (Ponnusamy et al. 2019). The three most common monomers present in lignin are sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol, corresponding to the three main structural units, which are syringyl, guaiacyl, and hydroxyphenyl, respectively (Ralph et al. 2019).

Lignin protects the plants from microbial attack and oxidation and gives rigidity and impermeability to their structure (Ponnusamy et al. 2019). The presence of lignin is one of the main drawbacks of using LMs in fermentation and AD, as it makes lignocelluloses resistant to chemical and biological degradation by reducing the hydrolysis rate (Reddy and Yang 2005). Organic solvents, thermal, and fungal pretreatment are generally suggested for efficient lignin removal (Amin et al. 2017; Singhvi and Gokhale 2019).

4.3 Parameters Affecting Lignocellulose Conversion to Biofuels

The biodegradation of LMs is influenced by four main factors, i.e. (1) accessible surface, (2) crystallinity and degree of polymerization of cellulose, as well as the (3) lignin and (4) hemicellulose content (Mancini et al. 2016a). Cellulose accessibility is a key factor in the bioconversion of LMs to fermentable sugars. Thus, the contact between cellulose and cellulase is one of the most critical factors affecting the enzymatic hydrolysis yield and rate. The contact area depends on biomass porosity and particle size (Meng and Ragauskas 2014; Xu et al. 2019). Cellulase accessibility to cellulose mainly depends on porosity, rather than the external surface of the substrate (Siqueira et al. 2017). Over 90% of the substrate enzymatic digestibility depends on the substrate porosity (Wang et al. 2012). In AD, a limited access to cellulose results in a scarce contact between biomass and hydrolytic bacteria, which reduces the release of fermentable sugars for the subsequent degradation steps. The accessible surface increases along the AD process proportionally with the degradation of the cell wall components (Xu et al. 2019). The microorganisms-substrate contact controls the hydrolysis efficiency, especially during the first days of AD. On the contrary, other factors prevail later, such as the compact structure and the degree of crystallinity of the remaining cellulose (Oliva et al. 2021; Xu et al. 2019).

The ordered structure and high crystallinity of cellulose are the main deterrents to convert it to biofuels. Nevertheless, amorphous regions, which are more accessible to enzymatic attack, are randomly present in the cellulose structure (Zoghlami and Paës 2019). The cellulose becomes more accessible by decreasing the crystallinity degree, enhancing the biofuel production from cellulose-rich materials (Jeihanipour et al. 2011). As described in Sect. 4.2.1, cellulose is a linear homopolymer composed of microfibrils, joint together to form fibrils and finally fibers. The degree of polymerization refers to the average length of the polysaccharide chains. An increase in the degree of polymerization is reflected in a higher density and tensile strength of the cellulosic component of LMs, making cellulose hydrolysis more difficult (Hallac and Ragauskas 2011; Mattonai et al. 2018).

A further factor affecting the hydrolysis of LMs is the presence of hemicellulose and lignin. Hemicellulose and lignin form a physical barrier around cellulose. It is important to remove or alter them, while avoiding the degradation of the hemicellulose sugars to obtain a high sugar yield (Singhvi and Gokhale 2019; Xu et al. 2019; Zoghlami and Paës 2019). Hemicellulose contributes to the resistance of the plant cell wall and reduces the overall hydrolysis rate of LMs (Xu et al. 2019). Nevertheless, hydrolysis and acidification of hemicellulose alone are faster than those of cellulose, suggesting that the methane production from hemicellulose can be optimised by controlling the organic loading rate (Li et al. 2018). Other studies reported that the hemicellulose-cellulose linkages contribute to reducing the crystallinity of cellulose, enhancing the hydrolysis step (Li et al. 2015; Xu et al. 2012). On the other hand, lignin is well known to negatively affect the AD process by reducing the biodegradability of LMs and the overall methane yield (Li et al. 2018). Lignin consolidates the cell wall structure and prevents contact of hydrolytic enzymes with carbohydrates. In addition, lignin is capable of adsorbing cellulase enzymes, further protecting the cellulosic component of LMs (Lu et al. 2016).

4.4 Pretreatment Methods to Enhance Methane Production from Lignocellulosic Materials

The use of LMs for methane production is limited due to their resistance to the enzymatic attack (Mahmood et al. 2019). Therefore, many studies have focused on developing cost-effective pretreatments to reduce the recalcitrance of LMs (Table 4.2) (Lee et al. 2021; Matsakas et al. 2020; Oliva et al. 2021). Pretreatments aim to increase the efficacy of lignocellulose hydrolysis by improving the accessibility to cellulose. This scope can be achieved by removing or altering the lignin and hemicellulose fraction of LMs (Fig. 4.2) (Ali et al. 2020a; Haldar and Purkait 2021).

To be efficient and economically advantageous, pretreatment methods should meet the following features: (1) high recovery of carbohydrates, (2) high digestibility of the cellulose in the subsequent enzymatic hydrolysis, (3) high solid concentrations as well as a high concentration of free sugars in the liquid fraction, (4) no destruction of hemicelluloses and cellulose, (5) no formation of possible inhibitors for hydrolytic enzymes and fermenting microorganisms, (6) cost-effectiveness and low consumption of chemicals, (7) low generation of residues, and (8) low capital and operational costs (Kumari and Singh 2018; Taherzadeh and Karimi 2008).

Pretreatment techniques can be differently classified. A first classification concerns the pH maintained during the process, with pretreatments grouped in acidic, neutral and alkaline (Ravindran and Jaiswal 2016). Nevertheless, the most common classification categorises pretreatments into physical, chemical, physicochemical and biological (Table 4.2) (Singh et al. 2015).

Table 4.2 Effectiveness of different pretreatment methods on the enhancement of the methane potential of lignocellulosic materials

Category	Pretreatment	Substrate	Δ CH_4	Reference
Physical	Ball milling	Wheat straw	+49%	Dell'Omo and Spena (2020)
	Microwave	Energy crop (*Sida hermaphrodita*)	+39%	Zieliński et al. (2019)
	Extrusion	Rice straw	+72%	(Chen et al. 2014)
Chemical	Alkaline (NaOH)	Wheat straw	+15%	Mancini et al. (2018a)
	Acid (H_2SO_4)	Cassava residues	+57%	Zhang et al. (2011)
	Ionic liquid ([C4mim]Cl/DMSO)	Rice straw	+137%	Gao et al. (2013)
Physicochemical	Steam explosion	Rubber wood waste	+670%	Eom et al. (2019)
	Liquid hot water	Sunflower residues	+173%	Lee and Park (2020)
Biological	Fungal (white-rot)	Rice straw	+114%	Kainthola et al. (2019b)
	Microbial consortia (WSD-5)	Napier grass	+49%	Wen et al. (2015)
	Microbial consortia (CS-5)	Catalpa sawdust	+76%	Ali et al. (2020b)

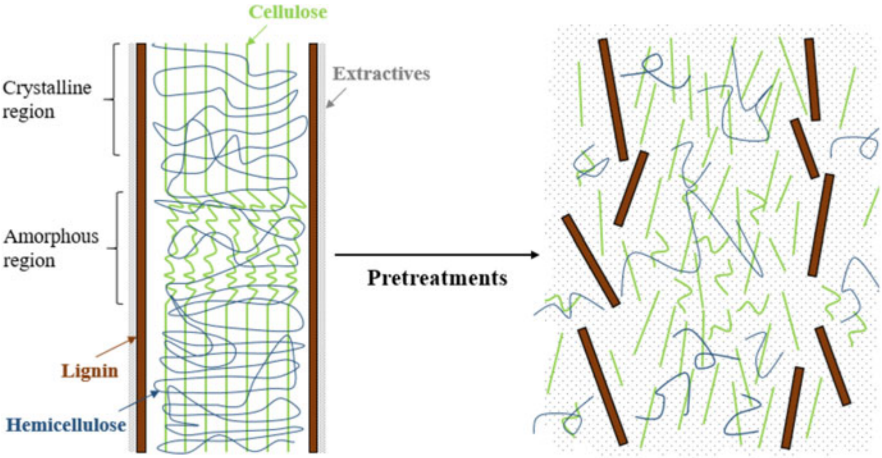

Fig. 4.2 Schematisation of the effect of pretreatment on the lignocellulosic structure

4.4.1 Physical Pretreatments

The most common physical pretreatments include different milling (e.g. ball, colloid, vibro-energy, roller, and hammer), extrusion and irradiation, with the primary objective of increasing the accessible surface area and decreasing cellulose crystallinity and degree of polymerisation (Amin et al. 2017).

Milling is a size reduction technique employed to increase the surface/volume ratio and alter the structure and the degree of crystallinity of LMs, making pretreated substrates more amenable to cellulase attack (Ravindran and Jaiswal 2016).

Irradiation pretreatments involve gamma rays, electron beam, ultrasounds (see Sect. 4.7) and microwaves, intending to improve the enzymatic hydrolysis of lignocelluloses (Taherzadeh and Karimi 2008). The pretreatment effectiveness is proportional to the lignin content, resulting in a lower efficiency on less recalcitrant (i.e. low lignin) substrates (Keikhosor et al. 2013).

Extrusion pretreatment relies on the spinning of a single or twin screw into a temperature-controlled barrel. The mechanical action causes strong shearing forces between the substrate, the screw, and the barrel, locally increasing pressure and temperature. Apart from the particle size reduction, those forces alter also the biomass structure and change the crystallinity of the cellulosic component of the biomass (Duque et al. 2017; Zheng and Rehmann 2014).

4.4.2 Chemical Pretreatments

Chemical pretreatments act directly on the main components of the biomass, removing lignin and hemicellulose or decreasing the crystallinity degree of the cellulose (Ponnusamy et al. 2019). The chemical agents employed are divided into four main categories: alkali, acids, salts, and organic solvents.

Alkaline pretreatment involves base solutions, e.g. NaOH, KOH, and $Ca(OH)_2$, aiming to enhance the digestibility of LMs. The main effects on LMs are lignin and hemicellulose removal, an increase in porosity and the reduction of polymerisation and crystallinity degree of the cellulose (Tu and Hallett 2019). Alkaline pretreatments occur at mild conditions, i.e. ambient pressure and temperature, but generally last over 24 h (Amin et al. 2017). NaOH and KOH are the most employed basic solutions for alkaline pretreatment, having particular effectiveness for lignin removal from low lignin content LMs (Baruah et al. 2018). Nevertheless, the recycling of alkaline solutions is challenging, and Na^+ and K^+ ions can inhibit the subsequent AD process (Bianco et al. 2021b). On the other hand, a $Ca(OH)_2$ solution can be more easily recovered but is less effective than NaOH and KOH based solutions (Amin et al. 2017).

Acid pretreatment is performed with diluted or concentrated solutions. Organic acids, such as formic acid, as well as inorganic acids, i.e. sulfuric, nitric, phosphoric, and hydrochloric, are widely employed (Baruah et al. 2018). Dilute acid pretreatment (0.1–5%) aims to remove the hemicellulosic component of the biomass and is effective at high temperatures (100–250 °C). On the other hand, acids concentrated at 30–70% hydrolise both cellulose and hemicellulose and require temperatures below 100 °C (Solarte-Toro et al. 2019). Acid solutions are unable to dissolve lignin but alter the cellulose-hemicellulose-lignin linkages, which increases the biodegradability of the solid residues (Amin et al. 2017). Nevertheless, the formation of inhibitory compounds can occur. Phenolic compounds, aldehydes and furfurals are the most know inhibitory compounds observed after acid pretreatments (Ali et al. 2020a). Acid-pretreated solid residues of LMs require abundant washing to be ready for AD or other biological processes (Rajan and Carrier 2014). On the other hand, before undergoing fermentation processes, the pH of the hydrolysate has to be neutralised with alkaline solutions (Gonzales et al. 2017), which increases the overall process costs (Castilla-Archilla et al. 2021) and can create further inhibition (Bianco et al. 2021b).

Ionic liquids and NMMO (see Sect. 4.6) act on the cellulosic component of LMs (Halder et al. 2019; Mancini et al. 2016b). Ionic liquids are salts in the liquid state at room temperature in which isolated ions and cations interact by Coulomb forces. NMMO is a zwitterion containing localised positive and negative charges in a single molecule (Böhmdorfer et al. 2017). Ionic liquids and NMMO dissolve cellulose, which can then be regenerated using an anti-solvent (Mancini et al. 2016a). The regenerated cellulose shows a lower crystallinity, which is a critical factor for the bioconversion of LMs (Xu et al. 2019). NMMO is effective at different concentrations in aqueous solutions (Wikandari et al. 2016), the mechanisms of which are thoroughly discussed in Sect. 4.6.

Organosolv pretreatment (see Sect. 4.5) involves organic solvents such as ethanol, methanol, and acetic acid, heated to high temperature to remove lignin and reduce the recalcitrance of LMs. Lignin is a valuable product and can be recovered at good purity levels after organosolv pretreatment (Ferreira and Taherzadeh 2020).

4.4.3 Physicochemical Pretreatments

Physicochemical pretreatment methods combine chemical and physical approaches. This category includes several pretreatment methods such as liquid hot water, wet oxidation, ammonia fiber explosion, steam explosion, and CO_2 explosion. Steam explosion and liquid hot water are the two most studied strategies.

Steam explosion combines thermal and pressure effects to hydrolyse the hemicellulosic component of the biomass (Jacquet et al. 2015). LMs undergo high-pressure (5–50 atm) saturated steam at temperatures between 160 and 260 °C. The pretreatment time is generally short (1–10 min) and inversely related to temperature (Amin et al. 2017). Water molecules firstly penetrate LMs and explosively escape once pressure is released, causing cell wall disruption (Ravindran and Jaiswal 2016). Higher temperatures lead to substantial hemicellulose hydrolysis into glucose and xylose monomers, liberating acetic acid, which acts as a catalyst to hydrolyse the remaining sugars (Baruah et al. 2018). However, harsh pretreatment conditions can generate inhibitors such as phenolic compounds, formic and levulinic acid (Cantarella et al. 2004; Martín et al. 2018). Alternatively, an external catalyst (e.g. H_2SO_4, SO_2, H_3PO_4, and CO_2) allows lowering the pretreatment temperature while maintaining a high hemicellulose hydrolysis rate (Duque et al. 2016).

Liquid hot water pretreatment, similarly to steam explosion, requires high temperature and pressure to remove hemicellulose and disrupt lignin bonds making the remaining cellulose more available for AD (Hashemi et al. 2019b; Qiao et al. 2011). Contrary to steam explosion pretreatment, water remains in the liquid state, and pressure allows maintaining this status at high temperatures (Ruiz et al. 2020). The hemicellulose sugars, together with other hydrolysable compounds, are hydrolysed, making liquid hot water pretreatment ideal for LMs rich in non-structural sugars (Ravindran and Jaiswal 2016). pH has to be controlled to avoid the formation of inhibitory compounds (Yang et al. 2018). Liquid hot water pretreatment does not need particle size comminution but demands a large amount of water (Baruah et al. 2018).

4.4.4 Biological Pretreatments

Biological pretreatments include enzymes, microbial consortia, and fungal strains (Baruah et al. 2018). Compared to physical and chemical methods, a biological pretreatment has various advantages, such as no requirement for chemicals and a lower energy input (Taherzadeh and Karimi 2008). Biological pretreatment methods are performed under mild environmental conditions, which reduce the risk of generating inhibitory compounds (Ravindran and Jaiswal 2016). Nevertheless, the long pretreatment time and the competition for carbohydrates between organisms carrying out pretreatment and biogas production limit biological pretreatments in commercial applications (Tu and Hallett 2019).

Several wood-decay fungi have been studied, and white-rot strains are most interesting for the biological pretreatment of LMs, since they can selectively metabolise lignin from LMs with low carbohydrate consumption (Amin et al. 2017). In contrast, soft-rot and brown-rot fungi use enzymes to degrade cellulose and hemicellulose with minimal lignin removal (Ravindran and Jaiswal 2016). White rot fungi have two enzyme systems: the oxidative ligninolytic system and the hydrolytic system. The first one makes use of three enzymes, i.e. lignin peroxide, manganese peroxide and laccase, which attack the phenyl rings in lignin. The second one degrades cellulose and hemicellulose to release fermentable sugars using cellulase and hemicellulase enzymes (Nadir et al. 2019). White-rot fungi degrade lignin with two modes of action, namely selective and non-selective decay. In selective decay mode, fungi selectively degrade the lignin and hemicellulose fractions, while the cellulose fraction is essentially unaffected. Non-selective degradation consumes similar amounts of cellulose, hemicellulose, and lignin for fungal growth (Baruah et al. 2018).

Microbial consortia employ mixed cultures to increase the total sugar yield and reduce the lignin content of LMs (Ali et al. 2020b; Wen et al. 2015; Zhong et al. 2016). Similarly to fungal pretreatment, enzymatic pretreatment uses pure enzymes (e.g. laccase, manganese peroxidase, cellulase, and xylanase) to achieve the same goals (Koupaie et al. 2019). Nevertheless, microbial consortia and enzymatic pretreatment are still attempting to meet a cost-effective balance beyond the laboratory scale (Koupaie et al. 2019; Wen et al. 2015).

4.5 Organosolv Pretreatment

4.5.1 Mechanism and Process Parameters of Organosolv Pretreatment

Organosolv pretreatment is the most efficient pretreatment method to remove lignin, which protects the polysaccharides against degradation (Ostovareh et al. 2015). Organosolv is a chemical pretreatment in which the LMs are mixed with an organic or aqueous organic solvent and heated to dissolve the lignin component. Besides, depending on the operating conditions, partial hemicellulose hydrolysis can occur (Oliva et al. 2021). After pretreatment, lignin can be extracted from the solvent by precipitation, membrane filtration (Arkell et al. 2014), and water electrolysis (Jin et al. 2013). Precipitation is the most employed strategy and is performed via acidification of the lignin-rich liquor (Mussatto et al. 2007).

A wide range of organic or aqueous organic solvents has been explored to pretreat LMs, with or without the addition of inorganic or organic acid catalysts (Table 4.3). The optimal process temperature depends on the type of biomass, solvent, and catalyst, and usually ranges from 150 to 200 °C (Taherzadeh and Karimi 2008). Organic solvents are classified into low boiling point alcohols (e.g. methanol and ethanol), higher boiling point alcohols (e.g. ethylene glycol and glycerol), and other classes of organic compounds (e.g. dimethyl sulfoxide, ethers and ketones) (Borand and Karaosmanoğlu 2018). In the choice of the solvent, the price and easiness of recovery should also be considered. The solvent should be separated and reused to reduce the operational costs of the process (Zhou et al. 2018). Also, solvent residues must be removed from the pretreated material to avoid the inhibition of the subsequent AD process (Behera et al. 2014; Harmsen et al. 2010). Due to the high cost of the solvents, ethanol and methanol are preferred over alcohols with a higher boiling point. The most employed catalysts to enhance the pretreatment effectiveness are hydrochloric, sulfuric, and phosphoric acid (Ferreira and Taherzadeh 2020), but organic acids such as acetic and formic acid have also been investigated (Borand and Karaosmanoğlu 2018).

After organosolv pretreatment, three separate components are obtained: a pure cellulose fraction, an aqueous hemicellulose stream, and a highly pure lignin fraction (Meng et al. 2020). Further, similarly to other pretreatments, organosolv causes a decrease in the crystallinity of LMs and enhances the accessibility of carbohydrates for microbial degradation (Mancini et al. 2016a). At higher temperatures, the cellulose fraction of the biomass is also degraded. Furthermore, to be effective, the pretreatment time varies between 0.5 and 2 h. Under these process conditions, organosolv is well suitable to dissolve hemicellulose, recover cellulose, and make

Table 4.3 Effectiveness of organosolv pretreatment for lignin removal (Δlignin) and increment of the methane potential (ΔCH_4) of different lignocellulosic materials

Substrate	Optimal pretreatment condition	Pretreatment effectiveness[a]	Reference
Rice straw	50% EtOH, 180 °C, 1 h	Δlignin: −18% ΔCH_4: +41%	Mancini et al. (2018b)
Rice straw	75% EtOH, 150 °C, 1 h, catalyst	Δlignin: −22% ΔCH_4: +32%	Mirmohamadsadeghi et al. (2014)
Wheat straw	50% EtOH, 180 °C, 1 h	Δlignin: −14% ΔCH_4: +15%	Mancini et al. (2018a)
Sugarcane bagasse	25% EtOH +10% Ammonia, 70 °C, 12 h	Δlignin: −49% ΔCH_4: +135%	Hashemi et al. (2019a)
Sweet sorghum stalks	50% PrOH, 160 °C, 0.5 h, catalyst	Δlignin: −25% ΔCH_4: +107%	Ostovareh et al. (2015)
Sunflower stalks	50% EtOH, 160 °C, 0.5 h	Δlignin: −26% ΔCH_4: +124%	Hesami et al. (2015)
Hazelnut skin	50% MeOH, 130 °C, 1 h, catalyst	Δlignin: −9% ΔCH_4: +1700%	Oliva et al. (2021)
Hazelnut skin	50% EtOH, 180 °C, 1 h	Δlignin: N.O. ΔCH_4: +10%	Mancini et al. (2018b)
Almond shell	50% MeOH, 200 °C, 1 h	Δlignin: N.O. ΔCH_4: +7%	Oliva et al. (2021)
Cocoa bean shell	50% EtOH, 180 °C, 1 h	Δlignin: N.O. ΔCH_4: N.O.	Mancini et al. (2018b)
Spent coffee grounds	50% MeOH, 200 °C, 1 h, catalyst	Δlignin: N.O. ΔCH_4: +10%	Oliva et al. (2021)
Forest residues	50% MeOH, 190 °C, 1 h, catalyst	Δlignin: −4% ΔCH_4: +320%	Kabir et al. (2015)
Elmwood	75% EtOH, 180 °C, 1 h, catalyst	Δlignin: −27% ΔCH_4: +73%	Mirmohamadsadeghi et al. (2014)
Pinewood	75% EtOH, 150 °C, 0.5 h, catalyst	Δlignin: N.O. ΔCH_4: +84%	Mirmohamadsadeghi et al. (2014)
Rubber wood waste	75% EtOH, 210 °C, 0.5 h	Δlignin: −74% ΔCH_4: +179%	Tongbuekeaw et al. (2020)

[a] N.O. means that no significant effect on the specific parameter was observed

it more susceptible to enzymatic hydrolysis (Ferreira and Taherzadeh 2020). Typically, an uncatalysed organosolv pretreatment is efficient only towards low-density hardwoods and agricultural residues. Softwoods or high-density hardwoods require more severe pretreatment conditions (Harmsen et al. 2010).

4.5.2 Benefits and Drawbacks

The benefits of organosolv pretreatment include: (1) production of high-quality lignin, which can be used for several applications, (2) reduced amount of waste produced, (3) lower energy use, (4) increase in porosity, (5) removal of lignin and the reduction of the hemicellulose fraction, which may shorten the hydrolysis stage, (6) low formation of inhibitory compounds, compared to the industrially most employed pretreatments, and (7) easy solvent recovery. On the contrary, potential drawbacks of the organosolv pretreatment are the high operational and investment costs, as well as the risk of explosion due to the use of organic solvents and the high temperatures employed (Ferreira and Taherzadeh 2020; Meng et al. 2020; Zhou et al. 2018).

4.5.3 Effectiveness of Organosolv Pretreatment on Different Lignocellulosic Materials

Organosolv pretreatment, performed with 75% ethanol using sulfuric acid as a catalyst, improves the methane production from hardwood elm, softwood pine, and rice straw (Mirmohamadsadeghi et al. 2014). The optimal process parameters vary depending on the substrate. Rice straw increases its methane potential by 32% when pretreated at 150 °C for 60 min. Instead, 30 min pretreatment is sufficient to enhance the methane production from pinewood by 84%. On the other hand, a higher pretreatment temperature (i.e. 180 °C) has a positive effect on elmwood (Mirmohamadsadeghi et al. 2014). Ostovareh et al. (2015) improved the bioconversion of sweet sorghum stalks to ethanol and biogas by organosolv pretreatment. Nevertheless, the use of the acid catalyst improves the methane yield only at lower pretreatment temperatures.

The organic solvent selection plays a key role when pretreating hazelnut skin (Table 4.3). The use of methanol and catalysed-methanol is more efficient than ethanol organosolv pretreatment (Mancini et al. 2018b; Oliva et al. 2021). In contrast, methanol-organosolv pretreatment is not strong enough to overcome the recalcitrance of nut shells, such as almond shell, and causes a loss of biodegradable matter from spent coffee grounds, decreasing the methane production (Oliva et al. 2021). On the other hand, ethanol-organosolv pretreatment is particularly effective on rice straw and wheat straw, raising the methane potential of the two LMs to 332 and 316 mL CH_4/g VS, respectively (Mancini et al. 2018a, b).

Organosolv pretreatment was effective on forest residues using three different organic solvents (i.e. ethanol, methanol, and acetic acid) with or without 1% w/w sulfuric acid, acetic acid, and hydrochloric acid as catalysts (Kabir et al. 2015). The methane potential of catalyst-free pretreated forest residues achieves 300, 230, and 330 mL CH_4/g VS for ethanol, methanol, and acetic acid pretreated LM, respectively, rather than the untreated biomass that reaches only 50 mL CH_4/g VS. The use of catalysts coupled to ethanol and methanol improved methane production from forest residues, but the methane yield decreased in the case of acetic acid catalysed pretreatment (Kabir et al. 2015). The economic analysis performed in that study showed that the methanol supply and recovery were cheaper than for the other two solvents (Kabir et al. 2015). Ethanol-organosolv pretreatment can also be combined with steam explosion to enhance the AD of birch and spruce woodchips (Matsakas et al. 2020).

Recent studies have focused on rubber wood waste valorisation using organosolv pretreatment under a biorefinery approach (Charnnok et al. 2020; Tongbuekeaw et al. 2020). Organosolv pretreatment (75% ethanol) significantly increases the methane production from rubber wood waste from 59 to 166 mL CH_4/g VS, reducing the lignin content by 74% (Tongbuekeaw et al. 2020). Sequential ethanol-organosolv and enzymatic pretreatments enhance the methane potential of rubber wood waste. The organosolv step removes almost 50% of the lignin, obtaining a glucose-rich hydrolysate for the subsequent enzyme-assisted AD (Charnnok et al. 2020).

4.6 N-Methylmorpholine N-Oxide Pretreatment

4.6.1 Mechanisms and Process Parameters of the NMMO Pretreatment

NMMO is a cyclic, tertiary amine, aliphatic oxide capable of dissolving cellulose by disrupting the original hydrogen bonds and creating new linkages with the dissolved polymer (Sari and Budiyono 2014; Satari et al. 2019). The effect on cellulose depends on the NMMO hydration (Fig. 4.3). A water content lower than 17% completely dissolves cellulose, while an NMMO content of 76–82% leads to the

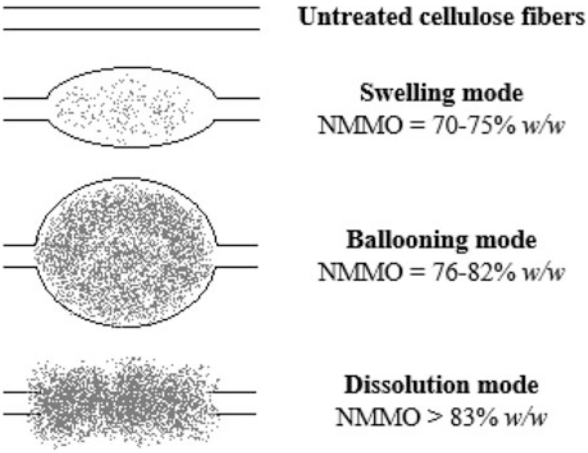

Fig. 4.3 Effect of NMMO pretreatment on cellulose fibers

swelling of the cellulose fibers by creating balloons, in which the cellulose starts to dissolve. A further increase of the water content (25–30%) reduces the cellulose dissolution and mainly results in the swelling of the cellulose fibers. An NMMO content lower than 65% proportionally decreases cellulose swelling, with no dissolution observed (Cuissinat and Navard 2006). The ability of NMMO in dissolving cellulose is attributed to its chemical structure, presenting weak polar N-O bonds with a negative charge on oxygen and positively charged on nitrogen. NMMO tends to form new hydrogen bonds with both water and cellulose, preferentially with cellulose until the water content of the aqueous solution is below 17% (Mancini et al. 2016a; Wikandari et al. 2016).

The interest in NMMO started in the early twentieth century with applications in the textile industry and culminating with its usage in the Lyocell process (Sayyed et al. 2019). Recently, the effectiveness of NMMO on cellulose has allowed its use as a pretreatment for LMs (Table 4.4) (Khoshnevisan et al. 2016; Shafiei et al. 2011; Sołowski et al. 2020). The dissolution mode (85% NMMO) is recommended for ethanol production, while a lower NMMO concentration results in a better improvement in terms of methane production (Jeihanipour et al. 2010). The dissolution mode foresees the complete solubilization and subsequent regeneration of the cellulosic component of the biomass. The rate of cellulose dissolution is inversely related to the cellulose concentration and degree of polymerization (Wikandari et al. 2016). The regeneration of cellulose occurs by adding an anti-solvent, such as boiling water (Cuissinat and Navard 2006). The regenerated cellulose shows a lower total crystallinity index (TCI) and lateral order index (LOI), which facilitate the microbial attack. On the other hand, NMMO pretreatment in swelling/ballooning mode allows a higher increase in porosity, with a lower decrease of the crystallinity indexes (Jeihanipour et al. 2010).

TCI and LOI of cellulose-based materials can be estimated by Fourier-transform infrared spectroscopy. TCI is expressed as the ratio of the absorbance value at 1375 and 2902 cm^{-1} and is proportional to the entire crystallinity of the sample. LOI is representative of the ratio between cellulose I and cellulose II, and is calculated as the infrared spectral ratio 1420/893 cm^{-1}. The LOI increases with the crystallinity of cellulose I and decreases with the increasing crystallinity of cellulose II (Carrillo et al. 2004; Nelson and O'Connor 1964a, b).

4.6.2 Benefits and Drawbacks

NMMO is often recommended as the most advantageous cellulose solvent compared to the well-known phosphoric acid, alkaline solutions, and other ionic liquids. NMMO offers the advantage of acting directly on the cellulosic component of the biomass, reducing the risk of losing carbohydrates, in contrast with other pretreatments such as steam explosion, alkaline, phosphoric acid, and biological pretreatments (Wikandari et al. 2016). Depending on the stage of hydration, NMMO acts differently on the cellulosic component of the biomass, by increasing the porosity or

Table 4.4 Effectiveness of NMMO pretreatment on glucan or total carbohydrates content (Δglucan, Δcarbo), crystallinity index (ΔLOI), water swelling capacity (ΔWSC), and increment of the methane potential (ΔCH_4) of various lignocellulosic materials

Substrate	Optimal pretreatment condition	Pretreatment effectiveness[a]	Reference
Cotton linters	73% NMMO, 90 °C, 1 h	ΔLOI: −22% ΔWSC: −23% ΔCH_4: +17%	Jeihanipour et al. (2010)
Rice straw	85% NMMO, 130 °C, 1 h	Δglucan: +16% ΔCH_4: +629%	Teghammar et al. (2012)
Rice straw	85% NMMO, 120 °C, 3 h	ΔLOI: N.O. ΔCH_4: +81%	Mancini et al. (2016b)
Triticale straw	85% NMMO, 130 °C, 15 h	Δglucan: +35% ΔCH_4: +583%	Teghammar et al. (2012)
Wheat straw	85% NMMO, 120 °C, 3 h	Δglucan: N.O. ΔWSC: +46% ΔCH_4: +11%	Mancini et al. (2018a)
Barley straw	85% NMMO, 90 °C, 7 h	Δcarbo: +5% ΔCH_4: +92%	Kabir et al. (2014)
Hazelnut skin	85% NMMO, 120 °C, 3 h	ΔLOI: −9% ΔCH_4: N.O.	Mancini et al. (2016b)
Cocoa bean shell	85% NMMO, 120 °C, 3 h	ΔLOI: +15% ΔCH_4: +14%	Mancini et al. (2016b)
Oil palm empty fruit bunch	85% NMMO, 120 °C, 3 h	Δglucan: N.O. ΔLOI: −76% ΔCH_4: +48%	Purwandari et al. (2013)
Forest residues	85% NMMO, 90 °C, 30 h	Δcarbo: +7% ΔCH_4: +114%	Kabir et al. (2014)
Forest residues	85% NMMO, 120 °C, 3 h	Δcarbo: +10% ΔCH_4: +162%	Aslanzadeh et al. (2014)
Birch wood (milled)	85% NMMO, 130 °C, 3 h	Δglucan: +8% ΔWSC: +57% ΔLOI: −18% ΔCH_4: +48%	Goshadrou et al. (2013)
Softwood spruce chips	85% NMMO, 130 °C, 15 h	Δglucan: +12% ΔCH_4: +1088%	Teghammar et al. (2012)
Pinewood chips	85% NMMO, 120 °C, 30 h	Δglucan: +12% ΔWSC: +280% ΔLOI: −6% ΔCH_4: +580%	Shafiei et al. (2014)
Cassava residues	85% NMMO, 90 °C, 2 h	ΔLOI: −19% ΔCH_4: +28%	Cheng et al. (2017)

[a] N.O. means that no significant effect on the specific parameter was observed

reducing the crystallinity of LMs (Jeihanipour et al. 2010). NMMO pretreatment can be operated in relatively mild conditions, with temperatures ranging from 90 to 130 °C and pretreatment times between 20 min and 30 h (Mancini et al. 2016a).

The pretreatment feasibility strongly depends on solvent recovery and recycling. The solvent recovery takes place by treating the liquid stream of the NMMO pretreatment with ion-exchange resins to remove contaminants and subsequent evaporation of the water, obtaining the monohydrate form of NMMO (Satari et al. 2019). NMMO pretreatment non-recyclable liquid waste streams can be treated with ozone, with ozonation products being easily biodegradable at neutral pH (Stockinger et al. 1996). The loss of NMMO during recovery is $<2\%$ (Sari and Budiyono 2014). Nevertheless, the use of NMMO as a pretreatment for LMs on a large scale is still limited because of the considerable amount of water required for the washing step (Mancini et al. 2016a).

The efficacy of recovered NMMO depends on the chemical composition of the LMs. In particular, the pretreatment of lignin-rich LMs reduces the efficiency of recovered NMMO (Millati et al. 2020), most likely due to negative side reactions and release of by-products such as tannins, resin acids, and phenolic compounds (Kabir et al. 2014). The NMMO action during pretreatment does not produce furans, reducing the risk of inhibition in the subsequent biofuel production processes (Wikandari et al. 2016). However, leftover NMMO after pretreatment can inhibit the AD process, even at low (0.5–1%) concentrations (Millati et al. 2020).

4.6.3 *Effectiveness of NMMO Pretreatment on Different Lignocellulosic Materials*

Recent studies show the effects of 85% NMMO pretreatment at 120 °C on rice straw, wheat straw, and hazelnut skin (Mancini et al. 2016b, 2018a). The pretreatment is particularly effective on rice straw, increasing the methane production by 82%, even though no significant effect on the LOI was observed. On the other hand, NMMO pretreatment significantly reduces the crystallinity index of pretreated hazelnut skin, resulting in a higher methane production during the first days of AD (Mancini et al. 2016b). Similarly to hazelnut skin, NMMO pretreatment increases the porosity of wheat straw, enhancing the specific rate constant R_m from 21 to 32 mL CH_4/g VS/d (Mancini et al. 2018a).

Teghammar et al. (2012) investigated the effect of 85% NMMO pretreatment on spruce wood, rice straw and triticale straw, observing that only for rice straw a longer pretreatment time (i.e. 15 h) leads to an inhibition of the AD process. On the other hand, 15 h NMMO pretreatment is particularly efficient for spruce wood and triticale straw, especially when no comminution is performed. The negative effect of a longer pretreatment time is due to the loss of glucan and xylan during pretreatment (Teghammar et al. 2012). On the contrary, all investigated pretreatment times (i.e. 1, 3, and 15 h) can positively affect the AD of pinewood, confirming that a longer time is required when larger particle size substrates undergo NMMO pretreatment (Shafiei et al. 2014). The dissolution mode pretreatment (i.e. 85% NMMO) increases the porosity and reduces the crystallinity of birch wood after 3 h pretreatment, enhancing the methane potential by 47% (Goshadrou et al. 2013).

To the authors' knowledge, only Purwandari et al. (2013) studied the effect of the NMMO concentration on pretreatment of LMs, although it is reported to be a key factor for cellulose hydrolysis and subsequent conversion to methane (Jeihanipour et al. 2010). The authors investigated 73, 79, and 85% NMMO pretreatment at 90 and 120 °C. A longer pretreatment time at 90 °C positively affects the subsequent AD of oil palm empty fruit bunches. In contrast, increasing the pretreatment temperature to 120 °C, the optimal pretreatment time is 3 h, and the significance of the NMMO concentration is attenuated (Purwandari et al. 2013).

4.7 Ultrasound Pretreatment

4.7.1 Mechanism and Process Parameters of Ultrasound Pretreatment

Ultrasound, or sonication, techniques have been widely employed in medical applications as well as chemical and food processing for decades using different frequencies depending on the purpose (Chemat et al. 2011; Miller et al. 2012; Suslick 1999). Recently, ultrasounds are getting attention as pretreatment method to enhance the bioconversion of lignocellulosic and other waste materials due to their environmental friendly approach (Table 4.5) (Bussemaker and Zhang 2013). Ultrasound pretreatment relies on diffusion of sound waves ($>$ 20 kHz) in liquid media, creating alternations of compression and rarefaction phenomena (Fig. 4.4a) (Yang et al. 2017). The alternation of high and low pressurised zones gives rise to gas bubbles that grow up with the sound waves diffusion until imploding for cavitation (Fig. 4.4b). The bubbles collapse releases a considerable amount of energy, creating zones with high temperature (2000–5000 K) and pressure (up to 1800 atm) (Hassan et al. 2018; Luo et al. 2014).

Ultrasonic cavitation is affected by several parameters. Firstly, the frequency (f) emitted by the ultrasonic device plays a key role. It is reported that a higher intensity is required to obtain cavitation at high sonic frequencies, overwhelming the cohesive forces of the medium (Luo et al. 2014; Santos et al. 2009). The intensity of sonication is proportional to the amplitude of vibration of the ultrasonic source. Generally, high amplitudes are not recommended, since they can easily lead to deterioration of the ultrasonic transducer. The optimal amplitude also depends on the viscosity of the medium. Higher amplitudes are required when the resistance of the sample to the movement of the ultrasonic device increases (Santos et al. 2009). Another important parameter to take into account when performing ultrasound pretreatment is the power density (P_d) (Zou et al. 2016b), calculated as:

Table 4.5 Effectiveness of ultrasound pretreatment on reducing sugars (Δsugars), crystallinity (ΔCrI), lignin removal (Δlignin), and increment of methane potential (ΔCH_4) for different lignocellulosic materials

Substrate	Optimal pretreatment condition	Effectiveness[a]	Reference
Wheat straw (co-digestion with dairy manure)	f: 40 kHz, P: 200 W, t: 20 min	Δsugars: +24% ΔCH_4: +80%	Zou et al. (2016a)
Maize straw (co-digestion with dairy manure)	f: 50 kHz, P: 250 W, t: 30 min	Δsugars: +16% ΔCH_4: +70%	Zou et al. (2016b)
Wheat straw	f: 20 kHz, P: 450 W, t: 10 min (ultrasound assisted with KOH)	ΔCH_4: +47%	Korai and Li (2020)
Cannabis straw	f: 40 kHz, P: 100 W, t: 30 min	ΔCrI: +21% ΔCH_4: +77%	Qi et al. (2021)
Corn stover	f: 40 kHz, P: 200 W, t: 90 min	ΔCH_4: +15%	Hassan et al. (2017)
Grape pomace	f: 50 kHz, P: 60 W, t: 70 min	Δlignin: −18% ΔCH_4: +10%	El Achkar et al. (2018)
Olive pomace	f: 20 kHz, P: 450 W, t: 10 min	Δlignin: −10% ΔCH_4: N.O.	Elalami et al. (2020)
Sida hermaphrodita (L.) Rusby (codigestion with cattle manure)	f: 25 kHz, P: 300 W, t: 10 min	ΔCH_4: +127%	Kisielewska et al. (2020)
Vinegar residues (grinded)	f: 40 kHz, P: 50 W, t: 60 min	ΔCH_4: +30%	Kong et al. (2021)

[a] N.O. means that no significant effect on the specific parameter was observed

$$P_d = \frac{P \cdot t}{V \cdot TS_0}$$

where P is the ultrasonic power (W), t is the pretreatment time (t), V is the volume (L) of the slurry undergoing ultra-sonication, and TS_0 is the initial total solid content (kg) of the slurry.

Apart from the characteristics of the ultrasonic wave, the operating conditions also impact the cavitation phenomenon. Temperature has a contrasting effect during ultrasound pretreatment. High temperatures break down the interactions between the solute and matrix, such as hydrogen bonds, Van der Waals forces, and dipole attractions. Nevertheless, the vapour pressure increases with the temperature of the solvent, with the solvent vapour filling the cavitation bubbles, thus reducing their

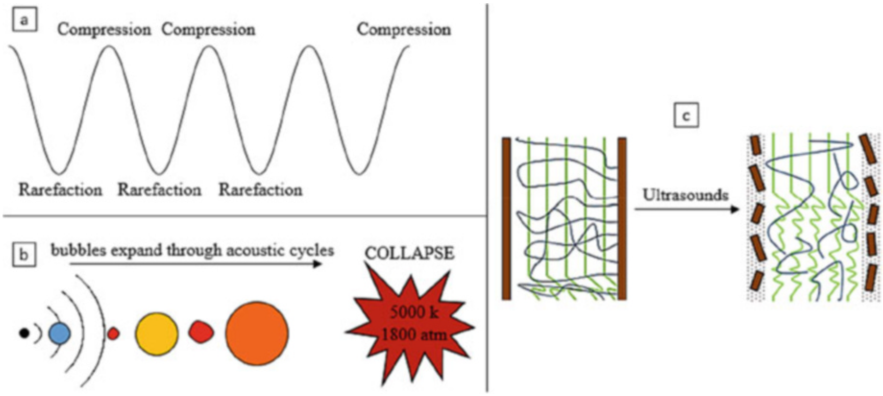

Fig. 4.4 Mechanisms of ultrasound pretreatment: (**a**) alternation of compression and rarefaction zones in the liquid media, (**b**) effect of ultrasonic waves on gas bubbles, (**c**) effect of ultrasounds on lignocellulosic structure

power of collapse (Bussemaker and Zhang 2013). While water is the most employed medium for ultrasound pretreatment, other liquids with a lower polarity (e.g. organic liquids) are also expected to be efficient. On the other hand, viscous liquids (e.g. oils) make cavitation harder (Santos et al. 2009).

4.7.2 Benefits and Drawbacks

Cavitation has both thermal and physical effects on the solid particles present in the media, contributing to the fractionation of the lignocellulosic structure and lysing of the membranes and cell walls of the LMs (Fig. 4.4c) (Rehman et al. 2013; Santos et al. 2009). Ultrasound pretreatment reduces the crystallinity and degree of polymerisation of cellulose, enhancing its hydrolysis and the solubilisation of the overall organic matter. Besides, ultrasound pretreatment modifies the surface of LMs and disrupts the lignin linkages, separating the lignin fraction from the cellulose and hemicellulose sugars (Bundhoo and Mohee 2018; Bussemaker and Zhang 2013; Hassan et al. 2018).

The main concern on ultrasounds techniques regards cost end energy aspects. Although some researchers reported the unfeasibility of ultrasound pretreatment on a laboratory scale (Bundhoo and Mohee 2018), other studies show its energetic convenience when employing commercial technologies on a larger scale (Cano et al. 2015). Apart from the energy and economic aspect, the possible degradation of cellulose and hemicellulose sugars should be considered when performing ultrasound pretreatment for LMs valorisation. Nevertheless, this aspect highly depends on the lignocellulosic substrate (Bussemaker and Zhang 2013).

4.7.3 Effectiveness of Ultrasound Pretreatment on Different Substrates

Several authors report that ultrasounds can reduce the particle size and increase the surface area of sewage sludge (Bougrier et al. 2006; Cho et al. 2013; Chu et al. 2001; Na et al. 2007) and manures (Elbeshbishy et al. 2011). Recently, the same effect has been observed on LMs, showing that the pretreatment duration is proportional to the substrate disruption. Scanning electron microscopic images show that the damages to the external surface of wheat straw and maize straw increase with the pretreatment time. Therefore, ultrasound pretreatment improves the vulnerability of LMs, thus increasing the available contact surface for the subsequent AD process (Zou et al. 2016a, b).

Ultrasound pretreatment also acts on the chemical composition of LMs. The cavitation phenomena lead to the formation of radicals that contribute to increased oxidative stress during pretreatment (Santos et al. 2009). This aspect, together with high pressure and temperature, reduces the lignin content of LMs, generally leaving the cellulosic component of the biomass unaffected. On the other hand, the removal of hemicellulose sugars is observed, most likely due to their amorphous structure and weak linkages (Perrone et al. 2016). Therefore, ultrasonic waves enable to obtain cellulose-rich materials, increasing the digestability of LMs during AD. Imam and Capareda (2012) investigated the effect of hot water and ultrasound-assisted hot water pretreatment on sweet sorghum residues. Hot water pretreatment alone is not effective on lignin removal. On the other hand, the ultrasonic implementation reduced the lignin content by 48%, compared to the untreated sweet sorghum. Similarly, ultrasound pretreatment of sugarcane bagasse reduced the lignin content from 27 to 21%, with minor effects on the cellulose and hemicellulose content (Ramadoss and Muthukumar 2014). Ultrasound-ammonia pretreatment removed 70% of the lignin from sugarcane bagasse (Velmurugan and Incharoensakdi 2016).

While ultrasound pretreatment generally does not change the cellulose content, ultrasonic waves may affect the cellulosic hydrogen bonds (Nakashima et al. 2016). In particular, ultrasounds reduce the crystallinity of the cellulosic part of LMs by rearranging the cellulose structure, leaving a more amorphous polymer, vulnerable to enzymatic attack (Bussemaker and Zhang 2013). On the other hand, some studies report an increase in the crystallinity index after ultrasound pretreatment. This is likely a consequence of the high lignin removal, resulting in a higher cellulose content remaining in the solid phase after the pretreatment.

The methane potential increases as a consequence of the changed structural and chemical characteristics of the ultrasound pretreated LMs (Subhedar and Gogate 2014). Qi et al. (2021) investigated the effectiveness of ultrasound pretreatment on the co-digestion of cannabis straw and municipal wastewater, obtaining a 77% increment of the methane production after 30 min pretreatment at 100 W. Zou et al. (2016a, b) observed a positive effect on methane production from wheat and maize straw co-digested with dairy manure after ultrasound pretreatment.

Interestingly, ultrasound pretreatment shows a great potential when combined with alkaline pretreatment (Hassan et al. 2017). The combination can occur using an alkaline solution as the medium of the ultrasound pretreatment or, simply, when ultrasonic irradiation follows the previously performed alkaline pretreatment (Hassan et al. 2017; Korai and Li 2020). Sequential NaOH-ultrasound pretreatment enhances the methane potential of corn stover from 148 up to 320 mL CH_4/g VS (Hassan et al. 2017). Similarly, ultrasound pretreatment of wheat straw using 2, 5 and 6% KOH as the medium allows a 47% increment of methane production (Korai and Li 2020). Despite the promising effects, other studies did not observe a significant effect on methane production after ultrasound pretreatment, most likely due to the low specific energy applied, which lowers the rate of sugar solubilisation (Elalami et al. 2020; Passos et al. 2015).

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Chapter 5
Biogas Production from Dairy Cattle Residues: Definition of the Pretreatment Approach Through a Bibliometric Analysis of Publications and Patents

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Abstract The use of bedding in livestock, such as wood shavings, is a technique that brings economic advantages, as it reduces the demand for water to clean the facilities and provides better animal welfare. On the other hand, the material used as litter is a lignocellulosic material which requires a pretreatment strategy for successful anaerobic digestion to produce biogas. This work examines the advances in science (articles) and technology (patents) to delimit pretreatment technology routes for lignocellulosic residues using a bibliometric approach. To identify the main articles and patents, search strategies were defined in such a way that all relevant documents were grouped and organized into four pretreatment routes (physical, biological, chemical, and combined). The number of published articles (2941) was 35% higher than patents (1923), and 70% of all the documents have been published in the last 10 years. The bibliometric analysis revealed that the chemical technological route has a higher technological maturity, as well as more research and development (R&D) effort applied. Articles using sodium hydroxide (NaOH) as an alkaline catalyst were analyzed and compared to judge its suitability. The work

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concludes that the combination of physical and alkaline pretreatment could provide degradation of cattle dairy residue and the costs and time in new R&D investigations can be reduced through the analysis of the technological maturity stage.

Keywords Biomass lignocellulosic · Alkaline hydrolysis · Search strategies · Technological routes · Technological maturity · Bovine manure · Renewable energy · Methane production

5.1 Introduction

Biogas as a renewable energy source can replace conventional fuels to produce heat, power, and vehicular energy. However, in anaerobic digestion the challenge is to degrade and convert biomass with high fiber content or lignocellulosic biomass, such as corn stover, rice straw, sugarcane bagasse, and some animal residue such as poultry litter and dairy cattle litter into biogas.

A considerable amount of dairy cattle rearing activity occurs in intensive or semi-intensive confined systems to increase the animal production capacity. In the intensive system, the lactating animal spends practically it is whole time in confinement, and in the semi-intensive system, the confinement time is 4 h. In both confinement methods, the environmental conditions in the housing area are controlled for increasing productivity (Perissinotto et al. 2009).

In intensive confinement, usually the animal is located in a shed. The number of animals is equivalent to the number of bays, from where it only goes out to feed itself, spending the rest of the time lying down ruminating. Traditionally, agriculture and wood residues such as sawdust, corn stover, rice straw, and wood shavings are used as litter for animals (Natzke et al. 1982). These substrates are rich in organic matter, which makes it interesting for the production of biogas through anaerobic digestion after their use is over.

The major challenge in the production of biogas from dairy cattle residues and cattle litter (manure + wood chips) is that they are difficult to degrade by anaerobic treatment due to the high lignin content. Wood residues (dust, sawdust, or wood shavings) and agricultural residues (wheat and corn stover, rice straw, among others) have high levels of cellulose, hemicellulose, and lignin when compared to animal waste. For non-residual biomass, the cellulose, hemicellulose and lignin concentrations vary between 51–31%, 17–7%, and 36–30%, respectively (Olsson and Hahn-Hägerdal 1996).

A possible solution for lignin removal from the dairy cattle residues is to implement a physical, chemical, or biological pretreatment system or a combination of these, allowing the anaerobic microorganisms to degrade cellulose and hemicellulose (Mosier 2005).

Data collection and analysis of patent databases from the literature can be used to set up the suitable pretreatment technology. This strategy has been employed in many areas of research recently, such as in the field of wind energy (Dubarić et al.

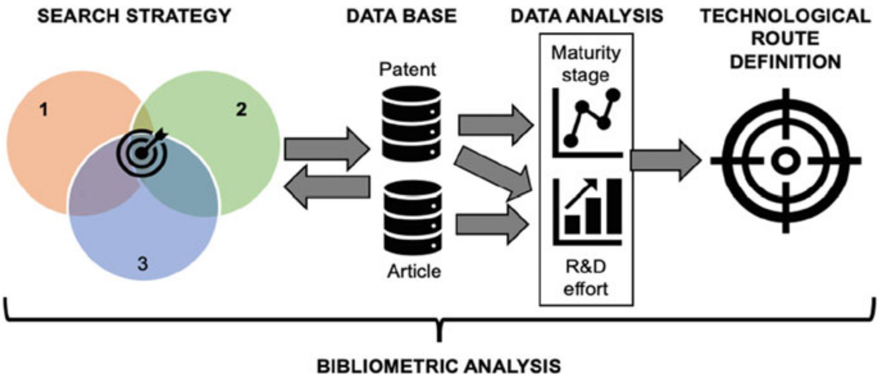

Fig. 5.1 Strategy steps for defining the technological pathway through bibliometric analysis

2011), solar energy (Zhao et al. 2015), ethanol production from lignocellulosic biomasses (Silva Schlittler et al. 2012), or in the field of lignocellulosic fuels (Toivanen and Novotny 2017), demonstrating that such information can be used to analyze the evolution and level of technology maturity in those respective fields. However, there are few similar studies in the field of biogas production, more particularly on pretreatment technologies for dairy cattle residue for biogas production.

Academic research is directly related to the technological development (demonstrated by patent registration) in the field of biogas production (Lora Grando et al. 2017). This is because companies, researchers, and universities around the world actively document their most relevant discoveries through patents to gain a technological and commercial advantage before engaging in any scientific publication.

In this context, this work aimed to analyze the stage of maturity and R&D efforts based on patent data and research articles to suggest which is the most promising and developed technological route, as demonstrated in Fig. 5.1. The case study used was the market challenges of dairy cattle litter residues for biogas production.

5.2 Main Routes of Pretreatments

There are many promising pretreatment technologies available that are carried out with some level of commercial success for marketable products and easily implemented on an industrial scale in the biogas production process. The Table 5.1 compares the main pretreatment processes and their effects on cellulose, hemicellulose and lignin.

The combination of alkaline and physical pretreatments stands out among the different technologies for promoting mainly the increase in surface area (ISA), decrystallization of cellulose (CD) and low formation of inhibitors (IF). These aspects are very relevant for the anaerobic process. Such pretreatment technologies

Table 5.1 Effect of different pretreatments on lignocellulosic substrates (Hendriks and Zeeman 2009)

	Effect					
Pretreatment	ISA	CD	SH	LS	ALS	IF
Mechanical	High	High	N/D	N/D	N/D	N/D
Irradiation	High	Low	Low	N/D	N/D	Low
Steam explosion	High	N/D	High	Low	High	High
Hot water	High	No effect	High	Low	Low	Low
Acid	High	N/D	High	Low	High	High
Alkaline	High	N/D	Low	Moderate	High	Low
Thermal + acid	High	No effect	High	N/D	N/D	Low
Thermal + alkaline	High	No effect	Low	Moderate	High	Low
Explosion of ammonia	High	High	Low	High	High	Low
Biological	High	N/D	High	High	High	N/D

ISA Increase of surface area, *CD* Cellulose decrystallization, *SH* Solubilization of hemicellulose, *LS* Solubilization of lignin, *ALS* alteration of the lignin structure, *IF* inhibitor formation, *N/D* Not determined

can be classified into three technological routes: physical (including mechanical shear, heat, pressure, and electric fields), chemical (acids, bases, and solvents), biological (microbial and enzymatic), and also the combinations of these processes (Bochmann and Montgomery 2013; Chen et al. 2017).

Since the potential of lignocellulosic biomass could be interesting for large-scale biogas production and the three main pretreatment technologies have a primary role in achieving this, there is need for relevant investigations to compare them. Many of the previous investigations have presented technical problems during large-scale operation, which often resulted from a limited understanding of the reality in an actual biogas plant. According to Achinas et al. (2017), there is a technological gap between universities and industry research, indicating that less mature technologies require more R&D efforts and resources.

Research achievements at universities are usually recorded through articles, easily found in scientific databases. While in the industry most of the scientific achievements are registered in patent documents in patent offices around the world and can be found in patent databases. Therefore, the joint analysis of these two databases could provide essential information for the review of research priorities for the technological development of problems still little studied (Russo and Ladisch 2008), such as the anaerobic digestion of dairy cattle litter residue, increasing the success of research and reducing the time and investments in R&D in this area of research.

5.3 Material and Methods

Considering the technological routes previously delimited, seven search strategies (set of keywords) were structured to collect patent and scientific articles data so that all relevant documents have been organized for further analysis of each technological route. The "Lens.org" platform, which has over 117 million patent applications from 95 different jurisdictions, has been used for the acquisition of patent data and "Scopus", which is the largest scientific database, with over 5 thousand journals and 70 million documents in its library, was used to acquire data from scientific articles. The keywords used were delimited based on the works of Lora Grando et al. (2017) and Magrí et al. (2017).

The search interval was carried out in the period 1998–2018, considering the "period of silence" of 18 months (2019–2020), the period between the request and its public release (i.e. the search time interval is defined according to the priority date). For patent searches, specific technical terms have been defined for each technology, applying them in the search fields delimited to "title", "abstract" and "claims"; in the scientific article's cases, technical terms similar to the patent search have been used, delimiting them to "title", "abstract" and "keywords". Both search platforms ("Lens.org" and "Scopus") have an automated truncation system and boolean operators (AND, OR, or NOT), as well as search delimiters (" "). These were used to restrict the fields of interest. It is important to note that the search process develops in an exploratory manner, so the current patent searches have not focused solely on specific IPC (International Patent Classification) codes. The searches were conducted based on strategic compositions between keywords and specific IPC codes following the proposal presented in Lora Grando et al. (2017).

The following is a list of keyword groups and IPC used in both platforms:

P: Patent—"Lens.org" Plataform

P1—(pretreatment OR treating);

P2—(biomass OR "raw material" OR "organic matter");

P3—(lignin OR lignocellulosic OR cellulose OR hemicellulose OR fiber);

P4—(residue OR waste OR manure OR sludge OR slurry OR dung OR sewage);

P5—IPC (B01, B02, B03, B04, B05, B06, B07, B08, B09, B23, B24, B25).

P6—IPC (C1, C2, C7, C8, C11, C12, C13);

P7—(chemical)

P8—(biological OR fungi OR bacteria OR enzymes)

P9—(alkaline OR NaOH OR "sodium hydride").

P10—(acid)

A: Article—"Scopus" Plataform

A1—(pretreatment)

A2—(biomass OR residue OR waste OR manure OR sludge OR slurry OR dung OR sewage)

A3—(lignin OR lignocellulosic OR cellulose OR hemicellulose)

A4—(physical)

A5—(biological)

A6—(chemical)
A7—(acid)
A8—(alkaline OR NaOH OR "sodium hydride")

Initially, five search strategies were established (general, physical, biological, chemical and the combination of these pretreatments). However, since the chemical route had a higher number of records, two more search strategies were set up for acid and alkaline chemical pretreatment. The rules for search strategies are listed below:

1. General pretreatment:
   Patent: (P1) AND (P2) AND (P3) AND (P4) AND ((P5) OR (P6))
   Article: (A1) AND (A2) AND (A3) AND (A4) AND (A6) AND (A7)
2. Physical pretreatment:
   Patent: (P1) AND (P2) AND (P3) AND (P4) AND (P5)
   Article: (A1) AND (A2) AND (A3) AND (A4)
3. Biological pretreatment:
   Patent: (P1) AND (P2) AND (P3) AND (P4) AND (P6) NOT (P7 OR P9 OR P10)
   Article: (A1) AND (A2) AND (A3) AND (A5)
4. Chemical pretreatment:
   Patent: (P1) AND (P2) AND (P3) AND (P4) AND (P6) NOT (P8)
   Article: (A1) AND (A2) AND (A3) AND (A6)
5. Combination pretreatment:
   Patent: (P1) AND (P2) AND (P3) AND (P4) AND (P5) AND (P6)
   Article: (A1) AND (A2) AND (A3) AND (A4 OR A5 OR A6)
6. Acid chemical pretreatment:
   Patent: (P1) AND (P2) AND (P3) AND (P4) AND (P6) AND (P9 OR P10) NOT (P8)
   Article: (A1) AND (A2) AND (A3) AND (A6) AND (A7) NOT (A8)
7. Alkaline chemical pretreatment:
   Patent: (P1) AND (P2) AND (P3) AND (P4) AND (P6) AND (P10) NOT (P8)
   Article: (A1) AND (A2) AND (A3) AND (A4 OR A5 OR A6) AND (A8) NOT (A7)

The databases were exported and processed with Microsoft Excel software. A graphical analysis of the level of technological maturity, as recommended by Achinas et al. (2017) was performed using the methodology proposed by Wang et al. (2016). The number of patent applications were considered as an indicator of technological maturity as shown in Fig. 5.2. The purpose of this comparison was to find out which technology is placed where on this curve, which contains four stages: germination, growth, maturity and decline.

The technical and scientific efforts in all pretreatment routes were measured and compared with articles using the Kiviat diagram, considering the total records of publication in the period from 1998 to 2018. Finally, a descriptive analysis of the pretreatment effects on lignocellulosic biomasses similar to the dairy cattle residues (with litter) was done. The observed parameters were: type of biomass, operating

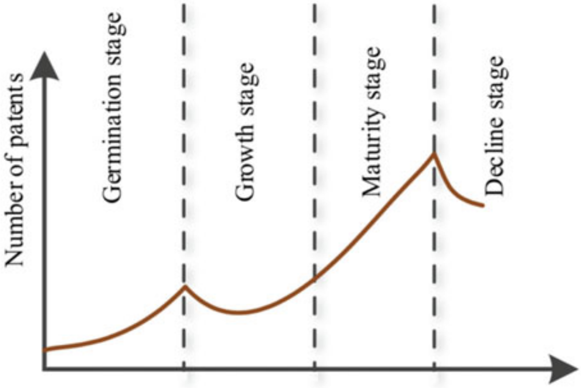

Fig. 5.2 The technological maturity prediction model (Wang et al. 2016)

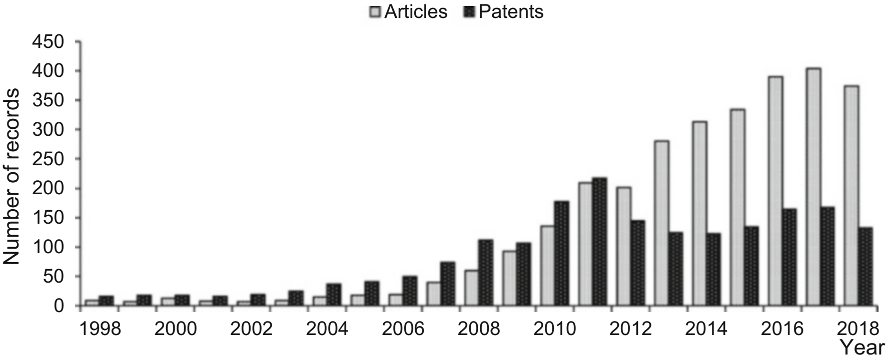

Fig. 5.3 Number of articles and patents worldwide in the period 1998–2018

conditions (temperature, exposure time and the dose of the catalyst solution), increase in methane content and biogas.

5.4 Results and Discussion

5.4.1 Analysis of Technological Routes Based on Patent Documents

There have been 1923 patent applications found worldwide, 50.9% of which were requested by China, 25.1% by the United States, and only four patents by Brazil. When correlating the number of articles and patents produced in the last 20 years, it was noticed that the number of publications of scientific articles (2941 publications) and patent applications (1923 applications) in the period 1998–2006 did not present significant changes, varying from 0 to 50 (Fig. 5.3). From 2007 onwards, an increase in the number of records was observed, which was also confirmed by Wang et al. (2016), who related the effect to the fossil fuel crisis, directly impacting the value of oil and stimulating investments in other energy sources, particularly on renewable ones.

Overall, the number of articles published was approximately 35% higher than the number of patents. Magrí et al. (2017) also observed a higher number of articles, twice as compared to patent deposits, while investigating the nutrients in the biodigester effluent. About 70% of patent applications and article publications occurred in the last 10 years, a convergence of the results was observed by Lora Grando et al. (2017). It can be assumed that the pretreatment routes are relatively new and emerging in the race for energy sustainability, especially to replace fossil fuels in the transportation sector.

Until 2008, the patents number was on average 56% higher than the published articles, after which the difference decreased, and in 2012 the number of articles exceeded the number of patents. A possible explanation is the very broad patent claims where one technology can have several applications in different segments (Lora Grando et al. 2017). However, as the technologies (patents) are tested in the laboratory and at the industrial scale with different types of biomass and experimental conditions, the number of articles is expected to increase more than patents. The difference between the number of articles and patents supposedly confirms the technological gap pointed out by Achinas et al. (2017). Conversely, the difference can represent the level of maturity of research in universities and the lack of alignment with the market needs.

Another important behavior to be observed is the decrease in the number of published patents after 2011, which may indicate the transition of maturity level from the germination to the growth stage. The number of patent documents is an indicator of the level of technology maturity and is useful to guide economic and scientific efforts (de Luna and Santos 2017), and can be used as an instrument for decision-making (Wittfoth et al. 2017). Therefore, the higher is the maturity of a technological route, the more aligned it will be with the market demand. On the other hand, the lower the maturity, there is more possibility of a disruptive discovery, consequently, more effort in R&D and investment.

The technological maturity stage for chemical, physical and biological pretreatments are shown in Figs. 5.4, 5.5, and 5.6, respectively. The chemical and physical route passed through the first and second stages and reached the third, maturity stage, where solutions supposedly are more accessible to the market and probably most competitive. The first stage, germination, was passed in 2011, and the second stage, growth, in 2016 for both pretreatments.

The biological route showed a conservative behavior in the germination stage, without any significant leap in the patent number. The analysis shown in Fig. 5.6 reflects the literature review, where biological pretreatment of biomass for biogas production is not commercially ready due to the low biogas increase or high operation and implementation costs.

For the combination of pretreatments, the graphical analysis is not representative due to the low number of patents. This type of combined pretreatment is at the

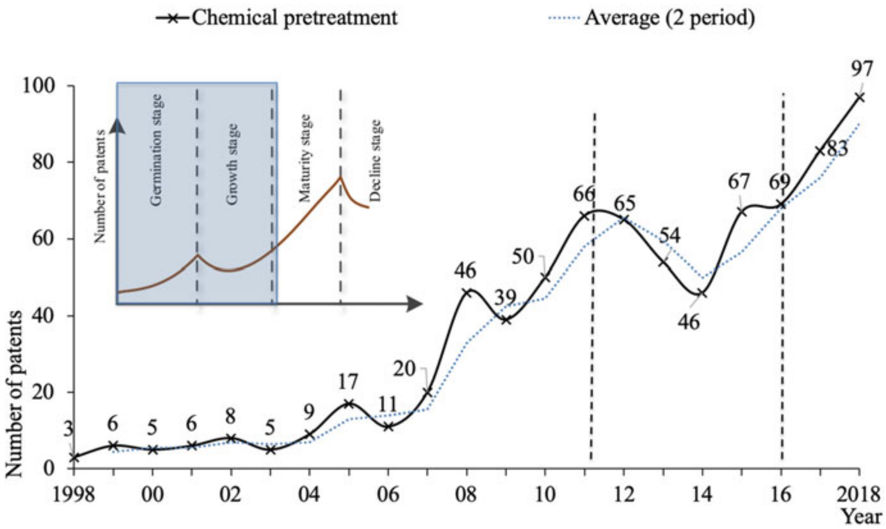

Fig. 5.4 Technological maturity analysis for the chemical pretreatment route

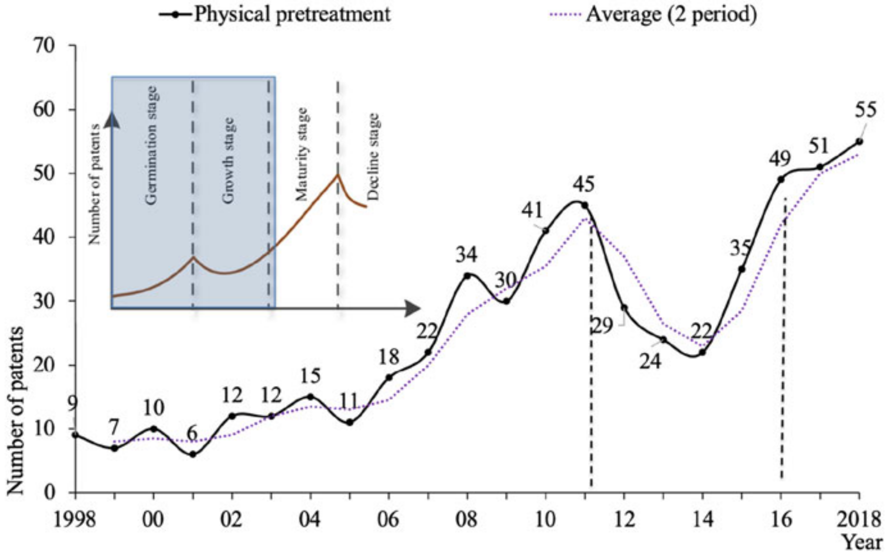

Fig. 5.5 Technological maturity analysis for the physical pretreatment route

germination stage. One possible explanation is that each component is generally intended to be patented in it's own right, to ensure a more wide-ranging claim.

Once the maturity stage of each pretreatment is understood, it is important to measure the R&D efforts, bringing together the total articles records and patents. The

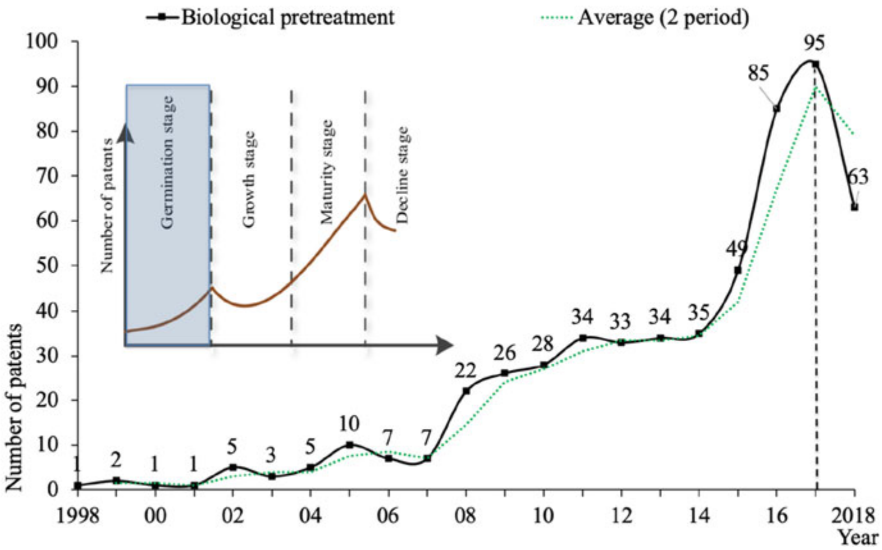

Fig. 5.6 Technological maturity analysis for the biological pretreatment route

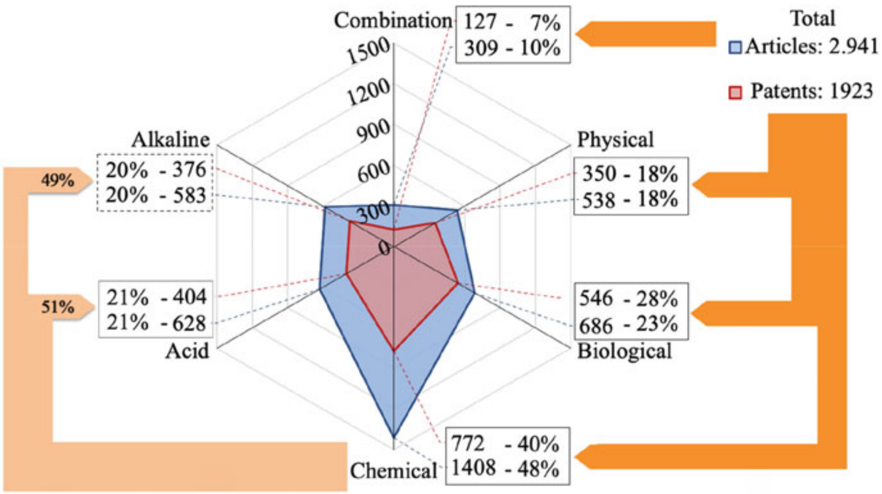

Fig. 5.7 The ration between patent and article documents number

Kiviat diagram was applied to compare different pretreatments and to define which one has the higher R&D effort (Fig. 5.7).

Considering the main pretreatments, the chemical route showed the best results, with 40% and 48% of the scientific (articles) and technical (patents) efforts, respectively, followed by biological and physical methods, which had no significant difference, and the combination of pretreatments with the lowest effort. These data confirm the hypothesis that chemical pretreatment is the most studied technique and has been widely used for the degradation of lignocellulosic biomass.

Acid and alkaline chemical pretreatments totaled 21% and 20% of all articles and patent documents and 51% and 49% in the chemical route, respectively. The total number of articles or patents can be different from the individual sum because some documents appeared in more than one search strategy. Other keywords to delimit the search strategy were tested without a positive effect or with an excessively restrictive result. For example, this was the case for alkaline pretreatment, where once the condition "NOT acid" was added; the results were not representative because most of the patents included the word acid in the claims to describe the process. The same was not observed in the case of acid pretreatment.

5.4.2 Chemical Pretreatment Methods

The chemical pretreatment, by acid or alkaline hydrolysis, is the most studied technique among the main categories of pretreatment, and it has been widely used for the delignification of different types of lignocellulosic biomasses. The commonly used chemicals for the acid pretreatment are H_2SO_4, HCL, HNO_3, among others. As for the alkaline pretreatment NaOH, $Ca(OH)_2$, CaO, KOH and NH_4OH are primarily used. Other chemical pretreatment methods such as use of ionic liquids are less conventional due to their high costs (Zheng et al. 2014).

The acid pretreatment process provides high hemicellulose solubilization, which allows better cellulose degradation during the enzymatic process, resulting in high biogas yield on biomass (Achinas et al. 2017). Another positive factor of the acid treatment when using HCl or HNO_3 is the decrease of the H_2S concentration in the biogas produced due to the lower amount of sulfate present (Hendriks and Zeeman 2009).

However, in this process if a low energy expenditure needs to be maintained, a high volume of reagent (30–70% v/v) is required. Otherwise, it is not possible to have satisfactory results in temperatures below 40 °C. This is one of the disadvantages of this process. The acid solution also causes corrosion of metal structures and equipment, has a high environmental risk, high operational cost and formation of inhibitory compounds during acid treatment and thus has limited its interest on an industrial scale (Zheng et al. 2014; Achinas et al. 2017).

In contrast to acid pretreatment methods, alkaline pretreatment can be carried out at ambient temperature and pressure, or even lower temperature conditions. This results in a lower degradation of sugars present in the biomass and can be beneficial for biogas production (Rabemanolontsoa and Saka 2016). However, at ambient temperatures, extended exposure of the fibers to the catalyst is required and may sometimes take hours or days, depending on the lignin content in the biomass (Pavlostathis and Gossett 1985; Neves et al. 2006; Pei et al. 2014; Rabemanolontsoa and Saka 2016). Contrary to the acid pretreatments, alkaline does not allow the recovery of the catalyst, because it is converted into salts, which are unrecoverable or incorporated into the biomass during the pretreatment reactions (Mosier 2005).

The alkaline pretreatment route showed better results on substrates with low lignin content such as grasses, agricultural residues, softwood residues, among others. In this method, the saponification of the intermolecular ester bonds causes lignin to rupture and separation of the bonds between hemicellulose and lignin structures leads to the solubilization of lignin and hemicelulose (Sun et al. 2005; Eggeman and Elander 2005; Achinas et al. 2017).

In most of the previous studies on alkaline pretreatment, NaOH is used as catalysts, because of its high efficiency, low production inhibitory compounds and low cost when compared with the other reagents (Amin et al. 2017). Moreover, NaOH stands out for being non-toxic or non-inhibitory to the subsequent anaerobic digestion even if there is any residual NaOH left in the treated biomass (Xie et al. 2011).

With this analysis, it can be assumed that the chemical alkaline pretreatment routes (particularly using NaOH) are more aligned with the market demand due to the technological maturity and total R&D effort.

5.4.3 Alkaline Hydrolysis with NaOH

Among the chemical pretreatment technologies, alkaline pretreatment using NaOH can be presented as a promising process with practical advantages such as operational simplicity and low cost. Besides, alkaline treatment contributes positively to the anaerobic digestion process. This is due to the fact that any alkaline catalyst remaining in the substrate can be useful during anaerobic digestion, controlling the reactor acidification by acting as the pH control agent (Pavlostathis and Gossett 1985). Neves et al. (2006), studying the methane yield from barley residue, concluded that alkaline hydrolysis increases the methane yield, by preventing digester acidification and reducing the TS (total solids) and VS (volatile solids) content of the residue. Even recalcitrant biomasses such as residues from the wood industry can have satisfactory results with alkaline hydrolysis as Mirahmadi et al. (2010) observed a 84% and 74% higher methane yield for hardwood (spruce) and softwood (birch) residues, respectively.

The substrate biodegradability also increases, since the structure and the functional groups of lignin, cellulose, and hemicellulose are broken after pretreatment with NaOH. Furthermore, it contributes to the modification of the chemical structure because the lignin originally has a high molecular weight and the three-dimensional network structure is replaced by low molecular weight molecules and becomes linear. Zhao et al. (2014) studying rice straw pretreatment using NaOH, observed a 26% increase in the biogas production and 30.4% increase in methane yield, associated with lignin solubilization and the degradation of cellulose and hemicellulose, which were 32.25% and 36.96%, respectively. NaOH treatment also accelerates the degradation activity of the microorganisms, as it expands the pore size of biomass (He et al. 2008), allowing the acidogenic bacteria to ferment the biomass more easily (Neves et al. 2006; Pei et al. 2014). In addition to a larger surface area, the alkaline hydrolysis releases soluble compounds that can be easily digested by methanogenic anaerobic bacteria directly, increasing the methane content in the biogas (Cheng and Liu 2010).

There are some factors that have significant influence on the alkaline pretreatment efficiency with NaOH; such as reagent concentration, fiber length and pretreatment (reaction/exposure) time. Selecting a proper dosage is very important, as this decides the process efficiency without hampering the process economics. Also, it needs to be mentioned here that just increasing the dosage does not always results in improved biogas production. At high NaOH dose (>5–9% by weight) along with lignin the sugars can also be solubilized which ultimately results in low available substrate for anaerobic digestion and lower biogas yield. But this phenomenon is highly depended on the biomass type. Moreover, a very high NaOH concentration can also be detrimental to the anaerobic digestion process due to the inhibitory function of high amounts Na^+ ions in the solution (Monlau et al. 2013; Pang et al. 2008; Pei et al. 2014; Xie et al. 2011; Zhu et al. 2010).

The length of biomass fibers can be a limiting factor in the pretreatment process, requiring the adoption of physical pretreatment to reduce the length/size of the biomass fibers. For example, during studying the efficiency of alkaline pretreatment of banana stem for biogas production, Pei et al. (2014) found that the shorter the fiber length, the higher is the biogas yield and the methane content.

The exposure time of the biomass to the alkaline catalyst (NaOH) also has a direct relationship with the degradation process but the type of biomass plays a critical role here. Some authors reported satisfactory results in minutes, hours, and days of pretreatment, depending on the type of biomass and other experimental conditions such as temperature (Table 5.2). For example, the residue from a vegetal extraction process treated with NaOH for 15 min can achieve a 55% increase in biogas production at the ambient temperature in comparison to the biogas produced from untreated residue. However, using the same pretreatment conditions, only 25% and 37% increase in biogas production were observed from corn stover and rice straw, respectively. (Zhao et al. 2014; Zhu et al. 2010).

As already mentioned earlier in the introduction that there are rarely any previous studies on biogas production from dairy cattle litter let alone on its pretreatment for process improvement. Hence, here previous studies on similar substrates to dairy cattle litter are compared for understanding the effect of NaOH pretreatment on biogas production (Table 5.2). From the NaOH pretreatment of different lingocellulosic biomass depicted in Table 5.2, it can be concluded that dairy cattle residue consisting of wood shavings as the litter can be treated using NaOH for enhancing biogas production. NaOH treatment definitely have a positive effect on the methane content and/or on the biogas production from different types of lignocellulosic biomass. However, depending on the fiber size and the degree of decomposition of the wood shavings, the use of a physical pretreatment, combined with NaOH, can help to achieve a more satisfactory results.

Table 5.2 Effect of alkaline pretreatment of different lignocellulosic biomass with NaOH along with the respective experimental conditions

Biomass	Temperature (°C)	Treatment time	NaOH dose (%)	Increase in methane (%)	Increase in biogas (%)	Reference
Woods residues						
Spruce shavings	−15; 0; 5; 50; 80; 100*	2 h	7	84	0	Mirahmadi et al. 2010
Birch shavings	15; 0; 5; 50; 80; 100*	2 h	7	74	N/D	
Banana stem	30–50	1, 2, 3*, 4, 5 days	3	50.9–56.2	37.2	Pei et al. 2014
	30–50	1, 2, 3*, 4, 5 days	6		85.6	
	30–50	1, 2, 3*, 4, 5 days	9		82.2	
	30–50	1, 2, 3*, 4, 5 days	12		58.3	
Agricultural residues						
Rice straw	Environment	24 h	5	32.8	25.8	Zhao et al. 2014
Rice straw + sewage sludge	Environment	24 h	5	28.4	19.7	
Residue of vegetal extraction	37	15 min	8	0	55	Cheng and Liu 2010
Rice straw	20	21 days	6	N/D	64.5	He et al. 2008
	37	3 h	1,5	70.9	50.0	Sabeeh et al. 2020
Corn stover	20	21 days	4	N/D	16.6	Pang et al. 2008
	20	21 days	6	71	23.8	
	20	21 days	8	N/D	23.7	
	20	21 days	10	N/D	22.9	
Sunflower stalks	55	3, 6, 12, 24*; 36 h	0,5	N/D	N/D	Monlau et al. 2013
	55	3, 6, 12, 24*; 36 h	2	N/D	N/D	
	55	3, 6, 12, 24*; 36 h	4	36	N/D	
	55	3, 6, 12, 24*; 36 h	6	N/D	N/D	
	55	3, 6, 12, 24*; 36 h	10	N/D	N/D	
Corn stover	20	24 h	1	0	0	(Zhu et al. 2010)
	20	24 h	2,5	0	0	
	20	24 h	5	0	37	
	20	24 h	7,5	(−)	(−)	
Energy crops						
Grass silage			1	10		

(continued)

Table 5.2 (continued)

Biomass	Temperature (°C)	Treatment time	NaOH dose (%)	Increase in methane (%)	Increase in biogas (%)	Reference
	20; 60; 100*; 150	48 h	2,5	23	N/D	Xie et al. 2011
	20; 60; 100*; 150	48 h	5	38	N/D	
	20; 60; 100*; 150	48 h	7,5	39	N/D	
	20; 60; 100*; 150	48 h			N/D	
Sorghum	55	12 h	4	0	N/D	Sambusiti et al. 2013
	55	12 h	10	0	0	

(*) Response with significant difference (N/D) Not determined (−) Negative effect

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Part III
AD of Specific Waste-Streams

Chapter 6
Anaerobic Digestion of Dairy Industry Wastewater

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Abstract Dairy industries are one of the major food industries which generate a huge amount of wastewater both in terms of volume and strength. The chemical composition of dairy wastewater ranges from 1000 to 4500 mg/l for COD, 500 to 3000 mg/l for BOD, and 160 to 800 mg/l for TSS. Such wastewaters, if discharged into the environment without proper treatment will pose serious detrimental effects on water, land and air. The major portion of the wastewater generated from dairies is highly organic which depicts its higher degree of biodegradability. Compared to the aerobic and physicochemical methods employed for treating dairy wastewaters, anaerobic treatment methods are highly promising, cost-effective, and provide a sustainable energy generation option. The present manuscript critically evaluates the effect of various factors like pH, temperature, organic loading rate, hydraulic retention time, availability of nutrients, and C/N ratio on the process of anaerobic digestion. Recent studies and older research are considered for this study which concludes that these factors have a pertinent influence on the performance of an anaerobic digester. To check the feasibility of adopting an anaerobic digestion technology in both small and large-scale dairy units, technical and economic analysis is a must. This chapter also provides a detailed techno-economic analysis (TEA) framework for biogas production from dairy wastes.

Keywords Dairy wastewater · Anaerobic digestion · Parameters · Techno-economic analysis (TEA)

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6.1 Introduction

"Operation Flood" also known as the "White Revolution" in the year 1970 transformed India from a milk deficient nation to the leading producer of milk in the world. Since 1997, India is the leading milk-producing country in the world. Dairy products are considered as nutritious food source. Further, it is also considered as the means for increasing employment opportunities and thereby boosting the economy. India is also a leading consumer of dairy products and has both private and cooperative dairies. In 2019, the milk production was 175 billion litres and by 2020 it is expected to increase by 4%. India contributes to about 22% of the global milk production. With the growing population, there is a tremendous increase in the demand for dairy products including milk, curd, cheese, butter, ghee (clarified butter), ice cream, custard and cream. The dairy industry is one of the food processing industries which consume large volumes of water in every process (Singh et al. 2014). During milk processing, around 2% of the processed milk comes out in the waste, and the wastewater generated is 0.2–10 l/l of milk processed (Mehrotra et al. 2016).

Milk processing in the dairy industry involves several unit operations such as receiving, storing, clarification, pasteurization, standardization, homogenization, deodorization, storage and packaging (Burke et al. 2018; Motarjemi et al. 2014). For cleaning the various units, different alkaline solutions, detergents, emulsifiers, and sanitizers are used. In the dairy industry, the wastewater produced is mainly categorised into three types (Britz et al. 2006):

(i) Processing wastewater: i.e. the wastewater formed while cooling the milk in coolers and condensers for evaporating milk or whey.
(ii) Cleaning wastewater or sanitary wastewater: The cleaning wastewater evolves during the washing of process units, storage tanks, and milk cans, in contact with milk and other milk products. Spillages, losses in packaging, breakdown of equipment, and by-products (such as whey and brine) spillages/losses are considered in this category. Cleaning wastewater is around 90% organic as it comes from milk and milk products manufacturing residues: whey, cream, cheese pieces, water from clarification and separation (Kolev Slavov 2017).
(iii) Industrial wastewater: includes water used in clean in point (CIP) of equipment in contact with milk products.

The composition and concentration of wastewater depend on the operation method, production process and design of the process plant. This wastewater is highly unstable and biodegradable (Sharma et al. 2008).

6.1.1 *Composition of Dairy Wastewater*

Water used in the dairy industry is generally contaminated by milk and various milk products produced in the processes. The characteristics of the effluents generated in a

Table 6.1 Composition of dairy industry effluents

Milk processing effluents	Characteristic (mg/l except pH)							Reference
	COD	BOD	pH	TSS	TN	TP	FOG	
Mixed dairy	2300	1250	6.04	2000	60	75	–	Porwal et al. (2015)
Yogurt	1500	1000	7.2	650	93	–	–	Bhavsar et al. (2012)
Whey (cheese effluent)	71,526	20,000	4.1	22,050	–	–	–	Deshpande et al. (2012)
Butter and Ghee unit	3218	1377	7.1	2240	–	2	1320	Mohanrao and Subrahmanyam (1972)
Milk processing	2580	1139	6.93	1233	–	–	–	Singh et al. (2014)
Skim milk powder and whey effluent	88,000	62,000	6.6	34,904	70–80	10–15	40–50	Mehrotra et al. (2016)
Butter washing	1498	650	9.55	260	–	–	–	Shivsharan et al. (2013)

dairy industry are summarised in Table 6.1. Wastewater from the dairy industry consists of milk solids, detergents, milk wastes and sanitizers. The organic fraction in the dairy wastewater is because of lactose, glucose, fat and protein present in the milk products (Hassan and Nelson 2012). The characteristics of dairy wastewater and its composition depend on the size of the dairy industry and the type of products produced in the industry. A typical dairy industry processing milk, curd, ice cream, butter and buttermilk generates wastewater having COD, BOD, TSS in the range of 2500–3000, 1300–1600, 72,000–80,000 mg/l, respectively and a pH of 7.2–7.5 (Raghunath et al. 2016). Whereas, the wastewater from fluid milk processing has a COD, BOD, and TSS in the range of 500–1300, 950–2400, and 95–450 mg/l, respectively, and the pH 5–9.5 (Demirel et al. 2005). Further, the COD, BOD, and TSS of the wastewater produced at the milk reception due to spillage and cleaning of the milk cans are 2540, 800, and 650 mg/l, respectively and the pH is 7.18 (Janczukowicz et al. 2008). Wastewater from the washing of equipment such as boilers has a COD, BOD, and TSS concentration of 14,640, 3470 and 3820 mg/l, respectively and a pH of 10.37 (Janczukowicz et al. 2008).

In many countries, large amounts of dairy products in the form of cheese and butter are consumed. Cheese whey streams contain protein, lactose and other mineral elements that can be utilized in the manufacture of different products such as lactic acid, vitamins, fermented whey drinks, baker’s yeast and antibiotics. However, recovery of whey or whey protein results in new wastewater streams that also need to be treated (Malaspina et al. 1995; Oreopoulou and Russ 2007). The wastewater produced from the cheese whey processing is 60–80 times more concentrated than domestic sewage. The whey stream has a COD and TSS concentration in the range of 80,000–90,000 mg/l and 8000–11,000 mg/l, respectively and a pH of 6 (Baroudi et al. 2012).

During yogurt and buttermilk production, the wash water produced contains a large amount of fat and curd solids. The pH of the effluent produced from these units is around 7.2 and the concentration of COD, BOD, TSS is 1500, 1000, 190 mg/l, respectively (Turan 2004). Due to higher temperature, i.e. 17–25 °C the dairy wastewater has faster biodegradability compared to domestic wastewater. Wash water and cooling water from processing units have an average temperature of 18 °C in winter and 23 °C in summer (Tsachev 1982). The BOD and COD of the dairy wastewater can be expressed in terms of the milk constituents as 1 kg of lactose is equivalent to 1.13 kg of COD, 1 kg protein is equivalent to 1.36 kg COD and 1 kg milk fat is equivalent to 3 kg COD (Singh et al. 2014).

In India, on average the wastewater generated from a dairy industry constitutes COD, BOD, TS, and SS in the range of 1000–4500, 500–3000, 900–1340, and 160–810 mg/l, respectively. The pH is 7.5–8, nitrogen concentration is about 6% of BOD, phosphorus 10–100 mg/l and COD is 1.5 times the level of BOD.

6.1.2 Environmental Effects of Dairy Wastewater

From the diary wastewater characteristics, it is evident that it contains a substantial amount of organic matter and nutrients leading to the deterioration of receiving water bodies and the environment. Figure 6.1 presents the pollutants from the milk processing unit and dairy wastewater.

6.1.2.1 Effects on Receiving Water Streams

Due to the high organic content and biodegradability, the dairy wastewater depletes the dissolved oxygen content of the receiving stream and creates anaerobic conditions resulting in foul odour. A higher concentration of COD and BOD is toxic to aquatic life. Suspended solids, soluble organics and trace organics in dairy wastewater lead to eutrophication of the receiving streams. Even if the BOD is low but the phosphorus and nitrogen content is too high, this could trigger the increased production of algae. Wastewater disposed into the streams causes the growth of algae and bacteria that consume oxygen and suffocate the aquatic life (Deshpande et al. 2012). Lactose, a low molecular weight organic compound present in dairy wastewater promotes the growth of sewage fungi.

Bacteria convert the nitrogen in protein to the inorganic forms of nitrogen as nitrate, nitrite, ammonia and ammonium ions. Different forms of nitrogen are harmful to both humans and livestock. Nitrate ions converted to nitrite ions in the bloodstream and haemoglobin converted to methemoglobin does not allow oxygen to be taken up by the blood. Methemoglobinemia is a disease observed in infants due to the presence of methemoglobin in the bloodstream. To avoid such effects, the

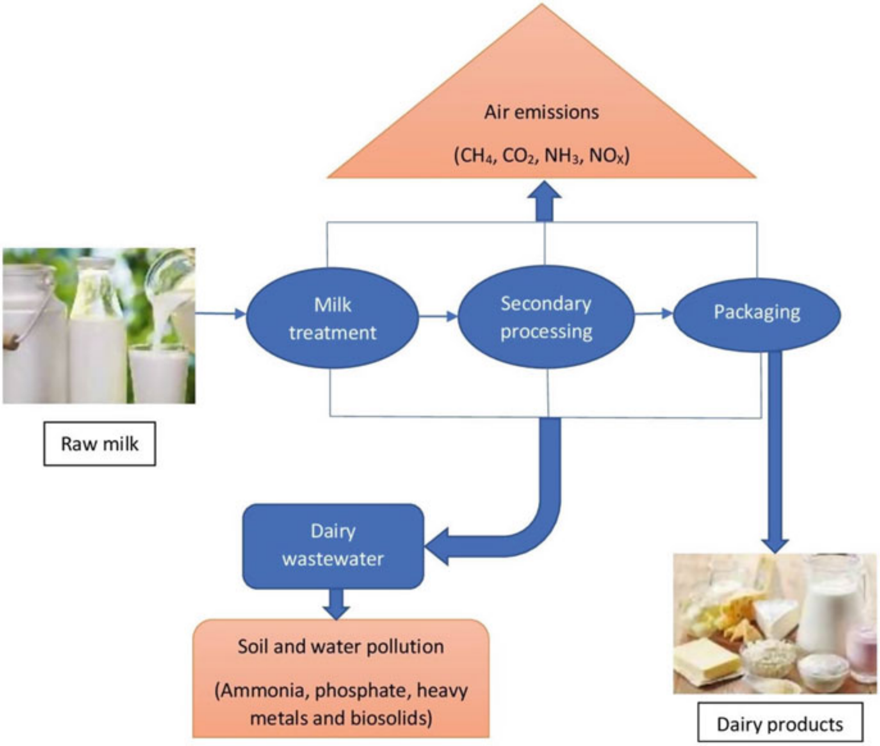

Fig. 6.1 Pollutants from the milk processing unit and dairy wastewater

nitrite-nitrogen concentration in drinking water must be below 10 g/m^3. All the inorganic forms of nitrogen and inorganic phosphorus act as nutrients for plant growth. To reduce the undesirable plant growth in the receiving streams, the inorganic nitrogen and inorganic phosphorus concentrations must be limited to 30–100 mg/m^3 and 15–30 mg/m^3, respectively (Shete and Shinkar 2013).

6.1.2.2 Effects on Land

Disposal of dairy wastewater on land is one of the treatment techniques. The nutrients present in the wastewater are removed through:

(a) Plant uptake
(b) Adsorption and immobilization in the soil
(c) Atmospheric losses
(d) Leaching into groundwater

Nitrogen and phosphorus uptake by plants account for 500 and 30 kg/ha/year, respectively. Up to 90% of nitrogen and phosphorus is recycled to pasture if the animals subsequently consume the pasture. Groundwater contaminated by nitrate is one of the limitations for treating dairy wastewater by disposing on soils. Groundwater when further used by humans can affect human health (Barnett et al. 1998; Shete and Shinkar 2013). Sodium, magnesium, potassium and calcium present in the dairy wastewater are immobilised by soils and occupy cation exchange sites on clay and soil collides. The pH of dairy wastewater can affect the pH of soil and nutrient availability, which may further affect the microorganisms present in soil and may alter the fertility of the soil.

6.1.2.3 Effects on Atmosphere

Anaerobic decomposition of dairy wastewater contributes to methane emissions. Further using the dairy wastewater for irrigation can add to nitrous oxide emissions (Milani et al. 2011). Moreover, the boilers used in the dairy plants account for carbon dioxide, sulfur oxides and nitrogen oxides into the atmosphere. Thus, carbon dioxide, methane and nitrous oxide are the greenhouse gas emissions from the dairy industry. Besides, dairy effluents have a very foul odour that is not pleasant. Volatile dust particles and particulate matter emitted from the powder driers and boiler stacks will settle on the surrounding buildings and can be corrosive (Deshpande et al. 2012; Shete and Shinkar 2013).

6.1.3 Treatment of Dairy Wastewater

The concentration of the dairy wastewater is rich in nutrients and organic matter thus conventional treatment techniques are not effective in removing them. Mechanical treatment followed by chemical or biological treatment are generally carried out (Birwal et al. 2017; Yonar et al. 2018). In a conventional dairy wastewater treatment system, the preliminary stage includes screens, grit chambers and a skimming tank to remove floating materials, inorganic soil material and oil and grease from the dairy effluents respectively. Solids removed from dairy wastewater, such as fats, oils and greases (FOGs), increase the biodegradability and methane production, but at the same time decrease the methane production potential by decreasing the BOD concentration. Figure 6.2 shows the possible treatment ways of dairy wastewater through mechanical, physico-chemical and biological methods.

Treatment of dairy wastewater through the biological process is promising since dairy wastewater effluent is mainly organic. Aerobic treatment processes are less efficient due to the growth of filamentous substances and acidification (high lactose and low buffer) (Nadais et al. 2010; Prazeres et al. 2012). Bulking and foaming, additional biomass production, as well as poor activity at low temperature, are the other disadvantages of aerobic treatment processes (Britz et al. 2006). Anaerobic treatment followed by aerobic treatment is the most commonly used process for treating dairy wastewater.

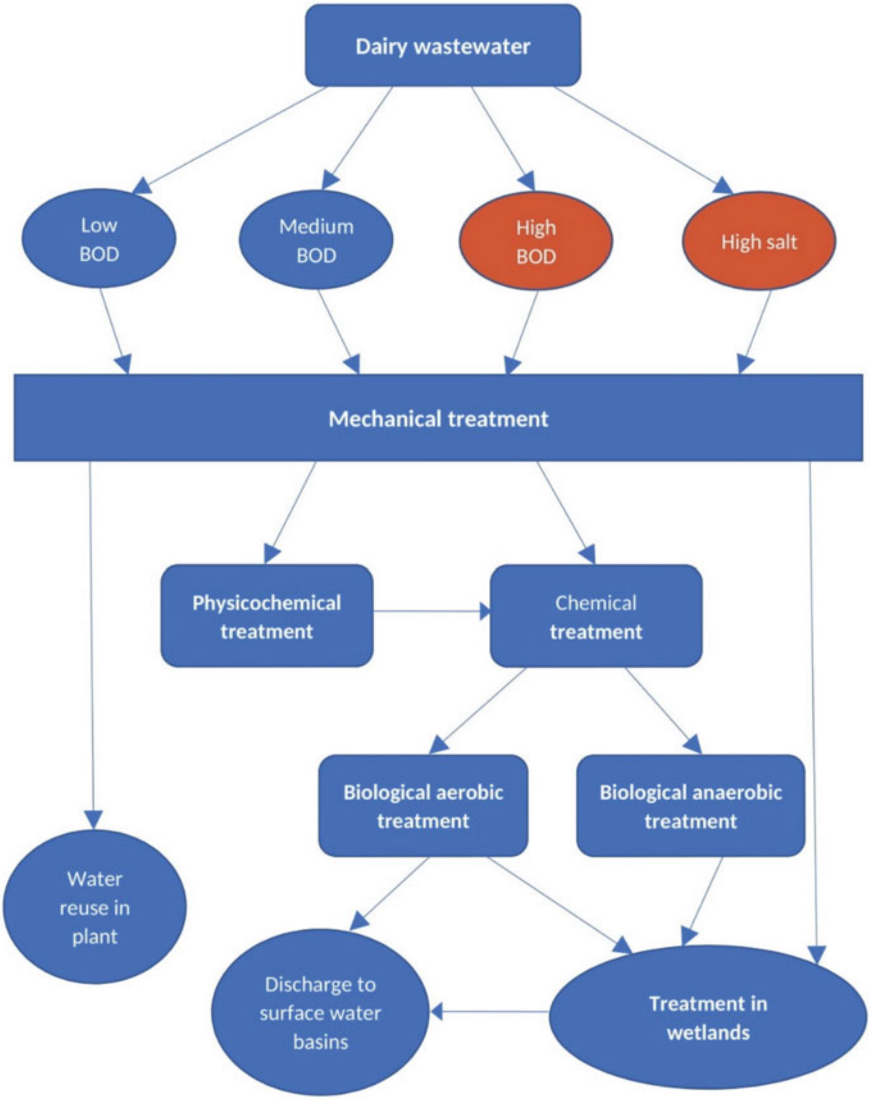

Fig. 6.2 Process diagram of the treatment of dairy wastewater

6.2 Anaerobic Digestion of Dairy Wastewater

Anaerobic systems used for the treatment of dairy industry effluent are anaerobic lagoon, contact digester, upflow anaerobic sludge blanket reactor, stirred tank reactor, fixed-film digester, anaerobic filter reactor, expanded bed digester, membrane anaerobic digester, separated phase digester and hybrid digesters (Hassan and

Nelson 2012). Anaerobic digestion of dairy wastewater produces organic acids such as lactic acid, propionic acid and acetic acid, and biogas with hydrogen, methane and carbon dioxide. In some cases, methanogenesis is inhibited for the production of other products such as hydrogen, propionic and acetic acid, which is called dark fermentation (Kasmi 2018).

There are many studies focusing on anaerobic treatment of dairy wastewater with very high treatment efficiency. The COD removal of various dairy wastewaters and biogas production presented in the literature is summarised in Table 6.2. Gavala et al. (1999) stated that an up-flow anaerobic sludge blanket (UASB) reactor under steady-state conditions removed 90% of COD from the influent having a COD of 2050 mg/l and organic loading rate of 0.031 kg of COD/m^3 day. An anaerobic UASB reactor followed by an aerobic reactor resulted in 90% and 85% removal of BOD and COD respectively, in a cheese manufacturing industry with a biogas production rate of 0.40 l biogas/g of COD removed (Malaspina et al. 1995). At an organic loading rate of 10 g/day, an anaerobic downflow-upflow hybrid reactor (DUHR) removed 98% COD followed by an anaerobic sludge blanket reactor (SBR) that achieved 90% removal of both nutrients and COD (Derramadero and Guyot 1995).

A combination of an anaerobic filter reactor and UASB reactor to treat dairy wastewater was evaluated by Calli and Yukselen (2002), and it was concluded that the digester generated 0.354 m^3 methane/kg of COD (Calli and Yukselen 2002). The performance of an anaerobic fixed film reactor treating dairy wastewater at 3 and 2 days HRT was evaluated by Koshta (2010) and observed a BOD removal efficiency of 87.69% and 89.42%, respectively. The performance of anaerobic sequence batch reactors (ASBR) was evaluated at an HRT of 6 h and a temperature of 58 °C and observed a removal efficiency of 62% and 75% of COD and BOD$_5$, respectively (Dugba and Zhang 1999). Further, Nadais et al. (2006) evaluated an intermittent feeding cycle, i.e. 48 h feed + 48 h without feeding, to the UASB reactor and observed that intermittent operation has a higher COD removal efficiency (22 g COD/l/day) compared with continuous feeding (3–6 g COD/l/day). Dębowski et al. (2018) treated the simulated dairy wastewater in an anaerobic biofilm reactor with magneto active microporous media. At a suitable organic loading rate ranging from 6 to 8 kg COD/m^3 day, the anaerobic reactor removed 80% of chemical oxygen demand, 70% of organic matter and 80% of phosphorous. The methane production was in the range of 420.6–557.1 l/day. Anaerobic digestion of the dairy wastewater as a substrate was performed by Karthiyayini et al. (2017) and observed 36% COD and 33.5% of volatile solids removal. Similarly, many recent studies suggest that anaerobic digestion is a more energy-efficient process for dairy wastewater treatment with increased biogas production (Shete and Shinkar 2017; Meegoda et al. 2018; Pilli et al. 2020).

The anaerobic digestion of milk fat (triglycerides) in dairy wastewater by microorganisms (*Clostridia* and *Micrococci* sp.) results in the products such as acetate, hydrogen and CO$_2$. But, the presence of long-chain fatty acids (LCFAs) in fats, oils and greases (FOGs) can cause inhibition of methanogenesis and digester instability. In anaerobic digestion, lactose generates acetate, lactate, formate, propionate and

Table 6.2 Process performance of the anaerobic digestion of dairy wastewater

Dairy waste type	Reactor	HRT (Days)	OLR (kg COD/ m^3 day)	pH	Temperature (°C)	COD removal (%)	Methane production (m^3/kg COD)	Reference
Ice cream	Anaerobic filter	0.5	6	–	–	85	0.32–0.34	Ince (1998)
Acid whey	CSTR	5	–	6.5	–	–	0.3	Saddoud et al. (2007)
Raw milk	Anaerobic filter	0.5	5–6	–	–	90	–	Omil et al. (2003)
Cheese plant waste	CSTR	5.7	60	7.0	-	-	0.28	Hwang (1997)
Cheese whey	Downflow fixed-film	6.6	8.3	–	30	76	0.34	Van den Berg and Kennedy (1983)
Deproteinized whey	Downflow fixed bed	5	2.8	7.25	–	–	27	De Haast et al. (1986)
Effluent of integrated plant	UASB	0.2083	8.5	–	30	87	–	Ozturk et al. (1993)
Synthetic dairy effluent	Hybrid	1.7	0.82–6.11	–	35	90–97	0.354	Ramasamy et al. (2004)
Pre-fermented whey	Up-flow anaerobic filter	2	3	7.2	–	–	0.28	Gannoun et al. (2008)
Cheese whey	Downflow fixed-film	4.9	13	–	–	75	0.28	Van den Berg and Kennedy (1983)
Whey	No mix anaerobic digester	6	10	7.0	–	–	0.6	Yang et al. (2003)
Cheese production wastewater	UASB	10–20	2.3–4.5	–	35	79–91	–	Gavala et al. (1999)
Cheese whey	Rotating biological contact reactor	3	–	–	37	85	–	Mawson (1994)
Synthetic ice-cream wastewater	CSTR	7.45	–	–	35	98	–	Ramasamy and Abbasi (2000)

(continued)

Table 6.2 (continued)

Dairy waste type	Reactor	HRT (Days)	OLR (kg COD/ m^3 day)	pH	Temperature (°C)	COD removal (%)	Methane production (m^3/kg COD)	Reference
Dairy wastewater	–	–	–	7.52–8.3	–	83.75	–	Asha (2014)
Cheese wastewater	Semi-continuous digester	9	0.633	–	35	78–90	–	Lebrato et al. (1990)
Synthetic dairy wastewater	Anaerobic diphasic fixed-film fixed bed digester	–	1.265	–	–	70.4	0.33	Srinivasan et al. (2009)
Dairy wastewater	Hybrid UASB	–	2.5–3.5	–	–	88	–	Thenmozhi and Uma (2013)
Dairy wastewater	Anaerobic biofilm reactor	–	0.0726	–	–	84	–	Sivakumar and Asha (2012)
Dairy effluent	Up-flow anaerobic fixed bed reactor	0.5	5.4	–	–	87	–	Deshannavar et al. (2012)
Dairy wastewater	Up-flow anaerobic packed bed bioreactor	56	–	–	–	59	–	Deshpande et al. (2012)
Dairy wastewater	Fixed bed fixed-film anaerobic reactor	–	–	–	–	80	0.318	Ramesh and Kumar (2007)
Dairy wastewater	Fixed Film and Fixed Bed Anaerobic Reactor	–	0.004	–	–	80.88	0.265	Ramesh et al. (2012)
Dairy wastewater	Anaerobic Sludge Blanket reactor	–	–	–	–	87.06	179.35 m^3/day	Gotmare et al. (2011)
Dairy wastewater	Combination of CSTR and baffled reactor	1.6	1.25–4.5	–	–	82	0.26	Jürgensen et al. (2018)
Dairy wastewater	Horizontal flow reactor	–	1–2			85	0.33	Dębowski et al. (2020)
Dairy wastewater	Internal circulation bioreactor	–	–	5–6	–	80	69.8	Charalambous et al. (2020)

ethanol as intermediate metabolites. The major products of lactose digestion by microorganisms (*Clostridium*, *Streptococci*, *Acetobacter* sp.) are methane, carbon dioxide, hydrogen, cellular carbon and ethanol. Milk proteins in dairy wastewater are digested by microorganisms (*Fusobacterium*, *Selenomonas*, *Eubacterium* sp.) to produce organic acids, carbon dioxide, ammonia and hydrogen (Hassan and Nelson 2012; Kasmi 2018).

6.3 Parameters Effecting the Anaerobic Digestion of Dairy Wastewater

There are many important process parameters in anaerobic digestion and by optimizing them, an increase in biogas yield and treatment efficiency can be achieved. The main parameters include pH, temperature, organic loading rate, HRT, nutrients and mixing (Abdelgadir et al. 2014), which are discussed in detail below.

6.3.1 pH

The pH value is the negative logarithm of hydrogen ion concentration. It is the expression of acidic or basic conditions of a solution (Shete and Shinkar 2017). In anaerobic digesters, the buffering system is required for the interaction of volatile fatty acids, bicarbonates and ammonia. Lactose present in dairy wastewater breaks down into short-chain fatty acids such as acetic, propionic, butyric and other acids by bacteria and cause a rapid decrease of pH in the digester. Low pH of dairy wastewater inhibits the growth of methanogens and reduces gas quality, quantity, and COD removal. The base (calcium, sodium) added to control the pH might affect the gas production when applied in exceeding amount. The optimum pH range for acidogenesis is around 5.5–6.5. The most suitable pH for methanogens is around 7.0 and the acceptable range for methanogenesis is 6.5–7.5 (Hassan and Nelson 2012; Abdelgadir et al. 2014). Therefore, maintaining the pH range within 6.6–7.4 is suitable in anaerobic digesters. Controlling the pH in digesters increases the digestion efficiency, but it increases the operation cost in anaerobic digestion of dairy wastewater as well due to the requirement of additional chemicals (Hassan and Nelson 2012; Nyaki and Njau 2016).

6.3.2 Temperature

Anaerobic digestion is a natural process that occurs in different temperature ranges such as psychrophilic (5–25 °C), mesophilic (30–37 °C), thermophilic (50–60 °C) and hyperthermophilic (>65 °C). Industrially, anaerobic digestion occurs in mesophilic (30–37 °C) and thermophilic (50–60 °C) temperatures (Hassan and Nelson 2012; Shete and Shinkar 2017). The rate of reaction and pathogens destruction occurs faster in thermophilic digesters, but it requires a lot of energy input to maintain elevated temperature. Thermophilic digesters are better capable to produce high methane gas with dairy wastewater to make the digester economically feasible. Thermophilic digesters facilitate treatment of a wastewater with higher organic loading rate. On the other hand, mesophilic digesters require less operating costs. An increase in wastewater temperature enhances turbulence, mixing, adsorption and sedimentation, thereby increasing biogas production (Meegoda et al. 2018). For example, the methane production gradually increased with an increase in temperature from 20 to 40 °C using cheese whey and animal waste as the substrate (Tabatabaei et al. 2011). With the decrease in temperature from 35 to 20 °C in the anaerobic digester the COD removal efficiency decreased by 40%. Some digesters do not require heat energy and rely on ambient temperature, but seasonal fluctuations affect the performance of these digesters. For example, the production of biogas in summer is faster when compared to winter (Tabatabaei et al. 2011; Abdelgadir et al. 2014).

6.3.3 Organic Loading Rate

The organic loading rate (OLR) of the anaerobic digester is the total amount of COD in kg/m^3/day of digester volume supplied to the digester. It is the total amount of organics fed into the digester in a day (Shete and Shinkar 2017). An increase in OLR beyond the optimum level decreases the methane production in the digester and the COD removal efficiency from the dairy wastewater. Overloading the digester causes wastewater to quickly hydrolyze and acidify thus creating over-accumulation of volatile fatty acids, which has the potential of inhibiting methanogenesis (Meegoda et al. 2018). A higher organic loading rate often causes inhibition of methanogens in the digester and causes reactor failure. Some reactors like fixed film, fluidized bed and expanded bed reactors can withstand high organic loading rates. The desired OLR of the digesters is the provision of the possible highest substrate concentrations to methanogens for methane production while compensating the inhibitory compounds (Tabatabaei et al. 2011).

6.3.4 Hydraulic Retention Time

Hydraulic retention time (HRT) is the mean length of time that liquids remain in a digester. A higher loading rate reduces the hydraulic retention time, which may affect the efficiency of digestion (Meegoda et al. 2018). Accumulation of volatile fatty acids increases with a decrease in hydraulic retention time. Long hydraulic retention is required in the digester to avoid cell wash out of slow-growing methanogens. Dairy wastewater requires less retention time when compared to the digestion of more complex compounds such as lignocellulosic waste. The HRT has great influence on the process economics as shorter retention time increases biogas productivity and reduces the running costs. The optimum hydraulic retention for mesophilic digestion ranges from 15 to 30 days (Abdelgadir et al. 2014; Hassan and Nelson 2012).

6.3.5 Nutrients

In the anaerobic digester, along with the substrate and inoculum, (micro-)nutrients are also essential for anaerobic digestion. Inorganic nutrients such as nickel, iron, cobalt and other trace minerals are added to the digester to enhance the anaerobic digestion by enhancing the microbial population growth (Shete and Shinkar 2017). In case of dairy wastewater, macronutrients such as nitrogen and phosphorous are already present. Calcium increases the granulation, which helps in retaining slow-growing methanogens in the digester and improve the treatment efficiency (Hassan and Nelson 2012; Demirel and Yenigun 2004).

6.3.6 C:N ratio

Carbon to nitrogen is another critical parameter influencing biogas production from wastewater. They are major nutrients present in wastewater that need to be removed before discharge into a water body. The optimum carbon-nitrogen ratio is in the range of 20–30. A higher C:N ratio reduces gas production and a lower C:N ratio causes ammonia accumulation (Hassan and Nelson 2012). Free ammonia accumulation in the reactor reduces the growth of microorganisms and highly inhibits the methanogenic process. A low amount of nitrogen can cause acidification in the digester and inhibit methanogens (Xue et al. 2020). Along with carbon and nitrogen, microbes require phosphorous and other micronutrients for their survival. Apart from the methane production, the percentage of biogas obtained also depends upon the C:N ratio (Shete and Shinkar 2017).

6.4 Techno-economic Analysis of Anaerobic Digestion of Dairy Wastewater

Biomass and various industrial wastes have been used as sources of renewable energy production through anaerobic digestion for biogas production. The biogas produced through anaerobic digestion has been used in ranges of 1–6 m^3 for household purposes and more than 1000 m^3 for industrial purposes (Deublein and Steinhauser 2011). Dairy industries have huge potential in producing biogas from the highly organic effluents it generates. But many dairies see the biogas generation strategy as a high-risk investment due to the high sensitivity of the process, variations in feedstock characteristics, segregation of wastes and operational problems (Schmidt 2014). Many governments have put several policy initiatives and off-take agreements to solve these issues. For this, at first, it is important to conduct an integrated analysis to assess the technical and economic feasibility and environmental impacts of employing anaerobic digestion technologies.

A techno-economic analysis (TEA) indicates the technical and economic analysis of a process/technology through various simulation approaches through software like Aspen plus and Intelligen Superpro Designer. The results provide an insight into the feasibility of a project. Also in certain cases, Life Cycle Assessments (LCA) are used to compare the impacts of various processes/products quantitatively on the environment (Li and Khanal 2016). The whole process of anaerobic digestion can be divided into three areas: collection and transportation of feedstock, pre-treatment and anaerobic digestion, and post-processing of biogas/co-product handling. Similarly, in TEA for the preparation of TEA framework, three basic sections can be identified namely (a) the unit operations involved in choosing, collecting and transporting feedstock to the digestion site, (b) processing stage of feedstock to produce biogas, and (c) final stage of upgrading the biogas generated for electricity generation, heating, liquid methane and house-hold purposes (Rajendran and Murthy 2019). Large dairy industries can utilise the wastes generated for electricity generation and heating purposes. by installing an anaerobic digestion plant within the industry, because the wastes generated may be large enough to generate the energy required for heating. Mostly large dairies can afford a one-time capital on setting up a treatment plant within the industrial premises. This will also help in reducing the collection and transportation cost in transferring wastes from the source to the digestion site. Hence, the first section in a TEA framework pertaining into operations involving the transportation of wastes can be neglected and this will help in reducing the complexity. Figure 6.3 represents a typical TEA framework for biogas production from dairy wastes.

The technical goals include maximising dairy waste utilization for AD, maximising biogas yield, and process stabilisation. The economical objective is to reduce the costs, i.e. capital, operational and maintenance costs. The whole waste processing value chain is determined by the TEA framework and through experimentally validated process specifics. The economic analysis involves cost assessments and investment analysis. The techno-economic analysis is conducted to estimate the cost required and energy generated over the value chain from feedstock digestion to energy production by various means like combined heat and power (CHP), electricity, or vehicle fuel. Studies on the use of biogas, as vehicle fuel are one of the leading technological advancements in the application of biogas. Table 6.3 shows a summary of AD studies on dairy wastes, which types of wastes used, OLR, other operational parameters, biogas yield and expenditures encountered are summarised.

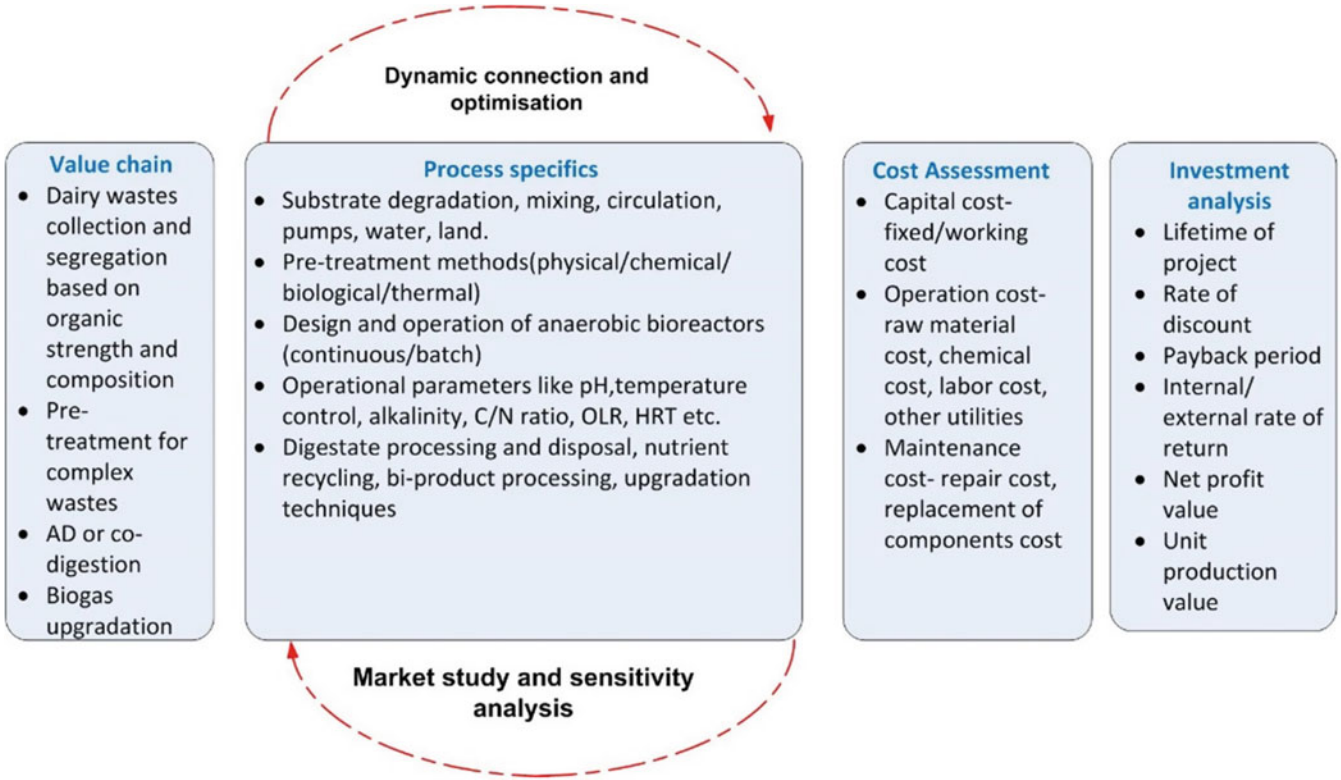

Fig. 6.3 TEA framework for biogas production from dairy wastes

Table 6.3 Techno-economic analysis of anaerobic digestion of dairy wastes

Type of dairy waste	Organic loading rate	Hydraulic retention time	T (°C)	Biogas yield	Payback period	Capital cost	Reference
Dairy manure	2.29 kg DM/m^3 day	33 days	40	30 m^3/tDM	3.4 years	11.5M$	Akbulut (2012)
Cheese whey	2.27–2.74 kg VS/m^3 day	25 days	35	437.3 N mL·CH_4/g VS_{added}	NA	NA	Mainardis et al. (2019)
Dairy manure	NA	20 days	35	97.3 m^3/t TS	6 years	2.26M$	Chen et al. (2015)
Dairy manure	2.6 kg VS/m^3 day	27 days	37	235 l_{biogas}/kg VS_{added}	11 years	NA	Imeni et al. (2020)
Cheese whey	NA	35 days	37	0.60 l CH_4/g VS_{added}	7 years	US$3860	Escalante et al. (2018)

6.5 Case Studies on Techno-economic Analysis of Anaerobic Digestion of Dairy Wastewater

Pilot-scale studies are conducted more in number than field scale/industrial scale set-ups. Some of the few recent anaerobic digestion studies on dairy wastes including their techno-economic analysis are discussed below.

6.5.1 Case Study 1

6.5.1.1 Case Description

Mainardis et al. (2019) has studied the techno-economic feasibility of diffused AD implementation in some selected dairies. Different kinds of cheese whey are analysed and their respective methane yield was evaluated using the biochemical methane potential (BMP) test. Results showed that digestion of cheese whey alone from a dairy could cover that dairy's electrical and thermal demand. Based on the results, pilot-scale anaerobic digesters were constructed. The study was carried out in the Friuli-Venezia Giulia region, located in the North-eastern part of Italy. This place is characterised by several small to medium dairy plants. A series of dairies present in the middle plain area of the Friuli-Venezia Giulia region is considered. The study used a territory-oriented based approach, and different varieties of cheese whey like fat, skimmed and mozzarella are considered. The anaerobic sludge is collected from a full-scale anaerobic digester of the wastewater treatment plant is used as an inoculum for all studies. Three varieties of cheese whey were collected from five local dairies depended upon their specific availability. Samples were sonicated for a treatment time of 5 and 10 min with 20 kHz frequency at 40 and 80 W. A biochemical Methane Potential (BMP) test was performed for the sonicated samples. Fifteen individual reactors having 650 ml volume each, inoculum and substrate volume up to 400 ml and equipped with stirrers were used. To overcome rapid acidification, a high inoculum to substrate (I/S) ratio of 6.0 was maintained. The temperature maintained in the reactors was 35 °C. The mixing regime adopted for the reactors was 30s off and 30s on.

6.5.1.2 Energy Analysis

Data regarding electricity, diesel, natural gas and water consumption by the five dairies are furnished. Heat and electricity that can be derived were calculated by burning biogas in a combined heat and power unit (CHP) having 50% electricity and 35% heat. Energy consumption of the five dairies is collected. Thermal consumption rates were high (0.247–0.557 MJ/kg milk) compared to the values presented in the literature. Among the five dairies, methane yield was high for dairies 2 and

4, i.e. 307.7 Sm^3/day and 317.8 Sm^3/day, respectively. Based on the values obtained, an appropriate digester size that can be installed in each dairy-based on cheese yield was proposed. Results showed that each dairy gets some surplus energy after covering most of the plant energy needs if they start digesting all the whey produced by themselves. Thus, the anaerobic digestion of dairy waste/wastewater approach is a way for sustainable development. Further, the transportation and management costs are significantly minimised along with renewable energy production and improved energy balance.

6.5.2 Case Study 2

6.5.2.1 Case Description

Tan et al. (2021) has conducted anaerobic digestion studies for determining the suitability of using an attached biofilm reactor with cattle manure as the substrate. Techno-economic evaluation of the biogas system was also done. The cow manure collected from a dairy at Ladang (Malaysia) was cultured overnight and then acclimatised using a sequencing batch reactor for use as an inoculum. The digester was set to operate at 37 °C, HRT of 7 days and pH 7. Granular Activated Carbon (GAC) was used as a support carrier on which the biofilm layer was formed. The percentage of GAC used was 25% (v/v) which means, 25% of the total working volume was attached over the support carrier, which helps in the accumulation of microorganisms on the biofilm layer formed. The maximum methane production of 934.54 mL/g VS was observed at 14 days HRT. Using the modified Gompertz equation methane production was estimated to be the maximum on 20 days HRT period.

6.5.2.2 Energy Analysis

An energy economic analysis was conducted for the study. The lifespan of the digester system is estimated to be 20 years and the rate of electricity is 0.35 Malaysian Ringgit (RM) /kWh. The cost spent on the digester set up was divided into fixed capital and working capital, where fixed capital is determined based on some factors (equipment cost, purchase cost, piping and site development cost) and working capital is 5% of the fixed capital. Also, operational cost is the sum of fixed operating cost and variable cost. The generated biogas was used for heating and electricity generation purposes. A combined heat and power (CHP) unit having 48% thermal efficiency and 38% electrical efficiency was operated using the methane generated. The revenue obtained from the sale of electricity generated using biogas was around RM 236.88 and RM 2842.56 in a year. This electricity can be effectively utilised within the farm which will reduce the electricity bills enormously. However, this alone cannot help in covering the total operational cost. Thus, fertiliser formed in the digester can also be supplied to the farmers which will help in expanding the revenue. At the initial stages, the cash flow was a little down as the profit was used to pay off the debts. Later, from 2 to 7 years the revenue from the biogas plant showed increment.

6.5.3 Case Study 3

6.5.3.1 Case Description

Fantozzi et al. (2015) studied the potential of energy production through anaerobic digestion of spoiled milk using a pilot-scale anaerobic plant. Spoiled milk comprises a major portion of waste generated from the dairy industry. Milk gets spilt out during many practices like collection, transferring milk from cans, processing units and packaging. The whole fresh milk that got expired and stored in warehouses are used for this study. The digestate from a secondary anaerobic digester fed with corn waste and sorghum silage was used as inoculum. The experimentation involves biomethanation (BM) tests in bottles and a pilot-scale set up. The substrate to inoculum ratio of 1:3 fixed from BM tests is used for the pilot-scale study. The study was carried out at a temperature of 35 °C for 40 days. Usage of the optimum amount of organic matter has avoided the rapid acidification problem and attained a maximum methane production of 0.362 Nm^3/kg VS.

6.5.3.2 Energy Analysis

The anaerobic digester plant consists of a CSTR reactor with a pre-tank load, a cogeneration unit to produce electricity and heat and a biogas storage unit. The power unit is in the micro-scale range (below 200 Kw). The net electric output power is around 105 kW and thermal power of 127 kW. The small to medium dairies located near the plant process around 15,000 tons of milk every year and 10% of the product normally becomes waste which is utilised for producing biogas. The digestion plant is operated and maintained by a dairy plant which collects raw material from the three other dairies. Since the dairies are located with a 50 km distance, transportation cost is not much high. Also, the benefit of supplier companies is their avoided transportation costs to landfills. The revenue from the incentives was calculated considering that about 8% of the electric power is consumed for plant operation. Disposal costs are imposed on other dairies which will also add to the revenue earned. Around 8% of the electric power generated is used for operating the plant.

6.6 Future Perspectives

From the bioreactor point of view, the two-stage and high-rate anaerobic digestion systems for dairy wastewater are attractive for achieving process energy efficiency. The production of hydrogen from dairy wastewater along with methane could also be a promising strategy (Demirel and Yenigun 2004; Karadag et al. 2014; Murari et al. 2019). In addition, highly polluting dairy wastes like whey wastes can be processed further to derive several value added byproducts (Asunis et al. 2020). The two-stage anaerobic digester consists of two reactors, an acidogenesis or hydrogenogenesis reactor and a methanogenesis reactor. In high-rate anaerobic digesters, the substrate is completely mixed, operated at elevated temperature and the retention time is lower. Such high-rate systems are more beneficial from an economic point of view. Further, techno-economic analysis is critical for establishing the full-scale process. Nutritional, chemical, mechanical and energy requirements and the innovative design of anaerobic digesters is essential to improve methane production and to reduce costs. Another strategy is co-digestion which utilizes multiple substrates for methane production in anaerobic digestion. Co-digestion of dairy wastewater with other organic feedstocks is advantageous to enhance methane production and to achieve a waste sustainable process. Demand for dairy products are increasing worldwide and as a result increase in dairy industries and the use of various chemicals (hormones, antibiotics and other drugs) are becoming more prevalent. Such new chemicals in dairy wastewater may seriously affect the anaerobic digestion process and the treated water quality. Hence, special care should be taken to develop innovative research ideas to tackle this problem in order to prevent toxicity in the anaerobic digestion of dairy wastewater and prevent environmental degradation.

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Chapter 7
Solid State Anaerobic Digestion of Agricultural Waste for Bioenergy Production

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Abstract Huge quantities of agricultural residues and stubbles are mainly disposed by burning on site causing air pollution. The organic matter present in the residues and stubble can be utilized in a planned manner, subsequently reducing the emission (greenhouse gases) caused by burning. These agricultural stubbles are an attractive feedstock for clean energy production through anaerobic digestion (AD). Conventional liquid anaerobic digestion systems may be profitable but have a high-water footprint. Solid-state anaerobic digestion (SSAD) not only helps to reduce water consumption, but it also allows for a high organic loading rate and prevent nutrient loss in the digestate. Nevertheless, process stability of an anaerobic digestion system running on high solid concentrations may have several constraints such as limited mass transfer and process inhibitors like ammonia, *p*-cresol and D-limonene if present in the feedstock for SSAD. In the case of lignocellulosic biomass, its recalcitrant nature may hinder the methane production under the SSAD. Apart from these, the high total solid (TS) content may inhibit the process stability by producing excess total volatile fatty acids (TVFAs) during SSAD.

Keywords Solid state anaerobic digestion · Lignocellulosic biomass · Agricultural residues · Biogas · Bioenergy

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7.1 Introduction

The modern world's economic status and growth rate are based on energy and its consumption (Cantarero 2020; Paritosh et al. 2020a). Depleting fossil fuel reserves, geo-political issues over crude oil reserves, greenhouse gas (GHG) emissions and its socio-environmental impacts are detrimental factors for a sustainable world. In the last decades, global energy demand has increased manifold and mankind has been forced to explore other alternative forms of energy from sustainable sources. Renewable sources like wind, solar, ocean, small hydro, geothermal and biomass have been accepted as major players for ensuring energy supply under a sustainable development goal (MNRE 2019). Keeping this in mind, many countries including the developing ones are investing in renewable energy sources. For example, total installed grid connected renewable energy capacity in India has increased to 85.9 GW at the end of 2019 as per Ministry of New and Renewable Energy, Government of India (MNRE 2019).

Bioenergy derived from biomass, i.e. biofuel, can be classified as liquid or gaseous biofuels. Liquid biofuels encompass bioethanol, biodiesel and biobutanol while example of gaseous biofuels is biomethane, biohydrogen and syngas. The biofuels are also classified as first, second, third and fourth generation biofuels based on the substrate used for their production. In first generation biofuels, food crops and grains are used for biofuel production while for second generation, crop residues such as rice straw, wheat straw, corn stover and millet straw are used. The third generation biofuels are derived from algae and fourth generation biofuels are those obtained from genetically modified microorganism. First generation biofuel is less desirables as it competes with food whereas the other three biofuels are attractive to the investors and stakeholder as they utilise renewable and waste biomass.

India produces around 634 million tonnes of agricultural stubbles on yearly basis (Kumar et al. 2018). Organic carbon present in the agricultural stubbles and residues may be processed for fuels and energy production. Due to the lack of effective and efficient technology, farmers are compelled to burn these stubbles on site as to clean it before the next crop season. This direct burning of the agricultural stubble may produce around 1600 kg of CO_2, 112 kg of CO, 9.2 kg of CH_4, 5 kg of particulate matter and 6 kg of hydrocarbons per ha land (Guo et al. 2020). Theoretically, burning of these stubbles not only contributes to high GHG emissions, but also causes immediate problems in the surrounding areas in the form of severe deterioration of air quality (smog formation), and hence crop burning is not at all a sustainable approach for its disposal.

Agricultural stubbles have huge energy potential and may substitute fossils for fuel or electricity and are a promising alternative to meet future energy demands (Hansen et al. 2020). Presently, bio-based energy has approximately 15% share in the Worlds' total energy use which is almost 45 EJ. Numerous studies have suggested that the potential market for bioenergy may increase up to 50% of the total energy use by the year 2050 (Perea-Moreno et al. 2019). As per a study, 220 billion tonnes of dry biomass are produced worldwide annually (Dahunsi and

Enyinnaya 2019). This biomass is equivalent to 4500 EJ of solar energy obtained every year and has the ability to support an annual market of 270 EJ. Because of the huge energy potential and sustainable nature of it, biomass seems to be an attractive substitute to fossil fuels (Maletta and Díaz-Ambrona 2020).

7.2 Anaerobic Digestion

Anaerobic digestion (AD) is a biological process, practiced extensively for conversion of biodegradable waste to renewable bioenergy (biomethane) using anaerobic microorganisms (Caposciutti et al. 2020). This method has capability of utilizing different organic wastes such as forest woods, lignocellulosic materials, agricultural crops, food waste and municipal solid waste with high efficiency and minimum by-product generation. Biogas produced from the AD process can be utilized as fuel having a high calorific value of 30–35 MJ/m^3 and has the potential of replacing other fuel sources like liquid petroleum gas and natural gas (Sheets et al. 2015). Other high energy requiring technologies and methods such as landfilling, pyrolysis and incineration are utilized to handle biodegradable waste, but AD is preferred due to its biological nature which is a lost cost and low energy operation. Also, AD can utilize various feedstocks at large or small scale and further provide help in the reduction of waste sludge, killing of pathogens, and provide essential nutrients in the form of digestate (Xu et al. 2018).

AD is a microbe driven, multi-phase and complex bio-chemical process. The AD process comprises of mainly four different biochemical phases namely hydrolysis, acidogenesis, acetogenesis and lastly, methanogenesis. These biological phases include application of microorganisms in order to decompose organic matter and produce biogas consisting of primarily methane (CH_4) and carbon dioxide (CO_2). However, the efficiency of AD process depends on different factors such as type of biomass feedstock provided and operational parameters such as temperature, pH, alkalinity, mass transfer rate, volatile fatty acid accumulation, carbon to nitrogen (C/N) ratio, recalcitrant nature of lignocellulosic residues, low concentration of micronutrient and ammonia inhibition. Operating bioreactor under non-optimal condition or imbalance of any of these factors can cause inhibition to the microorganisms and that can result in the deterioration of the methanogenesis performance (Thanh et al. 2016).

Various methods have been developed to resolve these issues such as solid concentration optimization in anaerobic digester for better mass transfer, buffering agent addition in the reactor to balance pH, substrate co-digestion to stabilize the C/N ratio, pre-treatment of biomass (particularly the lignocellosic ones) to disrupt the lignin complex for enhancement of methanogenesis (Jain et al. 2015). Other than that, to achieve good process stability and performance, many material supplementation such as carbon-based additives are added to anaerobic reactors for improving its performance and to enhance its economic feasibility (Paritosh et al. 2021). The carbon-based additives reinforce direct interspecies electron transfer in the system and improve syntrophic relations in the reactor. Moreover, the presence of materials such as biochar or activated carbon accelerate the utilization of volatile fatty acids (VFA) and ensure availability of substrate to methanogens. Whereas, addition of elements such as cobalt (Co), nickel (Ni), iron (Fe) and zinc (Zn). in the AD acts as micronutrients and accelerate the metabolic activities of methanogens which provides a better yield of methane (Paritosh et al. 2020b). Nanoparticles of the above mentioned trace elements have also been supplied by various researches to enhance anaerobic digestion of biomass and biogas production (Lee and Lee 2019).

7.3 Solid State Anaerobic Digestion

Anaerobic digestion can be categorized into two distinct forms based on their total solid (TS) content in the reactor medium. The first one is liquid state anaerobic digestion with a solid content $<15\%$, whereas the other one being solid state anaerobic digestion (SSAD) with a TS content $>15\%$. SSAD has the following advantages over liquid anaerobic digestion (LAD): feasibility of using higher organic loading rate (OLR), less energy requirement, smaller reactor volume and increased volumetric methane yield (Brown et al. 2012; Rico et al. 2015; Panjičko et al. 2017). Beside, pathogen inactivation may also be achieved in SSAD of biodegradable waste (Jiang et al. 2018).

However, SSAD has a few challenges which include slow mass transfer, process instability, end product needs additional treatment and lower biogas production (Karthikeyan and Visvanathan 2013; Carlos-Pinedo et al. 2019). These issues need to be addressed in order to enhance process efficiency, and to further ensure its feasibility at a larger scale for successful commercialization of this technology.

7.4 Feedstock Identification for SS–AD

Several types of feedstocks including various wastes such as the organic fraction of municipal solid waste (OFMSW), food waste, forest waste, agricultural waste, animal waste, solid manure, energy crops, industrial waste, residual lignocellulosic biomass, paper and pulp waste have been established as good substrates for biogas generation using the SSAD process (Fig. 7.1). The physical and chemical

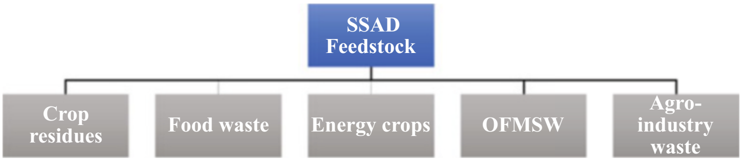

Fig. 7.1 Feedstock for solid state anaerobic digestion

composition of the substrate are very important and directly affect the process efficiency of AD system. For example, the presence of a high amount of recalcitrant compounds (such as lignin) in the biomass lower the biogas production whereas a high amount of easily utilizable compounds (such as sugars) enhances methanogenic activity (Paritosh et al. 2019). Hence, even before starting the process the suitability of any substrate, including lignocellulosic biomass for SSAD, should be determined by biomass characterization.

7.4.1 Organic Fraction of Municipal Solid Waste (OFMSW)

The organic fraction of municipal solid waste (OFMSW) comprises of yard trimmings, grass clippings, vegetable wastes, food wastes and fruit peel wastes (Kesharwani and Bajpai 2020). The approach for waste collection and transportation plays a major role in the SSAD process performance. Also, the seasonal variations and environment conditions can affect the composition of the OFMSW which in turn affects the SSAD process performance (Forster-Carneiro et al. 2007). Several studies have demonstrated that both physical as well as chemical properties of OFMSW have significant impact on biogas production.

Michele et al. (2015) performed SSAD of OFMSW by recirculation of the digestate. This liquid digestate flushing helped in removing fermentative products (such as volatile fatty acids (VFA)) inhibiting methanogenesis. The ratio of solid waste to digestate was in between 1:1.18–1:0.9 on w/w basis. The total solids removal was 36.9%, however the loss of organic matter was attributed to the washout with the percolate from the reactor. Hence, the percolate which was high in organic content was subjected to AD for biogas production in a second AD reactor (LAD). The mass balance showed that the methane content from the dry AD and the percolate were 18.4% and 49.7%, respectively, at a 21 d hydraulic retention time (HRT). However, only 20.4% and 25.7% of potential producible methane was generated by adopting 15 and 20 d of HRT using LAD of the same waste.

Food waste is also considered a part of OFMSW and contains organic materials which are transformed into simple molecules that are readily digested in the AD process. However, accumulation of VFAs caused by high soluble organic contents act as inhibitor by decreasing the pH of the system leading to reduction in methane yield of the AD process (Micolucci et al. 2018). Co-digestion of OFMSW with lignocellulosic biomass can be a beneficial approach for enhancing the process efficiency. Brown and Li (2013) examined the effect of feedstock to inoculum (F/I) ratio (1, 2 and 3) and substrate concentration (0, 10 and 20%) on co-digestion of food waste (FW) with yard waste on biogas production using SSAD. A high volumetric biogas production rate (8.6 L per L reactor volume) was achieved with 10% FW concentration and a F/I value of 2.

In another study conducted by Wang et al. (2012), the effect of different ratios of FW to distiller's grain on biogas production using SSAD was investigated. A 75.7% increase in the biogas production was observed with co-digestion compared with mono-digestion. Favourable synergistic effects were shown on the VFA/alkalinity ratio and propionate/acetate ratio when, distiller's grain and FW were co-digested. The optimum ratio for FW to distiller's grain was 8:1 with 20% TS in this study.

Zhu et al. (2014) examined co-digestion of soybean processing waste with addition of hay through SSAD for methane production. The authors studied the effect of the F/I ratio, leachate recirculation and pre-mixing of inoculum with substrate on biogas production. Maximum methane production was achieved at a F/I ratio of 3 (256 L/kg VS) and soybean processing waste and hay ratio of 75:25. The methane production during co-digestion was 148% and 50% higher as compared to mono-digestion of soybean processing waste and hay individually. The leachate recirculation accelerated the SSAD process, however no effect of premixing on the biogas production was observed.

Million tonnes of yard trimmings, grasses and leaves waste are generated in urban centres, and can be considered as a major component of OFMSW. These green wastes largely consist of hemicellulose and cellulose which are beneficial substrates for higher biogas production in the AD process. Xu et al. (2016) conducted research on yard trimmings by comparing SSAD digestate and dewatered LAD finished material as inoculum. The F/I ratio was varied from 0.2 to 2 whereas the TS content selected for the study was in between 20 and 35%. The highest methane production of 244 L/kg VS was obtained at a F/I ratio of 0.2 and TS content of 20%. The dewatered effluent at 24% TS and F/I ratio of 0.6 showed an increased volumetric methane yield compared with other experimental conditions.

7.4.2 Lignocellulosic Biomass and Residues

Lignocellulosic biomass is derived from plant based wastes such as agricultural residues, wastes generated from municipal parks and forests, and is one of the main sources of renewable energy production. Lignocellulosic material mainly constitutes of three main complex components which are cellulose, hemicelluloses and lignin. The carbohydrate part, i.e. cellulose (9–80%) and hemicelluloses (10–50%), is fermentable, whereas lignin presence is 5–35% in the biomass and is considered as inhibitory compound in the AD process (Fig. 7.2) (Yadav et al. 2019). The characteristic of lignocellulosic materials such as structural and chemical properties vary greatly depending on its source (biomass type). These properties are the main deciding factor for successful microbial degradation of the biomass and sometimes can cause complications for biogas production due to the higher presence of inhibitory substances.

Cellulose is a linear polysaccharide polymer of cellobiose which is connected by β-1, 4-glycosidic bonds. When the cellulose chain is linked by hydrogen bonds or van der Waals forces, high tensile strength microfibrils are produced. Cellulose is further comprised of two components, the first one is amorphous cellulose which is readily digestible and the other is crystalline form which is difficult to hydrolyse. Hemicellulose is more amorphous in nature and constitutes of pentoses

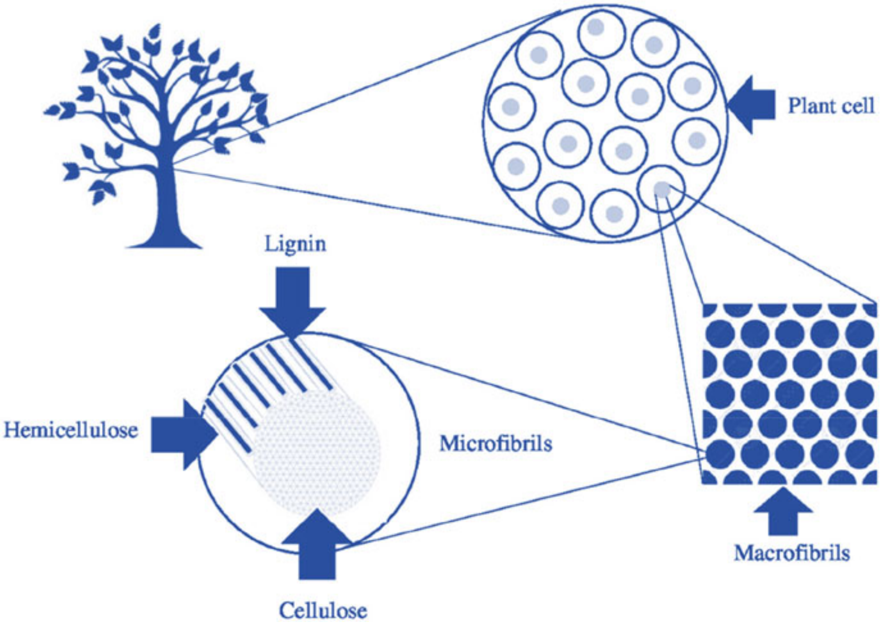

Fig. 7.2 Lignocellulosic biomass structure

(e.g. arabinose, xylose), hexoses (e.g. glucose, rhamnose) and acids (e.g. galacturonic acid). Lignin is a complex polymer consisting of sinapyl, coumaryl and coniferyl alcohol which is inert and insoluble in nature. These features of lignin make it recalcitrant and difficult parts of biomass to digest during AD process.

Brown et al. (2012) conducted a comparative study of a variety of lignocellulosic materials namely switch grass, yard waste, leaves, waste paper, wheat straw, corn stover, maple and pine biomass for biogas production using LAD and SSAD methods. For most of the biomass, there was no significant difference in methane production by SSAD and LAD method, except for pine and waste paper. However, due to the small volume used in SSAD systems, the volumetric methane productivity was higher in the SSAD reactor for all the feedstocks. Corn stover, wheat straw and switch grass produced comparatively more methane (2–5 times) than yard waste, maple and pine biomass.

Xu et al. (2013) studied biogas production by the SSAD process using corn stover as feedstock along with digestate of LAD from three distinct anaerobic systems under mesophilic conditions. Anaerobic digestate was collected from three LAD reactors that were fed with dairy waste, FW and sewage sludge, respectively. The anaerobic digestate to corn stover was mixed in such a manner that the F/I ratios will vary in between 2 and 6. The SSAD reactor at the F/I ratio of 2 showed the highest methane yield (238.5 L/kg VS) with digestate from a LAD reactor treating dairy waste as the inoculum. In case of the SSAD reactor inoculated with digested FW, the maximum methane production of 199.6 L/kg VS was at F/I ratio of 4. In a similar study, Liew et al. (2012) compared the biogas production potential of corn stover with yard waste, leaves and wheat straw using SSAD at F/I ratio of 2. The maximum methane yield of 81.2 L/kg VS was for corn stover as feedstock, while yard waste, leaves and wheat straw yielded 40.8, 55.4 and 66.9 L/kg VS of methane, respectively.

Methane production from albizia plant biomass was examined in two different anaerobic digestion systems, i.e. SSAD and LAD rectors (Ge et al. 2014). The study found higher methane production using LAD where the methane yield from albizia leaves and wood chips were 161 and 113 L/kg VS, respectively. The methane production from albizia leaves using SSAD was comparable (156.8 L/kg VS) to the LAD system, however, it was much lower (59.6 L/kg VS) in case of albizia wood chips using SSAD. Similar to other previously mentioned studies, the volumetric methane production was much higher (five times more) in the SSAD system in comparison to the LAD reactor.

Cui et al. (2011) compared raw wheat straw and spent wheat straw from horse stall for biogas production in a SSAD system. The experimental conditions used during the study were 20% TS, F/I ratio of 2, 4 and 6, and the inoculum used was digestate collected from a LAD reactor. The maximum daily methane yield from spent wheat straw was observed 8 and 3 days earlier in comparison to raw wheat straw with a F/I ratio of 2 and 4, respectively, indicating improved degradation rate for spent wheat straw. The maximum methane generation of 150 L/kg was with spent wheat straw when the F/I ratio was 4 and it was 56.2% higher than that of raw straw. Cellulose and hemicellulose digestibility was also, respectively, 24.1 and 49.4% higher in spent wheat straw compared with raw straw.

Yan et al. (2015) investigated the effects of different parameters such as solid concentration, temperature and C/N ratio on the digestion of rice straw employed for biogas production using a SSAD system. Maximum biogas production (447.4 mL/g VS) was observed with an initial TS of 20% and C/N ratio of 29.6 at 35.6 °C.

Sheets et al. (2015) investigated the influence of different factors, namely TS concentration (20 and 30%), temperature (36 and 55 °C) and controlled air exposure, on biogas production using switch grass as the substrate in a SSAD system. The air exposure did not show any positive effect on the methane production from switch grass. The biogas generation increased from 102 and 145 L CH_4/kg of VS with increase in TS concentration from 20 and 30% in mesophilic conditions. Under thermophilic conditions, the methane yields were 88 and 113 L CH_4/kg VS for 20 and 30% of solid concentrations, respectively.

Contrary to this previous study, biogas production decreased with increase in initial TS concentration from 8 to 38% during biogas production from giant reed biomass (Yang and Li 2014). The inhibitory effect was attributed to the high accumulation of VFA at high solids concentration. The maximum methane production (129.7 L CH_4/kg VS) was at a F/I ratio of 2 and TS content of 20–23% using the SSAD process (Table 7.1).

Table 7.1 Methane production from lignocellulosic waste using SSAD process

Feedstock	TS (%)	T (°C)	CH_4 yield	Remarks	Reference
Rice straw	20	37	263 L/kg VS	Incubation time and moisture significantly affected the lignin degradation	Mustafa et al. (2016)
Wheat straw	18	37	254 L/kg VS	Fungal treatment facilitated faster start-up of SS–AD reactor	Rouches et al. (2019)
Rice straw	20	37	258 L/kg VS	Fungal treatment showed linear relation between methane yield and lignin degradation	Mustafa et al. (2017)
Palm fruit bunches	20	40	73.3 m^3/tonne	Straw mushroom cultivation reduced the recalcitrance	Mamimin et al. (2021)
Sugarcane bagasse	15	35	143 L/kg VS	Lignin droplets formed during thermal treatment hindered the hydrolysis	Lima et al. (2018)
Rice husk	21	–	18 L/kg TS	Optimization of enzyme concentration is required	Nugraha et al. (2018)
Distilled grain	20	52	212 L/kg VS	*Methanoculleus* and *Methanosarcina* were detected in abundance	Wang et al. (2018)
Rice straw	21	37	190 L/kg VS	68% higher glucose yield was obtained at 60 min treatment	Momayez et al. (2018)
Wheat straw	25	35	1.2 m^3/m^3d	Startup time of SS–AD digester was reduced by 10 days	Zhu et al. (2020)
Rice straw + manure	15	35	357 L/kg TS	Gas productivity was improved by 2.85–5.88% per unit TS after treatment	Qian et al. (2019)
Rose stalk	12.1	55	117 L/kg VS	Treatment facilitated higher VS removal and lower digestion time	Liang et al. (2016)

7.5 Factors Affecting SSAD Process

7.5.1 *Solid Concentration*

Solid concentration is one of the most important parameters for the SSAD process and significantly affects the process efficiency. Hence, many of the previous studies have focused on optimizing the solids concentration in the digester. A very high solid concentration in the SSAD process contributes to reduced biogas production by limiting microbial access to the substrate (Bollon et al. 2013). The water content in the system is also relevant in this regard as it facilitates mass transfer and low water content can suppress the digestion process in the SSAD system (Le Hyaric et al. 2012).

Anaerobic digestion of municipal solid waste (MSW) was studied at two different solid concentrations of 20% and 30% under mesophilic conditions (Fernández et al. 2010). The dissolved organic carbon and VFAs removal was higher at low TS concentration of 20%, whereas at high TS concentration (30%) digestion of organic waste compounds decreased by 17%. Abbassi-Guendouz et al. (2012) investigated digestion of cardboard at various solid concentrations (10–30%). The results demonstrated that increase in the solid concentration was detrimental to the methane production rate. The threshold value for TS was 30% in this study, and beyond this methanogenic activity gets inhibited. In another similar study on methane production from organic wastes obtained from the palm oil industry (oil farm fronds, oil palm trunks and empty fruit branches) at three different solid contents (16, 25 and 35%) observed a negative correlation with increase in solid concentration in the AD process (Suksong et al. 2016). The maximum methane production (72 L/kg biomass) and total solids removal was at 16% solid concentration, whereas the methane yield decreased for the other two solid contents.

Hence, from the above studies it can be summarized that methane yield and methanogenic activity tends to decrease with an increase in solid concentration. The reason behind this trend is mainly related to the dysfunction of mass transfer at high solid content (Abbassi-Guendouz et al. 2012; Fernández et al. 2010). For example, Bollon et al. (2013) found that when solid concentration increased from 10% to 25%, the medium solutes diffusion coefficient reduced by 3.7 times.

7.5.2 Inoculum

Inoculum is another important factor as it provides the microbes, the main catalyst in the AD process (Cui et al. 2011; Shi et al. 2014). LAD effluents and digestate from the SSAD process are generally better inocula than activated sludge, rumen fluid and manure because the digestate from anaerobic processes provides high numbers of active methanogens that are more suited to the AD process. For example, Xu et al. (2016) established in their study that effluent from the LAD process is a better inoculum source than manure, rumen fluid, lake sediments and sewage sludge for initiating the SSAD process. In another study, Forster-Carneiro et al. (2007) noted that the lag phase in the SSAD process reduced from 20–30 days to 2–5 days when LAD effluent was used as inoculum instead of fresh manure. Suksong et al. (2019) reported a twofold increase in methane yield using LAD effluent as inoculum in comparison to SSAD finished materials. The LAD effluent used had high alkalinity (5.9 g/kg) and low VFA concentration (0.05 g/kg) which may have contributed to the better performance of the system (Suksong et al. 2019).

Often recalcitrant components in biomass prevent efficient utilization of the biomass for biogas production. In such cases, different process improvement strategies are applied, one among them is the use of hydrolytic microorganisms. Weiß et al. (2010) used enriched hydrolytic microbes for enhanced degradation of lignocellulosic biomass rich in hemicellulose. The study found an increase in xylanase activity by 1.62% as well as 53% increase in methane yield with supplementation of hemicellulolytic bacteria to the AD process. According to Ma et al. (2013) the optimal ratio of hydrolytic microbes to methanogens was recommended to be 24 in AD process, the hydrolysis process becomes the rate limiting step at a ratio below 24, while a ratio higher than 24 makes methanogenesis the rate limiting step. Similarly, enhancement in biogas production from corn stover due to the addition of dairy manure as inocula was attribute to the activity of hydrolytic microbes in the AD process (Xu et al. 2013). The biogas yield from corn stover using dairy manure was 30% and 100% higher than those using sewage sludge finished material and food waste as inoculum.

Gu et al. (2014) compared different inoculum sources such as digestates from dairy manure, chicken manure, municipal sludge, swine manure, paper mill sludge and anaerobic granular sludge for biogas production with rice straw as the substrate. Compared to sludge, digested manure as inoculum demonstrated significantly improved lignocellulose degradation and methane production due to the high enzyme activity (mainly cellulase and xylanase) in animal manure digestates.

The inoculation size in SSAD is another aspect which has the ability to increase methanogenic activity. The optimized concentration of inoculum can give a good start to the SSAD process and may as well reduce the lag phase of the AD process significantly (Yang et al. 2015). The inoculum size in AD is often described as food to inoculum (F/I) ratio. At mesophilic conditions, inoculation size as F/I ratio of 2–3 on VS basis is recommended for the AD process of lignocellulosic biomass (Zhu et al. 2014; Liew et al. 2012; Ma et al. 2013). Under thermophilic range, the optimal F/I ratio should be in the range of 4–6 when the experiment was performed on corn stover. This difference in optimum F/I ratio under different temperature conditions was also confirmed by Li et al., where the maximum methane yield for mesophilic and thermophilic conditions was at F/I ratio of 2.43 and 4.58, respectively. Lin et al. (2015) investigated SSAD of yard trimmings comprised of wood chips, maple leaves and lawn grass as substrate for biogas production and found a F/I ratio of 4–6 to be better for the digestion process under thermophilic conditions (55 ^{o}C). In another study, the F/I ratio of 1 showed best results for methane production under mesophilic temperature (Brown and Li 2013).

Mixing of inoculum with the substrate is another important aspect of the SSAD process. In this regard, mixing of inoculum with the substrate is required prior to the loading in the SSAD reactors. This pre-mixing is particularly needed in case of processes with high solid content. In large or pilot scale SSAD bioreactors, the interaction between microbes and feedstock sometimes fails due to improper mixing. Two different scenarios were created by Zhu et al. (2014) for analysing the effect of premixing and partial mixing on SSAD process stability and net methane yield. In the first scenario, the whole inoculum was completely mixed with the substrate at the start of the process. In the second scenario, half of the inoculum was mixed with substrate, following which the rest of the 50% inoculum was poured onto the top. Although, the methane yield was the same in both scenarios, the start-up time was less in the premixed SSAD reactor. In another study, three premixing strategies were employed to digest corn stover anaerobically in a SSAD reactor (Zhu et al. 2014). Comparison of the completely mixed scenario with partially mixed in one layer and two layers was performed. The reactor with two layered partial mixing of inoculum yielded the highest methane at F/I ratio of 4 to 6.

7.5.3 Temperature

Temperature is one of the most important determining factors for the growth and survival of microbes in the AD process at both laboratory and industrial scale systems (de Diego-Díaz et al. 2018). Reactor temperature can selectively enrich microbes and has the capacity to enhance the rate of biochemical reactions in the bioreactor. The temperature ranges used for the AD process are as follows: thermophilic (55–70 °C), mesophilic (20–45 °C) and psychrophilic (0–20 °C). Among these temperature ranges thermophilic and mesophilic conditions have been extensively practiced for the degradation process of lignocellulosic biomass (LCB) and OFMSW in SSAD. The mesophilic temperature range is more preferred when compared to thermophilic temperatures due to greater process stability as well as better growth of methanogens. Although the thermophilic temperature zone has its own benefits in the AD process, it requires more energy input in the process, making the process economics unsustainable. However, Sheets et al. (2015) during SSAD of switch grass concluded that under thermophilic conditions, net energy input can be decreased with the increase in methane production rate.

Furthermore, thermophilic temperature accelerates the process at initial level and drives the hydrolysis faster, but often methanogenic conversion is not satisfactory (Yang et al. 2015). Hydrolysis of substrate can be accelerated in thermophilic conditions due to enrichment of hydrolytic microorganisms inside the SSAD bioreactor. But faster hydrolysis of biomass often results in volatile fatty acids (VFAs) accumulation in the system, causing acidification of the reactor (Shi et al. 2014). This acidification further reduces methanogenesis, decreasing biogas production and also reducing stability of the SSAD system (Yan et al. 2015).

Shi et al. (2014) reported that the degradation rate of cellulose and hemicellulose was higher under thermophilic conditions in contrast to the mesophilic temperature range. In another study, a total 6–41% of cellulose and 2–34% of hemicelluloses digestion was observed during thermophilic SSAD of lignocellulosic biomass. These improved results were attributed to the increased (10–50 times) presence of cellulolytic and xylanolytic microorganisms in the thermophilic SSAD bioreactor (Fernández-Rodríguez et al. 2013).

7.5.4 Inhibition

There are many factors that can cause inhibition in the methanogenesis process in SSAD. For example, excess VFA accumulation can greatly affect methanogens, causing instability in the bioreactor (Carlos-Pinedo et al. 2019). Acidification results in decreased pH values, thus inhibiting methanogens which are most susceptible to the environmental conditions (Rocamora et al. 2020). The significant reason behind the increment in VFA accumulation in anaerobic digestion reactors is feedstock overloading (Eko and Chaiprasert 2020). Zhang et al. demonstrated that the use of alternative feedstock can avoid VFA accumulation for better stability of the AD process. The addition of packaging waste along with FW can avoid VFA accumulation during the SSAD process. The study suggested that choice of heterogenous waste as feedstock may permit high loading of substrate during the digestion. The ratio of VFA to alkalinity can assist to regulate digester stability. A VFA/alkalinity ratio within 0.3–0.4 is generally observed in AD plants, but a ratio in the range 0.4–0.6 can provide a stable and safe operation when high organic containing substrates are used (Lossie and Pütz 2008).

Besides VFA accumulation and alkalinity, the ammonia nitrogen content can also bring instability in the AD process. A study conducted by Duan et al. (2012) on sewage sludge found reduced methane generation even at a VFA/alkalinity ratio of 0.2 due to excessive ammonia nitrogen concentrations. This demonstrates that measuring the VFA/alkalinity ratio to monitor reactor condition could be deceptive in the long term operation of SSAD. A suitable knowledge of ammonium inhibition is required to predict the process steadiness.

Free ammonia (NH_3) and ammonium ion (NH_4^+) are available during the digestion of nitrogenous matter and feedstocks rich in protein (FW and OFMSW). The concentration of the ionic form as well as the non-ionic form of ammonia is influenced by both temperature and pH of the SSAD system as described by the following equations (7.1) and (7.2) (Calli et al. 2005).

$$pK_a = 0.09018\left(\frac{2729.92}{T + 273.15}\right) \tag{7.1}$$

$$FAN = \frac{TAN}{1 + 10^{(pK_a - pH)}} \tag{7.2}$$

where, pK_a is the dissociation constant of ammonium ions, T is temperature (°C), FAN is free ammonia nitrogen and TAN is total ammonia nitrogen.

During the ammonification process, about 60–80% of nitrogen in the substrate gets transformed into ammonium or ammonia ion (Yabu et al. 2011). Among these, free ammonia (FAN) is the major reason behind inhibition: when present in higher concentrations, it can cause potassium deficiency and proton imbalance within cells (Yang et al. 2015). Threshold values of the non-ionic form of ammonia is suggested in the range of 300–800 mg/L (Duan et al. 2012; Yabu et al. 2011).

Production of inhibitory compounds due to pretreatment of substrate is another concern, which has negative impact on the biogas production. During pretreatment of lignocellulosic feedstocks, furan derived compounds such as 5-hydroxyl methyl furfural and furfurals are produced which negatively affects the AD process (Barakat et al. 2012). According to Atelge et al. (2020), the inhibitory concentration of furan and 5-hydroxymethylfurfural on anaerobic digestion process is 1 mg/L and 3 mg/L, respectively, beyond which they can reduce the methane production rate.

Apart from these inhibitory substances, certain compounds present in specific substrates are also reported in the literature for their negative effect on the AD process. For example, a compound named D-limonene, found in citrus fruits peelings and processed fruits waste, has been described to be inhibitory to the methanogenesis process (Ruiz and Flotats 2014). D-limonene is a colourless and aqueous secondary plant metabolite that contains cyclic terpenes. It is inhibitory to methanogens and can destroy the microbial cell membrane. Hence, this compound needs to be removed in order to successfully utilize citrus fruit waste for methane production in SSAD. D-limonene can be removed by steam distillation and solvent extraction methods, but this will increase the process step and can make the process more energy and cost intensive (Calabrò et al. 2020). Another such inhibitory compound is *p*-cresol, present as degradation product in brewery spent grains. However, two stage SSAD utilizing granular biomass has shown capability to reduce the negative effect of *p*-cresol in the methanogenic reactor (Panjičko et al. 2017).

7.6 Approaches for Enhancing SSAD Performance

Lignin present in lignocellulosic biomass is inhibitory to the SSAD process due to its recalcitrant nature. In order to increase the production of biogas and reduce inhibition, different pretreatment methods can be applied (Kumar et al. 2018; Saha et al. 2018). Chemical pretreatment involves acid, alkali, ionic liquids (ILs) and organic solvents to disrupt linkage between complexes in the lignocellulosic matrix (Kumar et al. 2018). Whereas, physiochemical pretreatment involves usage of carbon dioxide explosion, ammonia fibre explosion (AFEX) and wet oxidation. AFEX treatment includes pressurized ammonia given to biomass with rapid decompression (Stoklosa et al. 2017). As a result, hydrolysis and ammonolysis reactions break the ester cross links in the cell wall biopolymers. With the help of biomass pretreatment, various advantages can be achieved such as lignin removal, decrystallization of cellulose, increase accessible surface area, alteration of inter-linkage of hemicelluloses and cellulose in biomass structure (Rouches et al. 2019). The cellulose decrystallization causes cellulose to become more porous and readily available to the microbes, which enhances its bioconversion efficiency (Paritosh et al. 2021; Yadav et al. 2019).

Pretreatment for decrystallization of cellulose before digestion can be carried out with the help of acids. Inorganic acids such as hydrochloric acid (HCl), sulphuric acids (H_2SO_4) and phosphoric acid (H_3PO_4) are commonly employed for this purpose. However, in the recent times ionic liquids (ILs) have also been used for biomass pretreatment. ILs are less corrosive in nature, connect with the hydroxyl group of cellulose by breaking hydrogen bonds and this ensures dissolution of cellulose (Han et al. 2020). The pretreatment process using ionic liquids is efficient in recovering decrystallized cellulose with the help of anti-solvents such as methanol, acetone, ethanol or water and also, the ILs can be recovered to a very high extent (even 100% in some cases) (Han et al. 2020).

The most preferred ionic liquid used for pretreatment of lignin containing biomass is N-methyl morpholine-N-oxide monohydrate (NMMO). Akhand and Méndez Blancas (2012) reported a total of 47% increase in methane yield when rice straw biomass was subjected to NMMO pretreatment. The pretreatment increased the substrate surface area which facilitated increased microbial degradation of the feedstock to produce biogas.

Physical pretreatment such as size reduction was applied for methane production from napier grass with three sizes of 6, 10 and 20 mm (biomass passing through respective size sieves) (Surendra and Khanal 2015). A higher methane yield was found for the smallest biomass size of 6 mm as compared to the two other biomass sizes (10 and 20 mm). This improved results is again attributed to the increase in specific surface area for microbial degradation of biomass.

Various pretreatment methods such as steam explosion, irradiation, dilute acid application and liquid hot water have been developed to enhance biogas production and reduce inhibition (Kumar et al. 2018). In addition, other methods such as wet oxidation, alkaline treatment and biological methods (fungal or enzymatic) can be applied for lignin removal (Kumar et al. 2018). Zhao et al. (2014) investigated pretreatment of yard trimmings using white rot fungi (*Ceriporiopsis subvermispora*) for improving the SSAD process. *Ceriporiopsis subvermispora* pretreatment at 40% solid concentration showed the highest methane production (44.6 L/kg VS) which was 154% higher than methane produced from raw yard trimmings. Similarly, when albizia chips were pretreated with the same fungal strain of *Ceriporiopsis subvermispora*, 370% increase in biogas yield was reported (Ge et al. 2015). Pretreatment of rice straw with combined physical (milling) and biological (fungal) methods for improved biodegradability of feedstock in the SSAD system was studied (Mustafa et al. 2017). A 1 month long incubation with *Pleurotus ostreatus* and subsequent milling of the rice straw achieved 30.4% lignin removal and 165% higher methane production in comparison to the experiments with untreated rice straw.

However, to degrade a higher lignin content in feedstocks such as spruce (29% lignin content), the alkaline pretreatment method is more suited. In a study by Mohsenzadeh et al. (2012), birch and spruce biomass was pretreated with different alkaline reagent combinations (NaOH/urea, NaOH/thiourea, NaOH/urea/thiourea, and NaOH/polyethylene glycol) at four different temperatures (−15, 0, 22 and 80 °C). The pretreament with combinations of NaOH/thiourea at −15 °C showed the best results in terms of 59.9% and 45.3% increase in yield using birch and spruce biomass, respectively. Although lignin removal was not maximum at this pretreatment condition, product yield was the highest, indicating other factors such as crystallinity of sugars in the biomass have more significance. According to the authors, a decrease in crystallinity index has positive correlation with the hydrolysis rate.

Zhu et al. (2010) studied alkali (NaOH) pretreatment of corn stover at different concentrations (1–7.5% w/w) in order to increase methane production. The lignin removal increased from 9.1 to 46.2% by increasing the NaOH concentration from 1 to 7.5% and at optimum condition, a high biogas production of 372.4 L/kg VS was realised. Pretreatment of poplar waste with NaOH showed improved lignin reduction by 19.2% and a high methane production (98.2 L/kg VS) from the resulting biomass by SSAD process (Yao et al. 2017).

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Chapter 8
Food Waste Biorefinery for Bioenergy and Value Added Products

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Abstract Food loss and waste (FLW) is becoming a general environmental and societal problem as well as an opportunity for its valorisation to a plethora of energy vectors, chemicals and bio-based materials. Food loss is related to the primary and industrial sectors (i.e., farms and fish farms, factories), while food waste is produced by retailers and consumers. This leads not only to direct FLW but also indirect loss of energy and resources devoted to food production. While societal and political awareness is rising, with the subsequent actions resulting in an efficiency boost along the food supply chain, unavoidable FLW amounting to more than 1000 Mtons/year exists due to personal preferences, safety issues and supply inefficiencies. Likewise, huge amounts of plant biomass by-products (pomace, bagasse, straw, stover, peels and pulp) over 5000 Mtons/year are generated. First, second and third-generation biorefineries can be built based on such biomass as well as that from forest, cattle, fish and algae. Biorefineries are based on thermal, physical, chemical and biological treatments and can produce a great variety of energy vectors, namely hydrogen, biogas, bioethanol, biokerosene, biodiesel and biochar; chemicals (similar to petrochemicals), materials (biomonomers and biopolymers) and energy (heat). Even feed and food products could be considered as biorefinery products, ultimately.

Keywords Food Waste · Sustainability · Biorefinery · Biofuel · Biopolymer

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8.1 Introduction

Food Losses and Food Waste (FLW) are considered a major burden to achieve Sustainable Development on a global basis. Together with other inefficiencies in the production, distribution and consumption chains of other basic commodities, such as energy and water, FLW affect the so-called food-energy-water nexus (Slorach et al. 2020). Process efficacy in the production and distribution of food, drinking water and energy must be promoted to achieve several of the Sustainable Development Goals (SDGs) included in the United Nations (UN) Agenda 2030. In particular, one can think of the following SDGs as the most directly affected goals: Zero Hunger (2), Good Health and Well-Being (3), Clean Water and Sanitization (5), Affordable and Clean Energy (7), Decent Work and Economic Growth (8), Build resilient infrastructure, promote sustainable industrialization and foster innovation (9), Ensure sustainable consumption and production patterns (12) and Conserve and sustainably use the oceans, seas and marine resources (14). However, all 17 UN SDGs are affected by the non-optimal extraction, distribution and consumption of these critical basic commodities (United Nations 2021).

According to the Food and Agriculture Organization (FAO), about 1300 Mtons of food was wasted or lost in 2013, with an impact on the global economy above US $750 million (Xue et al. 2017). In fact, when considering the UN SDG 12, by 2030 Responsible Production and Consumption strategies aim to half the current FLW (Target 12.3) by increasing loss/waste prevention, reduction, recycling and reuse (Target 12.5). In this sense, there are several indicators proposed and monitored by FAO. In particular, indicator 12.3.1. is named “Global Food Loss and Waste” and focuses on FL from production to retail level, but not including the latter (subindicator 12.3.1.a) and on FW at the retail and consumer levels (subindicator 12.3.1.b). While the former is being applied through 10 main food commodities by country and annual period, the latter is less amenable to monitoring and only a proposal for measurement has been created. If we look at the first subindicator, worldwide FL in 2016 almost reached 14%, with values as low as 5.8% (FAO 2021). From this perspective, with FL reaching almost 16% of produced food, Europe and North American countries are far from the less than 6% FL attained in Australia and New Zealand. FL in the Asia-Pacific region were, in general, low in 2016, less than 8%, which points to a relatively efficient food supply chain to retailer level. However, these figures could be misleading, most probably due to lack of monitoring or rapid changes in food consumption (India, China). Ample efforts have been taken in industrialized countries by international agencies (WRAP, FAO, World Resources Institute and more) to promote adequate monitoring of FLW, defining a first global standard as recently as June 2016. Nevertheless, several major pitfalls remain, indicating that global FLW is notably underestimated, even if it is highly probable than FLW figures for Europe and Northern America are more reliable (Xue et al. 2017).

The trends of the World population, GDP per inhabitant, total crop production, and consumption of fossil and biomass-based fuels are compiled in Fig. 8.1a. In

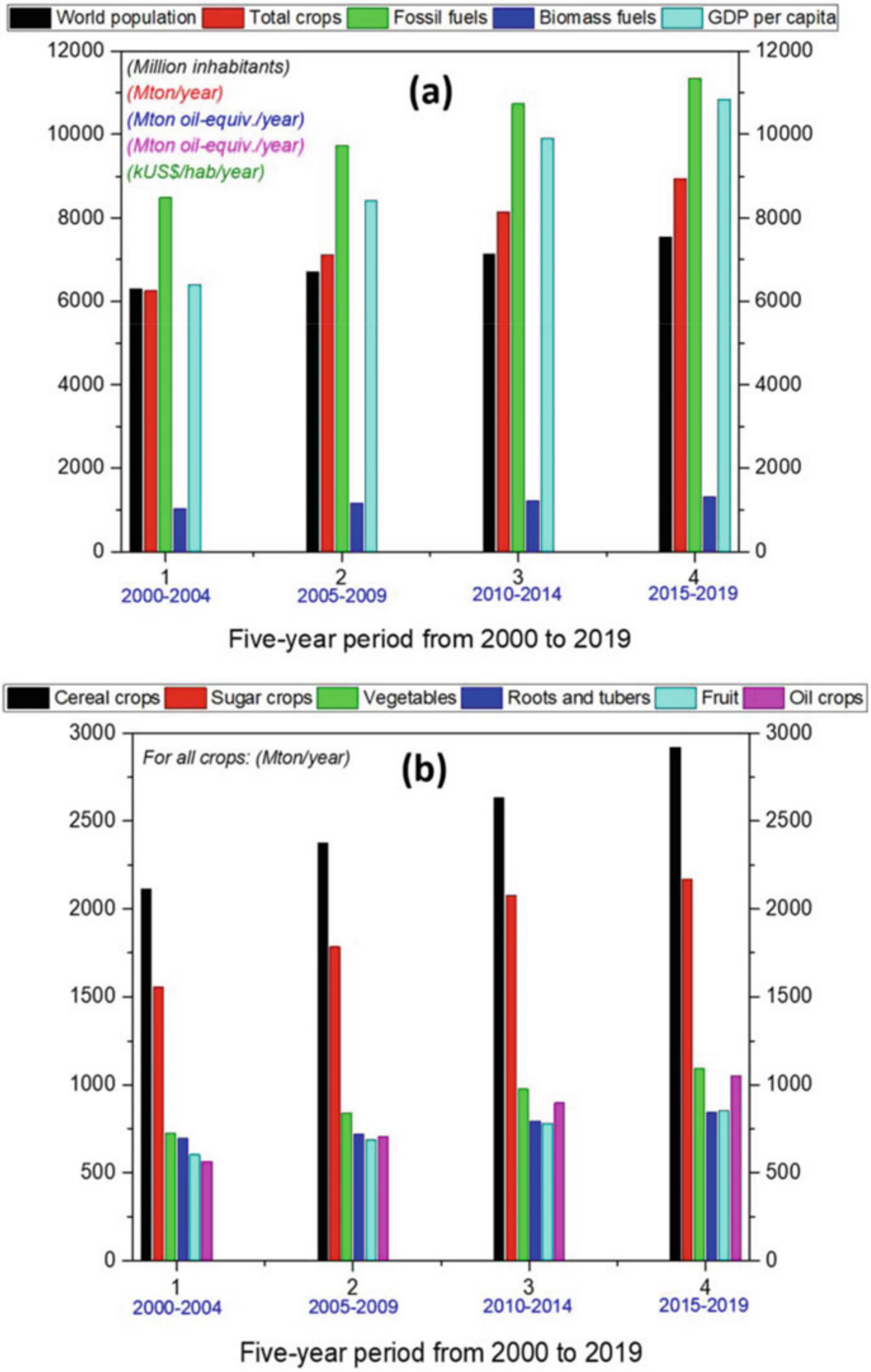

Fig. 8.1 (**a**) Several key parameters regarding the World population, economic growth and resource production in the 2000–2019 period (FAOSTAT 2021; World Bank 2021, IEA 2021); (**b**) Production of critical crops from 2000 to 2019 (FAOSTAT 2021)

addition, Fig. 8.1b shows the worldwide trends in the main crops during four 5-year periods starting in 2000. Although the steady linear growth in the World population results in an increase of all other variables, it is evident that trends are relatively different. Some are linear, such as population and crops, whilst other are asymptotic (GDP/cap; fossil fuels). A closer look at the evolution of different crops (Fig. 8.1b) indicates that cereal crops, the most abundant, strongly increase (38% growth in the 2000–2019 period), while roots and tubers only experience a growth slightly higher than 20%. On the contrary, oil crops dramatically increase by 87% in the mentioned 20-year period. Thus, crops maintain the same linear trend as the World population, but with an increase of 43% in comparison to 19.78%, respectively. This leads to an economic growth and an increase in the general well-being, as shown by GDP per inhabitant increments, though the latter seems to be reaching a stable value around US$12,000 (2010 value) per inhabitant and year. The last 20 years have undergone a booming hyperbolic economic growth, much in line with the progressive reduction in consumption of fossil resources. By 2000, the World seemed to reach another stable value of about US$5400 (2010 value)/cap/year. In this period, there were important political and economic paradigm shifts (Euro introduction, Gulf crisis, globalization), which led to a dramatic increment in global wealth growth. As we reach another plateau, it seems evident that new paradigms are to arrive, possibly including concepts such as sustainable growth, circular economy, bioeconomy, big data analysis and industry 4.0 (Dantas et al. 2021). If we considered the exponential growth in renewable electricity sources (wind and solar) [378% from 2000 to 2018, reaching a 2% share of the global energy consumption] and the steady increment in biomass resources for energy, these are called to complement and, ultimately, substitute fossil energy resources. Notwithstanding, considering an increase of 44% and 52% in gas and coal production in the last 20 years, substitution will need political action, social perception changes and dramatic technological advancement on energy production, distribution and consumption (LLNL 2021).

European consciousness on the problem posed by food waste (FW) is reflected in the shift of municipal solid waste (MSW) fate in the last decade. MSW contains up to 50% FW and, by 2005, was mainly disposed of in landfills, while, by 2015, >25% of it is recycled, with the EU objective to get to 60% in 2025 (Carmona-Cabello et al. 2018). In this valorization strategy, the development of second generation biorefineries is a must, not only to cope with an important, though, hopefully, decreasing amount of FW in the future, but also to profit from biomass created during the food production activities in the primary sector.

Thus, biorefineries are intended to be relevant in an industrial ecology strategy focused on the use of renewable resources (biomass) through closely integrated processes in the fashion of existing refinery processes to the plethora of chemicals, materials, fuels, food and feed needed by mankind. In this sense, both bioeconomy and circular economy can be established with the aid, among others, of tools such as life cycle assessment (LCA) and life cycle cost (LCC) in the design of processes and products (Lam et al. 2018). An integration of human activities in nature, if adequate,

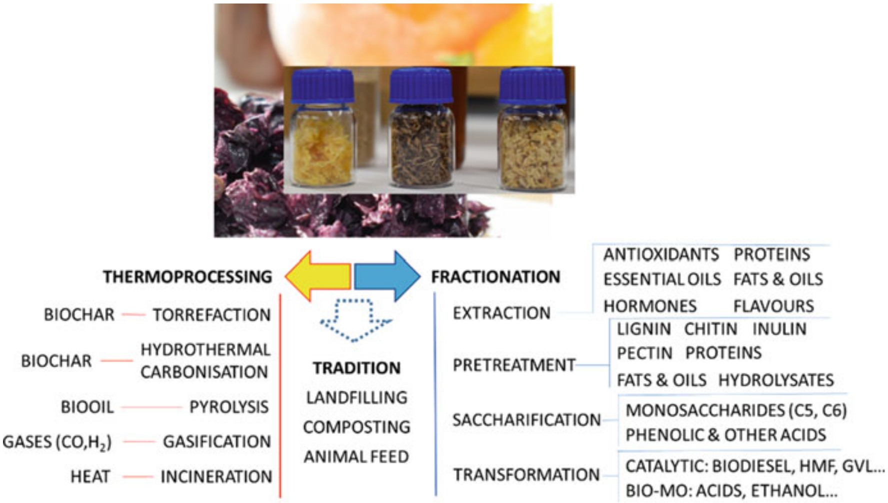

Fig. 8.2 Biorefinery approaches to FLW and food-related biomass valorisation: The thermochemical and the fractionation approximations

can tackle complex problems such as global climate change, resource scarcity and increasing demands due to growing population and global living standards (Mohan et al. 2019).

In biorefinery schemes, the chemical composition and physical structure of any biomass feedstock should be considered to establish its potential for the generation of products and to obtain positive synergism with other resources of similar or complementary nature (Carmona-Cabello et al. 2018), including fossil resources (for example, in the production of hydrotreated vegetable oil (HVO)). Likewise, the water content can drive towards the need of drying or the selection of fermentation or hydrothermal processes instead of pure thermal or catalytic ones. In such cases pyrolysis or other operations common to the thermochemical biorefinery (Kim et al. 2020) could be undertaken. Additionally, the pretreatment-saccharification-transformation scheme typical of the fractionation bio-chemical biorefinery (Rastogi and Shrivastava 2017) could be approached (Fig. 8.2).

In the fractionation biorefinery, carbohydrate-rich biomass has been typically addressed by a series of pretreatments, saccharification and/or transformation by chemical and biological means to bioethanol, biokerosene and biodiesel (as a mixture of fatty acid methyl ester (FAME)). Since food-designed resources have been firstly approached due to their reactivity/accessibility, first-generation biorefineries have encountered some problems due to the food/fuel controversy. Therefore, due to its greater availability and non-edible nature, lignocellulosic and algal biomass is being considered of high interest as feedstock. Lignocellulosic biomass is well-known for its recalcitrant nature, mainly related to its lignin content. Hence, pretreatment processes are required to make the carbohydrates accessible for enzymes and microorganisms. Overall, such processes can be divided into four general categories: physical or mechanical, chemical, physicochemical and biological, and are applied both in the thermochemical and in the fractionation biorefinery schemes, as explained in Sect. 8.2.1.

Pretreatment and transformation stages (upstream processes) aim to get liquid streams with high concentrations of monosaccharides (glucose, fructose, galactose, xylose) and, in general, monomers contained in the biopolymers in lignocellulose or other biomass. To this end, complex enzymatic mixtures containing cellulases, amylases, xylanases, arabinases, lipases, and other hydrolytic and oxidative enzymes (polysaccharide monooxygenases), are applied (Carmona-Cabello et al. 2018). Biological approaches, called consolidated bioprocess (CBP), combine three successive processes. These processes are the production of cellulase, the hydrolysis of cellulose and hemicellulose and, finally, the fermentation of hexose and pentose sugars. They involve the use of microorganisms, such as fungi (white, brown and soft rot fungi), bacteria, or consortia of bacteria (Huzir et al. 2018; Amiri and Karimi 2018).

8.2 Biobased Energy Vectors from Food Waste

8.2.1 Bioethanol

Ethanol, as obtained from fermentation of renewable resources, has emerged for decades as an alternative fuel in internal combustion engines due to its physical and combustion properties; as well as its power generation capacity (Ilhak et al. 2019). The octane number of ethanol is higher than that of gasoline, which allows the use of ethanol in a spark ignition engine with a high compression ratio. On the other hand, ethanol has a high volumetric efficiency due to its latent heat of vaporization value (Ilhak et al. 2019). Moreover, this biofuel produces less carbon oxides on combustion. However, ethanol as a fuel is not without problems. Its difficulty to ignite at low temperatures makes cold starting difficult, which means that combustion is not complete. In addition, it is corrosive to some of the engine parts, which should be fabricated with materials featuring adequate physical resistance. Therefore, although engines could work, in theory, with a blend of ethanol with gasoline up to 85:15, the real practical limit seems to be 20% in engines without any engine mechanical modification (Ilhak et al. 2019). Finally, ethanol is more expensive than petroleum-based fuels, although its price is expected to decrease by about 8% in the coming decades (OECD/FAO 2018).

Since the early 2000s, the production and use of biofuels has been prioritized in the policies of various countries, however, the market for biofuels is expected to be limited due to low investment in their research and development, with a projected global expansion in the case of ethanol from 102.106 m^3 in 2010 to 140.106 m^3 in 2029 (OECD/FAO 2020).

The largest bioethanol producing country is the United States, with around 55% of world production, followed by Brazil (30%), the European Union (5%), China, Canada, India, Thailand and Argentina. The main expansion of this biofuel is expected to take place in developing countries, with Brazil, India and Thailand, together with China, being the most important (OECD/FAO 2018).

However, the feedstock currently used for its production is corn, sugarcane, barley, wheat, sugar beet and sweet sorghum; agricultural products used for food, whose use in obtaining bioethanol is framed within first generation biofuels (Cooper et al. 2020). First generation biorefineries are based on raw materials usually employed for food and feed, very rich in simple sugars (monosaccharides, disaccharides) or edible polysaccharides (as starch). Therefore, as food production, in term of mass, is far from the production of fuels need by Humanity (several billions of tons annually), a high stress is created on food market, this being the main reason for the search for other raw materials. A main advantage of first-generation ethanol production is the process simplicity—very well-known due to its long-time use in the food industry. Although the cost of biomass purchasing is high, up to 65% total costs, lower technology and process-related costs in comparison to other raw materials makes first-generation bioethanol production the first and most developed option nowadays. As for the use of non-edible lignocellulose-based feedstock (second-generation biorefineries), it involves 20–25% higher costs due to the technical complexity of required pretreatment and saccharification steps and the higher complexity of the fermentation step, related to the antimicrobial activity present in hydrolysates (Esmaeili et al., 2020). Thus, tax policies and monetary incentives are needed for the transition from first to second generation biorefineries.

Fermentation varies depending on the raw material used, but most of its stages are maintained with certain changes in process variables, such as pH (between 3.7 and 5.5) or temperature (between 30 and 40 °C). Milling, fermentation and distillation are performed in-series when using sugarcane and other sources of soluble sugars. It is necessary to add gelatinization and hydrolysis stages (enzyme-based mashing-saccharification) prior to fermentation when polysaccharide-rich feedstock is employed (Ayodele et al. 2020). In both cases, up to 95% glucose or sucrose present in the feedstock can be obtained. Fermentation is usually carried out with *Saccharomyces cerevisiae*, having genetically modified yeasts proven to enhance its productivity. Finally, in a multistage distillation process, 95% ethanol is obtained, which can be subsequently dehydrated to 99.99% using azeotropic distillation (Ayodele et al. 2020) or membrane technology (Khalid et al. 2019). This technology has been used in the United States, Brazil and the EU for more than two decades.

First-generation bioethanol production competes for farmland with food production. This issue is at the centre of sustainability debates as large areas of arable land with a high need for rainfall or irrigation are required (Ayodele et al. 2020). Thus, most recent research focuses on obtaining the so-called second-generation (2G) bioethanol. The raw materials used to produce 2G ethanol are classified into three main groups: agricultural residues, forestry residues and energy crops. This chapter puts the spotlight on agricultural and agrofood residues due to their abundance, particularly sweet sorghum and sugar beet bagasse, and straw and corn stubble. The chemical composition of these residues presents some variation in their components: cellulose (between 33 and 48%), hemicellulose (between 18 and 27%) and lignin (between 7 and 21%) (Ayodele et al. 2020; Jeevan Kumar et al. 2020). Lignocellulose pretreatments are more complex than those applied to starch or feedstock rich in free simple sugars (first-generation biorefineries). These pretreatments aim at obtaining cellulose, hemicellulose and lignin fractions with adequate purity to boost the development of 2G ethanol (Romaní et al. 2018; Cheah et al. 2020). They are critical to the economics of 2G ethanol.

The pretreatments studied are very varied and can be classified into different categories: physical processes (milling, extrusion, freezing, microwave and ultrasound processes), chemical processes (treatment with acids, bases or ionic liquids, organosolv, oxidation with sulfite, alkaline wet oxidation and ozone), physicochemical processes (steam explosion, treatment with liquid hot water and ammonia fibre explosion) and, finally, biological processes (digestion by fungi and bacteria) (Cheah et al. 2020; Dhiman and Mukherjee 2020; Jeevan Kumar et al. 2020).

Hydrothermal treatments enclose the use of supercritical water as a quite established operation, which requires temperatures higher than 374 °C. This condition provokes both the denaturalization of the walls of plant cells, the degradation of hemicellulose and the transformation of lignin into its monomers. The advantages of this pretreatment are high energy conversion, low corrosion and no need for catalysts (Ayodele et al. 2020). There are some problems related to the high temperature and pressure values required, entailing the use of sophisticated equipment, special materials and reducing gases. Hydrothermal treatment includes emerging technologies as the use of ionic liquids. Ionic liquids modify the lignocellulose biomass structure in a way that requires subsequent stages of regeneration, filtration, washing and distillation prior to hydrolysis and fermentation (Ayodele et al. 2020).

An effective pretreatment must provide large amounts of cellulose and hemicellulose prior to hydrolysis to monomers (mainly glucose and xylose). In addition, pretreatment causes the generation of inhibitory compounds for subsequent stages (enzymatic hydrolysis, if applicable, and fermentation). The pretreatments that generate highly inhibiting compounds are acid pretreatment, organosolv and steam explosion (Cheah et al. 2020).

The following hydrolytic stage is an enzymatic process that can be combined with the fermentation stage (Jeevan Kumar et al. 2020). The basic operation uses two separate stages and is known as 'Separate Hydrolysis and Fermentation' (SHF). Its main disadvantage is the inhibition of cellulolytic enzymes by the accumulation of reducing sugars in the reaction medium during the enzymatic stage. Also, since two reactors are needed, the investment in process equipment becomes more expensive (Jeevan Kumar et al. 2020). To solve the problems posed in the SHF approach, the 'Simultaneous Saccharification and Fermentation' (SSF) process was developed, in which the hydrolysis and fermentation stages are carried out jointly in a single reactor. Obviously, this procedure is possible only with similar optima conditions for both transformations (Jeevan Kumar et al. 2020). Another advancement is 'Consolidated Bioprocessing' (CBP), which consists of simultaneous enzyme production, saccharification and fermentation by the same microorganism, decreasing the need for exogenous enzymes and reducing operation costs (Jeevan Kumar et al. 2020). A last alternative is the partially consolidated bioprocess (PCBP), a combination of simultaneous pretreatment and saccharification and subsequent fermentation (Jeevan Kumar et al. 2020).

Pretreatment and saccharification stages can jointly result in a complex mixture of hexoses (glucose, mannose and galactose) and pentoses (xylose and arabinose). Therefore, microorganisms (as pure or mixed cultures) capable of transforming all of them to ethanol whilst being highly ethanol tolerant are needed (Ayodele et al. 2020; Jeevan Kumar et al. 2020). *S. cerevisiae* is the most widely used microorganism in the production of 1G bioethanol from glucose. However, 2G bioethanol production faces the described challenges, requiring other microorganisms in addition (Ayodele et al. 2020; Jeevan Kumar et al. 2020) or to obtain ad hoc cell factories to produce bioethanol using different approaches such as metabolic engineering, genetic engineering or adaptive evolution (Sakar et al. 2020; Sharma and Arora 2020).

One strategy is the use of ethanol-producing bacteria (EPB), such as *Zymomonas mobilis*, capable of fermenting both types of sugars. Another strategy is based on the use of mixed cultures, called co-fermentation. In this case, microorganisms capable of fermenting pentoses, such as *Candida shehatae*, *Kluyveromyces marxianus*, *Pichia stipis* and *Pachysolen tannophilus*, are used together with *S. cerevisiae*. In the case of using co-fermentation, the SHF and SSF processes (SHF, SSF) are referred to as 'separate hydrolysis and co-fermentation' (SHCF) and 'simultaneous hydrolysis and co-fermentation' (SSCF) (Ayodele et al. 2020; Jeevan Kumar et al. 2020). Finally, the combined production of 1G and 2G bioethanol can lead to profitable processes (Ayodele et al. 2020).

As for starch-rich FW, although fermentation approaches are similar to those addressed above, the enzymatic saccharification is achieved by amyloglucosidases, α-amylases, fungal mixtures, including proteases for more complex food matrixes still rich in carbohydrates (Saeed et al. 2018). In fact, the treatment of household FW benefits from the use of complex mixing systems within the reactors and the use of several enzymatic cocktails (Loizidou et al. 2017). Finally, ethanol fermentation is a valuable pretreatment in the process of biogas (or methane) production by anaerobic fermentation (Sun et al. 2020; Karimi and Karimi 2018).

8.2.2 Biobutanol

Butanol is a 4-carbon alcohol ($C_4H_{10}O$) receiving increasing attention as a substitute to conventional transportation fuels. It can be produced from biomass (as "biobutanol") as well as fossil fuels (as "petrobutanol"), both having the same chemical properties.

1-butanol (or n-butanol), iso-butanol and tert-butanol are valuable gasoline additives due to their physiochemical properties. Compared to ethanol, butanol can be blended to any ratio with gasoline as well as diesel without additional infrastructure.

Table 8.1 Main processes to produce n-butanol and isobutanol

Product	Processes	Feedstock	Conditions	Performance	Challenges
n-butanol	Traditional (Oxo synthesis)	Propylene + syngas	T ≈ 100 °C, P ≈ 20 atm, cat = Rh, Co	Conversion ≈ high Selectivity ≈ medium	Fewer energy requirements by developing new catalysts
	From ethanol	Ethanol	T ≈ 150 °C, P = 1 atm, cat homog. = Ru,Ir	Conversion ≈ 40% Selectivity ≈ 90%	Reduce environmental pollution and non-reusability problems of the catalyst
	ABE	Waste biomass	*C. acetobutylicum* or *E. coli*	Productivity = 0.5–6.5 g/(L·h)	Evolve enhanced microorganisms with higher tolerance to the solvent Develop continuous fermentation and new methods of product recovery
Isobutanol	Traditional (Guerbet reaction)	Methanol + n-propanol	T ≈ 200 °C, P ≈ 80 atm, cat = Ni/MeONa	Yield ≈ 75%	Reduce energy consumption through new catalysts
	From ethanol	Methanol + Ethanol	T ≈ 180°C, P = 1 atm, cat homog. = Ru	Conversion ≈ 75% Selectivity ≈ 99%	Reduce environmental pollution and non-reusability problems of the catalyst
	ABE	Waste biomass	*C. acetobutylicum* or *E. coli*	Productivity ≈ 0.2 g/(L·h)	Evolve enhanced microorganisms with higher tolerance to the solvent Develop continuous fermentation and new methods of product recovery

It also shows easy transportation and less corrosion because of its low vapour pressure, has a vaporization heat slightly higher than gasoline and its low solubility in water reduces the potential of groundwater contamination (Pugazhendhi et al. 2019; Bankar et al. 2013). A summary of the different processes to produce n-butanol and isobutanol is shown in Table 8.1.

Although bio-n-butanol had been used on a large scale and its biologically fermentative production has a long history, the higher octane number of isobutanol has attracted increasing attention in the fuel industry. However, biological isobutanol is harder to separate and purify due to its low concentration in the fermentation broth (Fu et al. 2020; Bankar et al. 2013).

In the petrochemical route, n-butanol can be produced using three industrial processes: propylene oxo synthesis, conversion of n-butanol from ethanol and the Reppe synthesis, oxo synthesis being the most common in industry. In this process, propylene and syngas feed streams are converted with cobalt or rhodium catalysts (Huzir et al. 2018; Jin et al. 2011).

n-Butanol serves as a precursor for producing paints and plastics and is also an intermediate in the production of butyl acrylate, methacrylate and as a solvent in the production of dyes, oils and waxes. The n-butanol market size is forecasted to reach US$6.74 billion by 2025 with an estimated annual growth rate of 6.5% during 2020–2025. Major players in the n-Butanol market are Arkema (France), BASF (Germany), Dow Chemical (US), Eastman Chemical (US) and Mitsubishi Chemical (Japan) (The Express Wire 2020). However, butanol and its isomers present the disadvantage of a quite low production compared with ethanol fermentation, which is 10–30 times higher (Bankar et al. 2013; Chen et al. 2014).

On the other hand, the global isobutanol market is expected to reach US$1.18 billion by 2022. In 2014, synthetic isobutanol accounted for 58% of the total market, while bio-based isobutanol is expected to grow 7.0% from 2015 to 2022. Some of the main companies involved with biobutanol production are Butamax (US), Gevo (US), BUTALCO (Switzerland), Green Biologics (UK) and Cathay (China) (Grand View Research 2016).

Agricultural and food residues with a high content of cellulose and hemicellulose and low lignin content are an ideal substrate for biobutanol production. This production occurs in two different steps, mainly extracellular breakdown of polymeric carbohydrates of biomass and intracellular two-stage ABE fermentation using *C. acetobutylicum*. In the first step, hydrolysis of the polymers is made by the numerous enzymes secreted, while in the ABE fermentation acetone, butanol and ethanol are produced in 3:6:1 ratio (Pugazhendhi et al. 2019; Bankar et al. 2013; Chen et al. 2014).

Butanol toxicity due to its accumulation is the major problem during fermentation. Producing >7.4 g/L of butanol suppresses *Clostridium* growth and limits butanol yield leading to an increase of the production and recovery costs. To solve this issue, there is an ample toolbox in genetic engineering of the biosynthesis pathways. Thus, researchers have developed solventogenic *Clostridia* tolerant strains towards butanol production and have restricted their spore formation. Besides, interest has also been shown in *E. coli* and *S. cerevisiae*, which are well tractable and rapidly growing (Pugazhendhi et al. 2019; Fu et al. 2020; Bankar et al. 2013)

Batch bioprocessing is the most used method to conduct the fermentation, although, in an economical comparative investigation, continuous fermentation was found to be preferred for large-scale production. Among the techniques to recover butanol from the fermentation broth, distillation is the most traditional and widely applied method. However, due to water having a lower boiling point than butanol, researchers have developed new recovery techniques to decrease the cost of the separation, like adsorption, gas stripping and pervaporation (Pugazhendhi et al. 2019; Bankar et al. 2013).

Due to the problems associated with the ABE fermentation and the increasing urgency to substitute petrochemical routes, ethanol upgrading to butanol has received much attention in recent decades. There are two main pathways to achieve this transformation, namely: the direct dimerization of two molecules of ethanol and the multistep tandem synthetic route known as the Guerbet reaction. The later includes the dehydrogenation of ethanol, followed by aldol condensation (under a strong inorganic base like NaOEt), dehydration and final hydrogenation to produce n-butanol or isobutanol (Wu et al. 2018; Kulkarni et al. 2018; Wingad et al. 2016). To carry out this upgrading, recent progress in catalyst development has been made, which involves homogeneous catalysts, such as iridium and ruthenium complexes; and heterogeneous catalysts, including metal oxides and zeolites like MgO or Al_2O_3, hydroxyapatite (HAP) and supported metal catalysts like Ni/Al_2O_3 have been explored. These reactions are performed under relatively high temperatures and pressures (Wu et al. 2018; Kulkarni et al. 2018; Wingad et al. 2016).

8.2.3 Biodiesel

Biodiesel is defined as the monoalkylesters of long chain fatty acids derived from renewable liquid feedstocks for use in compression ignition engines. Biodiesel is a worldwide recognized potential alternative for substituting petroleum-based diesel. Biodiesel has a series of advantages compared with conventional diesel, including its renewable origin, biodegradability, non-toxicity and the virtual nonexistence of sulfur and aromatics compared to diesel. In addition, biodiesel is of geostrategic value for countries as it provides support to local economies and reduces energy dependency (Hajjari et al. 2017; Foroutan et al. 2020; Hamza et al. 2020).

The key aspects of biodiesel application are the choice of feedstock and the design of a suitable production process. The main drawbacks for the implementation of biodiesel are the production costs, associated to raw material costs, and their effective supply as well as the development of efficient production processes to satisfy the demands as fuel. The properties of biodiesel as fuel and the required process production (including previous treatment and purification) development are strongly correlated with the fatty acid content or degree of unsaturation of the feedstock. Conventionally, biofuels including biodiesel are classified based on their feedstock and production technologies into different generations. These generations include biofuels produced from edible oil seeds, non-food oil crops and wastes, algae, and the genetically engineered oil crops. The debate between using edible and non-edible oil feedstock for biodiesel is driven by feedstock availability and cost, greenhouse gas emission, economic efficiency of using fertile lands as well as fuel vs. food/feed competition. A suitable alternative for biodiesel relies on non-edible vegetable oil; however, controversy arises regarding the use of soil resources for the massively needed supply. In this context, waste-oriented oils/fats have been proposed as the excellent options to produce biodiesel (Ramos et al. 2019) with a major dual advantage: cost and environmental impact. Utilizing it as feedstock for biodiesel means a double contribution in making the environment safe and cleaner. Hence, waste based-oil is considered an economically and socially viable feedstock for low cost biodiesel production on a commercial scale (Hamza et al. 2020; Goh et al. 2020).

Biodiesel is synthetized by the process of esterification or transesterification reactions of fatty acid or vegetable oil in the presence of monohydric alcohol, catalyst, and defined conditions of temperature over a period of time. Transesterification is the catalysed process of trading the alkoxy group of an ester by an alcohol such as methanol and ethanol (acyl acceptor) to convert the triglycerides of the oil to fatty acid alkyl esters and glycerol. In biodiesel production, different alcohols can be used. Methanol and ethanol, and the reaction product produced when methanol is used is called a fatty acid methyl ester mixture (FAME), whereas if the alcohol is ethanol, the product obtained is a fatty acid ethyl ester mixture (FAEE). The mild reaction conditions needed, the fast reaction time and the easy phase separation combined with its low-cost and industrial availability make methanol the most used alcohol in biodiesel production, although it is not a renewable bioresource as ethanol (Ramos et al. 2019).

Besides the properties of the original feedstock, the type of catalysts used in the transesterification reactions is another critical element affecting the biodiesel production. They could be chemical compounds, such as acids and/or bases, and enzymes, working in homogenous or heterogeneous phase. The overall process involves three consecutive reversible reactions which produce intermediate molecules of di- and monoglycerides. Reactions involved and catalysts have been reviewed in detailed in recent literature (Ramos et al. 2019; Changmai et al. 2020; Hamza et al. 2020). The following paragraphs cover the basics of reaction catalysis in the interplay with feedstock properties.

Homogeneous base catalysis was vastly implemented due to its simplicity, mild reaction conditions and high productivity and conversion. However, it is very much limited by the free fatty acid content. The homogeneous acid-catalysed reaction is an alternative since it can simultaneously catalyse esterification and transesterification. However, it deals with a slower reaction rate and the energy and methanol demand is higher. As a consequence, general drawbacks of the homogeneous catalysis are the result of side reactions of saponification and hydrolysis; or the high capital cost and energy required for the process, the high cost of separation and purification of catalysts and glycerol as well as the need for neutralization and wastewater treatment (Ramos et al. 2019).

To overcome the previous disadvantages, heterogeneous catalysed reactions have been developed involving different solid materials. Heterogeneous catalysts facilitates separation and are less sensitive to high FFA content. As drawbacks, they are costly and energy intensive as high temperatures and high alcohol:substrate ratios are needed (Ramos et al. 2019).

Finally, enzyme catalysis based on lipases has been considered. Enzyme-catalysed reactions offer simple biodiesel purification procedures with reduced energy requirement due to the mild operating conditions. Additionally, a high selectivity of transesterification can be achieved with regards to the feedstock, offering a vast range of substrate because of the capability to esterify both glyceride-linked and non-esterified fatty acids in one step, not resulting in side reactions such as saponification. This shows the additional advantage of producing high-grade glycerol as by-product whilst also being environmentally accepted. However, the use of enzymatic catalysis is limited, mainly due to their higher cost compared to chemical catalysts, slower reaction rates than that using alkaline catalysts, and enzyme inhibition (Ferrero et al. 2016; Ramos et al. 2019; Ching-Velasquez et al. 2020). The inactivation by the alcohols used as substrates (mainly methanol) and glycerol produced in the reaction is another problem in this process. Advances in biodiesel manufacturing techniques from natural oils and fats using conventional and advanced technologies, to improve transesterification and biodiesel productivity have been recently reviewed (Kirubakaran and Arul Mozhi Selvan 2018; Ambat et al. 2018; Gebremariam and Marchetti 2018; Tabatabaei et al. 2019; Goh et al. 2020).

FW-based oil has been acknowledged as a suitable renewable source for biodiesel production. Waste oil can be waste edible oil (WEO) or animal fats derived. Each year, large amounts of WEO are produced by the food industry, restaurants and households around the world. It has been estimated that European countries alone produce 100,000–700,000 tons of WEO per year with a potential cost reduction by 60–90% (Foroutan et al. 2020). Use of waste oil as feedstock is very much related to the current regulatory frameworks for waste oil collection and recycling practices (Goh et al. 2020). However, the application of waste oil has some limitations, including their high free fatty acid and water content, which influences the final ester yield in the base catalysed reactions. Hence, to improve the yield and efficiency of biodiesel production, it is imperative to perform an oil characterization, especially regarding the acid value (Kirubakaran and Arul Mozhi Selvan 2018; Ching-Velasquez et al. 2020). Animal fats, which are the waste produced after meat processing and cooking, are another source for biodiesel production. Animal waste feedstock has economic, environmental, and food security advantages over edible oils (Kirubakaran and Arul Mozhi Selvan 2018; Ambat et al. 2018; Ching-Velasquez et al. 2020). However, animal waste fats with higher saturated fatty acids and free fatty acids require complex production techniques (Kirubakaran and Arul Mozhi Selvan 2018; Ambat et al. 2018; Ching-Velasquez et al. 2020).

Generally, waste-based oil must be submitted to some preliminary characterisation and processing before subjecting it to biodiesel production. First, the collected waste oil must be freed from debris or other impurities through a simple filtration technique. The water content can be removed through drying. Further pretreatment stages may be needed to reduce the FFA value to<1%; otherwise, saponification will occur, which will greatly affect the biodiesel yield when basic catalysts are used (Kirubakaran and Arul Mozhi Selvan 2018; Hamza et al. 2020; Hamza et al. 2020). Regarding the limitations during the reaction, although the methods vary in terms of reaction mechanisms and conditions, the emphasis is to improve the blending of the solvents to enhance the rate of reaction and produce higher biodiesel yields (Kirubakaran and Arul Mozhi Selvan 2018; Hamza et al. 2020; Hamza et al. 2020).

Before commercialization, some purification procedures may be performed to maintain quality standards for the final product to be considered biodiesel. Impurities come from solids, unsaponifiable materials present in the feedstock itself, including catalyst residues, water, glycerol and excess alcohol from the reaction, such as polar compounds, dimers, mono and diacylglycerols and free fatty acids. There are several methods for removing such impurities, such as membrane filtration, centrifugation, and distillation as well as wet and dry washing (Fonseca et al. 2019; Ramos et al. 2019).

Last trends of manufacturing biodiesel from waste oil focuses on developing new heterogeneous catalysts, enabling technologies, reactor concepts (Gupta et al. 2020) and reaction media to intensify the reactions and increase productivity (Banković-Ilić et al. 2017; Degfie et al. 2019; Ching-Velasquez et al. 2020). New heterogeneous chemical catalysts include waste egg shell and heterogeneous base catalysts or carbon based nanocatalysts (Banković-Ilić et al. 2017). Immobilized lipases as heterogeneous biocatalysts are under constant development to increase productivity and decrease production costs (Cavalcante et al. 2021). Recent examples are the application of lipases from *Rhizomucor miehei* (RML), lipase B from *Candida antarctica* (CALB) and lipase from *Thermomyces lanuginosus* to overcome current limits of enzyme catalysis to increase the biodiesel production yield and rate (Babaki et al. 2017; Badoei-dalfard et al. 2019; Ching-Velasquez et al. 2020). Intensification of the reaction is being assisted by enabling technologies as microwave assisted intensification of biodiesel production from waste cooking oil using heterogeneous base catalysts (Gupta and Rathod 2018) or ultrasound system for the enzymatic transesterification of oils using combi-lipases as biocatalyst (Poppe et al. 2018). Among new reaction media, the use of low-cost deep eutectic solvents (DESs) has been investigated as a new reaction medium for enzymatic biodiesel production from waste oils with reuse of the catalyst (Merza et al. 2018).

8.2.4 Biogas, Biohydrogen, Biohythane and Volatile Fatty Acids

The fermentation of organic substrates, including FW, can lead to gaseous products of interest mainly in the energy sector, but also as building blocks for many other industries. Biogas is one of such products, which is defined as a mixture of methane, CO_2 and small amounts of other gases produced by anaerobic digestion (AD) of organic matter. Commonly, the methane content is in the range from 45 to 75% v/v, with most of the remainder being CO_2. The composition varies with the feedstock and the fermentation process used, which will inevitably affect the energy content of biogas, whose lower heating value (LHV) varies from 16 to 28 MJ/m^3. Globally, the production of biogas has steadily increased over the last two decades from 0.28 EJ in 2000 to 1.33 EJ in 2017, with the EU contributing as much as half of the supply, followed by Asia with about a third. However, as of 2017, this is only about 2% of the overall bioenergy supply and has potential to represent a higher share in estimated growing capacities that only in the EU could increase up to 20×10^9 m^3 (World Bioenergy Association 2019).

Biomethane, also referred to as renewable natural gas, consists mainly of pure methane, which can be obtained by purification and upgrading of biogas by removing CO_2 and other gases or by gasification of solid biomass followed by methanation. It has a LHV of 36 MJ/m^3 and can use the distribution channels and be applied in technologies that currently use natural gas. The biomethane market prospects also show an outstanding potential increase in demand. The International Energy Association estimates growths up to about 45 Mtoe by 2030 and 75 Mtoe under a Stated Policies Scenario, which could reach as much as 110 Mtoe by 2030 and above 200 Mtoe by 2040 under a Sustainable Development Scenario with developing countries in Asia leading the way. This product sees a broad-based growth across all sectors where natural gas is present (buildings, power and heat, industry), whilst also tapping into markets like transport (International Energy Association 2021).

Hydrogen shows great advantages as fuel candidate, as it has a high energy yield (142.4 kJ/g) and heating efficiency (about 2.75-fold with respect to hydrocarbons). It is a clean fuel as only water is produced from combustion and can made use the infrastructure associated with the rapid development of fuel cell technologies (Wang and Yin 2018). Current worldwide hydrogen value chains currently indicate a production of hydrogen from fossil-based natural gas and coal amounting to 196 Mtoe and 75 Mtoe, respectively. The production of hydrogen as by-product of other processes is about 48 Mt H_2, only 0.3 of which comes from renewables, which points towards an opportunity of increasing the share. By 2050 transport, industrial energy and particularly the use of hydrogen as industrial feedstock will have an increased market share, such as in methanol and ammonia production (International Energy Association 2021). As for biohydrogen in particular, it was calculated that about 15.5 Mt could be produced using waste from crops like potatoes, wheat, corn, sugarcane or barley by 2030 (Alavijeh et al. 2020).

In connection with methane and hydrogen, the term hythane was coined and patented by the company Hydrogen Component Inc., which tested mixtures of these gases in internal combustion engines. Mixtures containing 20% v/v H_2 showed a reduction of NOx emissions whilst maintaining energy efficiencies. Significantly, these mixtures did not require changes in engines or infrastructures.

Finally, the term volatile fatty acids (VFA) typically refers to organic acids of chain length from two to up to six carbons. VFAs have been used in many applications, including energy related technologies, such as the generation of electricity in microbial fuel cells, in the synthesis of complex polymers or in textiles, food and pharma products. In general, the market value of VFAs is related to the length of the chain, which drives the production towards heavier products rather than lighter, there is even a trend towards the generation of higher fatty acids (Esteban and Ladero 2018).

Policies to promote the generation of all of these gaseous products from renewable substrates, particularly FW and other agricultural wastes show a particular alignment with the UN SDGs, particularly SDG 7 (Affordable and clean energy) and SDG 12 (Responsible consumption and production). The drive towards the production of each of the mentioned products from organic substrates will greatly depend on the fermentation technology used. The following epigraphs will cover the particularities of their production with a focus on FW. Table 8.2 summarizes the main results of selected references of processes to obtain the mentioned products.

Biogas is produced by single-stage AD of organic matter such as wastewater sludge, manure, crop residues or, naturally, FW. AD is a process that consists of four steps, namely: (1) hydrolysis, where lipids, proteins, carbohydrates and other large polymers are broken down into smaller molecules by anaerobic bacterial consortia including *Cellulomonas clostridium*, *Bacillus thermomonospora*, *Ruminococcus baceriodes* among others; (2) acidogenesis, during which bacteria like *Streptococcus*, *Lactobacillus* or *Bacillus* transform the monomers into short chain organic acids and alcohols; (3) acetogenesis, where the former products are converted into H_2, CO_2 and acetic acid by bacteria like *Clostridium*, *Acetobacterium* or *Syntrophomonas*; and (4) methanogenesis, in which *Methanolobus*, *Methanosarcina* or *Methanococcus* reduce the previous products to CH_4.

The first AD plant treating FW dates from 1939 in the USA, although this type of processes has attracted interest in Europe in the last decades, reaching a capacity of 150 Mton/year (Bolzonella et al. 2018). The quantity and quality of biogas, i.e., its biomethane content, depend on the type of inoculum and operational factors like pH, temperature, hydraulic retention time (HRT), solid retention time (SRT), stirring and loading rate (Tabatabaei et al. 2020). Largely, the biogas produced is also influenced by the composition of the feedstock. In the case of FW, this can be disadvantageous as they could have low C/N ratios, high lipid concentrations, insufficient macro- and micronutrients or there could be toxic compounds, all of which may trigger different inhibition mechanisms that may unfavour the steps of AD to different degrees (Tabatabaei et al. 2020).

Biogas production is a slow process owing to the long doubling time of the microorganisms involved in these stages, being methanogenesis the rate-limiting stage in the AD process leading to higher HRTs. In other cases, the hydrolysis stage can be cumbersome if complex organic substrates are used, hence leading to toxic byproducts and VFAs. To decrease HRTs and enhance biogas production, one possible solution involves the upstream pretreatment of the feedstock to increase its digestibility. In this sense, biological pretreatment using fungi, microbial consortia or enzymes is beneficial as they are relatively simple, do not require additional chemicals and the investment is typically low. On the other hand, such pretreatments require long reaction times and may be hard to apply in some substrates. Further lines of work on pretreatment feature techniques like microaeration and metabolic engineering of microorganisms (Tabatabaei et al. 2020). Additionally, components like fats or terpenes need to be removed to enhance the productivity as they show inhibition effects and methane formation can be reduced. In the case of terpenes, these compounds are known to have antimicrobial and antioxidant properties and are

Table 8.2 Examples of biological processes to obtain biogas, biohydrogen, biohythane and VFA from FW sources

Food waste	Type of AD	Inoculum	Pretreatment reactor	Operating conditions	Main results	Reference
Fruit, vegetable and kitchen waste	Two-stage (acidogenic and methanogenic)	Activated sludge from wastewater treatment plant	Mechanical homogenization Pilot plant CSTR (2 and 4 m^3)	T = 35 °C HRT = 10 days + 20 days OLR = 4.5 g VS/ (L day)	Y_{CH4} = 460 mL/g VS C_{VFA} = 2582 mg/L	Wang et al. (2014)
Tomato pomace	Mainly methanogenic	Methanogenic sludge from UC Davis	Lycopene extraction and enzymatic saccharification CSTR	T = 55 °C HRT = 90 days OLR = 1 g VS/ (L day)	Y_{CH4} = 105 mL/g VS	Allison and Simmons (2017)
Kitchen waste	Full four-stage operation codigested with sludge	Activated sludge from wastewater treatment plant	Lipid extraction Shaken bottles (120 mL)	T = 55 °C HRT = 30 days OLR = 4.24 g VS/ (L day)	Y_{CH4} = 531 mL/g VS C_{VFA} = 510 mg/g VS	Algapani et al. (2017)
Household food waste	Two-stage (acidogenic and methanogenic)	Brown water from University toilets	None for FW; preheating for sludge CSTR (10 and 40 L)	For H_2: T = 37 °C; HRT = 0.3 days; OLR = 47.8 g VS/ (L day) For CH_4: T = 37 °C; HRT = 20 days; OLR = 37.2 g VS/ (L day)	Y_{CH4} = 728 mL/g VS Y_{H2} = 99.8 mL/g VS $C_{VFA}{}^{b}$= 2200 mg/L	Paudel et al. (2017)

also used as food colorant, so isolation of this type of compounds could be interesting not only from the perspective of increasing yields of biogas, but also towards an integral valorisation of FW (Allison and Simmons 2017).

Hydrogen from different biomass sources can be obtained through different (thermo)chemical methods that include the gasification of hydrocarbons, steam or aqueous phase reforming and the corresponding water-gas shift reactions. In addition, a number of biological processes using lignocellulosic and carbohydrate-rich substrates like FW have attracted interest in the last few years, including direct and indirect biophotolysis (Sampath et al. 2020). Both require phototrophic microorganisms like cyanobacteria or microalgae like *Chlorella* or *Chlamydomonas* to capture solar radiation and perform oxygenic photosynthesis, by means of which H_2 can be generated in a single or two-step process.

In dark fermentation, bacteria like *Clostridium*, *Enterobacter*, *Cellulomonas* or *Thermotoga* can be used, in which hydrogenases are the key catalyst for the generation of H_2, which is produced without any oxygen or light inputs. Feedstock like FW or other type of waste can be used, although it appears that lipid and protein-rich substrates are detrimental to H_2 production compared to others rich in carbohydrates (Ntaikou et al. 2010).

In photofermentation, light-dependent purple sulfur and, especially, non-sulfur bacteria like *Rhodobacter sphaeroides* or *Rhodopseudomonas palustris* are suitable to decompose organic acids to H_2 with nitrogenases and hydrogenases catalyzing the process (Hitam and Jalil 2020).

Hybrid systems can increase biohydrogen productivity combining non-photosynthetic and photosynthetic bacteria. The organic acid byproducts generated during dark fermentation by bacteria like *Clostridium butyricum* serve as substrate for photoautotrophic microorganisms like *Rhodopseudomonas faecalis* in the presence of light in the second stage (Azwar et al. 2014).

Apart from physical pretreatments that are also applicable to the production of biogas to make the complex polymeric structure more accessible in FW or other biomass, certain chemical pretreatments are meant to increase the yield to hydrogen. For example, chloroform, BESA and O_2 inhibit methanogenic species (Wang and Yin 2018).

Owing to the importance of hydrogen production processes, a techno-economic analysis of a dark fermentative hydrogen production process from FW in China recently showed that it could be profitable operating with a supply of above 0.3 ton/day of FW. The unit production cost of the product would be US$1.02 per cubic meter with labour having the highest impact on the costs (Han et al. 2016).

In the past few years, the production of biohythane has attracted a good deal of attention, for which the use of FW and sewage sludge have had prominent use. Contrary to the sole production of biogas, the substrates are subjected to a two-stage AD consisting first of a dark fermentative phase followed by a methanogenic step. This operation allows the reduction of the overall required fermentation time and reactor volumes, which makes it attractive from the operation point of view (Bolzonella et al. 2018). The two main types of feedstock typically used are FW and sewage sludge or codigestion of both. LCA research on biohythane shows that a two-stage AD process produces a methane amount similar to the single-stage configuration, although the concomitant production of H_2 helps to reduce an additional 10% the overall CO_2 equivalent emissions of the process (Franchetti 2013).

Acetic, propionic, (iso)butyric and (iso) valeric acid are commonly denoted as VFAs. These are the main byproducts generated following AD of biomass as intermediates of the different stages. Their production will vary depending on the composition of the substrate used, especially if they are complex and have high organic load rates, lipid content or low C/N ratios. Additionally, the operational conditions used will determine to what extent the metabolic pathways in the acido- and acetogenesis stages of AD will occur. In general, low solid to inoculum ratios and low HRT lead to an increase in VFA production. Also, the quality of VFAs is dependent on the temperature conditions as under mesophilic conditions acetic acid is the main VFA produced during hydrolysis and acidogenesis; on the other hand thermophilic operation favours the generation of butyrate (Zhou et al. 2018; Srisowmeya et al. 2020).

8.3 Biobased Chemicals from Food Waste

8.3.1 5-Hydroxymethylfurfural and Furfural

Lignocellulosic biomass consists of cellulose (35–50%), hemicellulose (20–35%) and lignin (10–25%) as major components. From the hydrolysis of the former two fractions, hexoses like glucose and fructose and pentoses like xylose maybe obtained, from whose dehydration 5-hydroxymethylfurfural (HMF) and furfural can be obtained (Esteban et al. 2018). Both are very highly valued compounds that act as building blocks for further chemicals given their chemical functionality.

From transformations of HMF, further furan derivatives like 2,5-diformylfuran, 2,5-furandicarboxylic acid or 5-hydroxymethyl-2-furan carboxylic acid may be obtained with interest as pharmaceuticals, agrochemicals, flavors and fragrances or dimethylfuran and methyl tetrahydrofuran, valuable fuel additives. As for furfural, compounds like 2-methyl tetrahydrofuran and 2-methylfuran are derivatives that have proven to be bioadditives that improve fuel performance. Their industrial relevance has led to the first plants for HMF (between US$330,000 and US $386,000 per tonne) production having been established in the last few years, such as the ones by AVA Biochem or GF Biochemicals, the latter of which focuses on levulinic acid using HMF as intermediate. As for furfural, with a market price of US $2800–US$3300 per tonne, its market is estimated to grow from US$551 to about US$700 million from 2019 to 2024 (Bhaumik and Dhepe 2015), which has led to an increasing number of industrial efforts. Starting with Quaker Oats Company in the 1920s, many companies have patented technologies for furfural production, such as Petro Chemie, Krupp or Stake Technologies (Esteban et al. 2020).

The source of sugars from which the dehydration takes place are (hemi)cellulosic fractions from lignocellulosic biomass, including FW. With the generation of furans

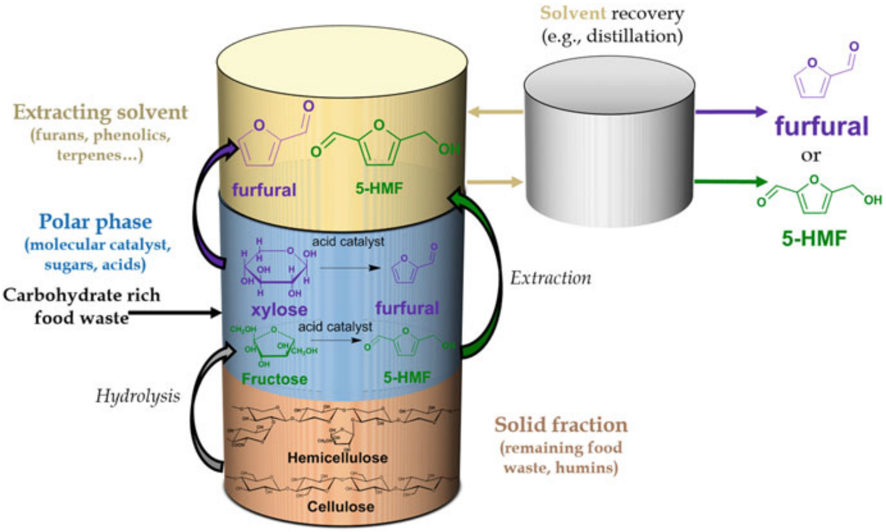

Fig. 8.3 Concept for the production of furans from carbohydrate-rich FW using a biphasic liquid system

in mind, ideally FW with a high fraction of carbohydrates would be most productive. Unlike most of the other products covered in this chapter, HMF and furfural are obtained through chemocatalytic processes as these compounds are inhibitors of microorganisms. For the reaction to occur, hydrolysis to obtain individual sugars happens first, followed by the dehydration in a polar phase, usually aqueous, by an acid catalyst. FW like pasta, potatoes and bread have been used to obtain HMF, furfural and other furans using green solvents like γ-valerolactone (GVL) as medium (Lui et al. 2019; Yu et al. 2018).

However, in the continued presence of acid catalysts and water, HMF can rehydrate to levulinic and formic acid and both HMF and furfural can polymerize and form undesired humins. For this reason, many authors have followed a biphasic approach, whereby nonpolar solvents extract the furans in situ as they are generated and hence avoid the aforementioned reactions. By doing this, the furans can afterwards be isolated and the organic solvent be recycled into the process. In addition, if a molecular catalyst is used, it can remain in the aqueous phase and be reused. Figure 8.3 depicts this concept.

Following the latter approach, some works have reported the production of HMF using FW. For instance, melon rind waste has been used as carbon source to obtain HMF under microwave irradiation using montmorillonite KSF as catalyst, with which the hydrolysis to hexoses like glucose and fructose and their dehydration was achieved. A biphasic H_2O/THF was used to improve the performance of the system by extracting HMF with respect to single phase operation, reaching a 6% overall recovery from the original FW source (Lucas-Torres et al. 2016). Typically water is used as the polar phase, although it has been found that choline chloride-based (ChCl) deep eutectic solvents can help hydrolyse carbohydrate polymers. A biphasic system with ChCl-H_2O as polar phase and GVL as extracting phase was reported for the production of HMF from carbohydrate-rich FW like bread or rice waste, for which $AlCl_3 \cdot 6H_2O$ was used as catalyst. Yields up to 18.60% were obtained with GVL greatly helping to increase the extraction efficiency, thereby avoiding the degradation of HMF. Very importantly, the ChCl-H_2O solvent showed high recyclability (Ji et al. 2020).

8.3.2 Citric Acid

Citric acid (CA) is one of the most widely used organic acids: its production was 2 Mtons in 2020, with China being the world's largest producer. The global market could reach US$3.6 billion in 2025, growing more than 5.24% by then. Currently, it is mainly consumed in the food, pharmaceutical and personal care industries as acidulant, antioxidant, preservative, flavouring, buffer and astringent. Other applications include leather tanning, metal finishing and phosphate replacement in detergents (Amato et al. 2020, Mores et al. 2021). Great research efforts have focused on the production of citric acid through fermentation processes. *Aspergillus niger* is the main producer due to its easy manipulation and its high selectivity/yield towards the acid of interest in comparison to other microorganisms such as *Yarrowia lypolytica* yeast, which also generates isocitric acid (Mores et al. 2021). *A. niger* can produce CA from glucose, sucrose, maltose, galactose, mannose and fructose. This is a good reason to employ impure raw materials with high carbohydrate content such as cane molasses or corn starch.

In recent years, several studies have focused on FW valorisation to reduce costs (Amato et al. 2020). Ozdal and Kurbanoglu (2019) produced 68.6 g/L citric acid through the most widely used method in the industry, submerged fermentation. The best results were observed with 0.15 g/L of KH_2PO_4 and 4 g/L of chicken feather peptone (CFP). This nitrogen source was obtained from a complex pretreatment with two consecutive hydrolysis with 6 N H_2SO_4 at 70 °C, 24 h and 130 °C, 4 h, followed by the addition of different hydroxides, filtration and evaporation. The carbon source was obtained by pretreatment of sugar beet molasses with H_2SO_4 1 N at 90 °C, 15 min and its subsequent addition of 0.1 g/L of $K_4Fe(CN)_6$. Employing the same type of operation, Liu et al. (2018) used waste cooking oil as a carbon source, co-producing 12.6 g/L of citric acid and 4 g/L of erythritol at pH 6 and an osmotic pressure of 0.75 osmol/L. Hou and Bao (2018) produced 136.3 g/L of citric acid by simultaneous saccharification and fermentation (SSF) of corn stover, pretreated with H_2SO_4 5% w/w, 175 °C, 5 min and detoxified with *Amorphoteca resinae* ZN1 at 28 °C, 4–7 days. Roukas and Kotzekidou (2020) obtained 351.5 g/kg dry pomegranate peel by solid state fermentation, a promising method with low or no pretreatment or complex equipment, although with a lower capacity to use nutrients (Table 8.3).

Table 8.3 Citric acid production processes from FW

Substrate	Microorganism	Type of operation	CA production and yield	Reference
Sugar beet molasses with CFP	*A. niger* MO-25	Batch, submerged, 30 °C, pH 6, 200 rpm, 7 days, 4 g/L CFP. 0.15 g/L KH_2PO_4	68.8 g/L 0.48 g/g	Ozdal and Kurbanoglu (2019)
Waste cooking oil	*Y. lypolytica* M53	Batch, submerged, 28 °C, pH 6, 200 rpm, 7 days, 0.75 osmol/L	12.6 g/L 0.48 g/g	Liu et al. (2018)
Corn stover	*A. niger* SIIM M288	Batch, SSF. Reactor 1: 50 °C, pH 4.8, 12–48 h. Reactor 2: 1 vvm air	136.3 g/L 0.75 g/g	Hou and Bao (2018)
Pomegranate peels	*A. niger* B60	Solid state, 25 °C, pH 8, 8 days, 3% methanol, moisture 75%	351.5 g/kg 0.78 g/g	Roukas and Kotzekidou (2020)

8.3.3 Lactic Acid

Lactic acid (LA) is a very versatile compound that arouses much interest, accounting its production through fermentative processes for around 80–90%. The global demand for LA is estimated to increase from 1220 kt in 2016 to 1960 kt in 2025 (López-Gómez et al. 2019). The chemical route generates racemic mixtures of this acid, requiring expensive separation processes. However, through microbial fermentation, D- or L-lactic isomers can be generated. LA is widely used as acidulant in the food industry. Furthermore, it is used in the manufacture of topical ointments, lotions, parenteral solutions, cleaning agents, solvents, humectants and in the generation of oxygenated chemicals such as esters. In addition, polylactic acid (PLA) is a green, biodegradable and biocompatible polymer obtained by ring opening from lactide, a cyclic lactic acid dimer. Table 8.4 presents some LA production routes from FW.

Among LA-producing microorganisms, the bacteria of the genus *Lactobacillus* should be highlighted, being the most abundant genera. In recent years, numerous studies have been carried out based on the use of FW as a cheap source of nutrients (López-Gómez et al. 2019; Rawoof et al. 2020). Ahmad et al. (2020) studied the effect of different pH and total solids content on dark fermentation of FWs without inoculation of external microorganisms. The authors obtained a maximum LA concentration of 12.87 g/L after having carried out an enzymatic pretreatment with a cellulase at 50 °C, pH 5–5.5 for 72 h. In order to reduce production costs, Jiang et al. (2019) obtained 79.1 g/L of L-lactic acid through a simultaneous saccharification and fermentation (SSF) in fed batch from 100 g/L of corncob residues supplemented with 15 g/L peanut meal, 30 g/L $CaCO_3$, 10 U/g cellulose, 15 U/g glucosidase and 0.3 g/L protease. Through a continuous operation, Peinemann et al. (2019) achieved a yield of 0.86 g/g with the addition of glucoamylase. However, Costa et al. (2021) did not need to add any enzyme in their process, reaching a yield

Table 8.4 Lactic acid production processes from FW

Substrate	Microorganism	Type of operation	LA production and yield	Reference
Food waste	Indigenous microbiota	Batch, mode dark, 50 °C, pH 6, 10 days 150 gTS/L, 10 days	12.87 g/L 0.09 g/g	Ahmad et al. (2020)
Corncob residue	*Bacillus coagulans* H-1	Fed-batch, SSF. 50 °C, pH 6, 150 rpm, 84 h, 15 g/L peanut meal, 30 g/L $CaCO_3$, 10 U/g cellulose, 15 U/g glucosidase, 0.3 g/L protease	79.1 g/L 0.76 g/g	Jiang et al. (2019)
Food waste (university canteen)	*Streptococcus* sp.	Continuous (0.44/day), SSF, 35 °C pH 6. 160 rpm, 148 h, 1 mL/24 h glucoamylase	74 g/L 0.86 g/g	Peinemann et al. (2019)
RCW and PP	*L. casei* DSM 20011	Batch, 37 °C, pH 7, 50 rpm, 48 h, RCW:PP 90:10	65.4 g/L 0.78 g/g	Costa et al. (2021)

of 78.3% in a batch operation from ricotta cheese whey (RCW) and centrifuged pear processing (PP) residue in a 90:10 ratio.

8.3.4 Succinic Acid

Succinic acid (SA) is widely used in the food and pharmaceutical industry as an additive, while it is an intermediate of the production of polybutylene succinate, polyesters, polyols, resins, coatings and pigments in the traditional chemical industry. In the bioeconomy era, SA is used mainly in the generation of intermediate chemicals such as tetrahydrofuran, hydroxysuccinimide or maleic acid, among others. In addition, the potential application of this acid in the manufacture of biodegradable polymers should be highlighted (Dai et al. 2020). In 2017, the bio-derived SA market was estimated at US$175.7 million and a compound annual growth rate of 20% was forecasted, reaching a value of US$900 million by 2026 (Li et al. 2020). Table 8.5 features some studies on SA production starting from FW.

Bacteria isolated from the rumen of ruminants, including *Actinobacillus. succinogenes*, *Anaerobiospirillum succiniciproducens*, and *Mannheimia succiniciproducens* are the most promising candidates that can naturally produce SA as the main product during anaerobic fermentation. However, some processes have also been developed using fungi like *Saccharomyces cerevisiae*, *Yarrowia lipolytica*, *Byssochlamys nivea* and *Paecilomyces varioti*. To achieve sustainable production of bio-based SA, expensive sources of carbon and nitrogen, mainly glucose and yeast extract, can be replaced by FW (Dai et al. 2020; Li et al. 2020). For this reason, after optimizing the hydrolysis conditions, Li et al. (2018) used fruit and vegetable waste (FVW) pretreated with 2% glucoamylase, 1% cellulase, 2% hemicellulase and 0.25% pectinase at 55 °C, pH 5, 300 rpm for 48 h. The authors

Table 8.5 Succinic acid production studies starting from FW

Substrate	Microorganism	Type of operation	SA production and yield	Reference
FVW	*Y. lypolytica* PSA02004	Fed batch, isFBB, 28 °C, pH 6, 600 rpm, 2 L/min air, 324 h	140.6 g/L 0.46 g/g	Li et al. (2018)
Sugarcane bagasse	*Y. lypolytica* PSA02004	Batch, 28 °C, pH 6, 600 rpm, 2 L/min air, 102 h	33.2 g/L 0.58 g/g	Ong et al. (2019)
FVW	*Y. lypolytica* PSA02004	Batch, isFBB. 28 °C, no pH control, 600 rpm 3 L/min air, 54 h	32.6 g/L 0.61 g/g	Li et al. (2019)
HSCBs	*A. succinogenes* DSM 22257	Batch. 37 °C, no pH control, 150 rpm, $MgCO_3$ 30 g/L, 400 h	24.1 g/L 1.1 g/g	Ferone et al. (2019)

conducted a fed-batch type fermentation in an in situ fibrous bed bioreactor (isFBB). They employed *Y. lypolytica* as a biocatalyst to reach a SA yield of 0.46 g/g. From these results, Li et al. (2019) used the same substrate and pretreatment but without pH control for the first time, achieving a yield of 0.61 g/g. Ong et al. (2019) needed two pretreatments to obtain a yield of 0.58 g/g through a free cell batch type fermentation with the same strain. In order to effectively use sugarcane bagasse, this substrate was submitted to an alkaline treatment with NaOH 0.5 M, 80 °C, 2 h and an enzymatic treatment with cellulase 40 FPU/g at 50 °C, pH 5, 150 rpm, and 96 h. To valorise a by-product stream from the beverage industry, Ferone et al. (2019) used high sugar content beverages (HSCBs) as feedstock for SA batch production by *A. succinogenes*. After adding 30 g/L $MgCO_3$ to activate the metabolic pathway of succinic acid generation, they obtained 1.1 g/g from not-supplemented ACE juice without pretreatment.

8.3.5 Fumaric and Itaconic Acids

Fumaric acid (FA) and itaconic acid (IA) are included by the United States Department of Energy on the list of top 12 building blocks to be obtained biotechnologically (Zhang et al. 2013). Both are known to be produced best using filamentous fungi.

FA ((E)-2-butanodioic acid) production was linked to the *Rhizopus* genus until 50s in the XX century, when the petrochemical production route was developed. Presently, FA is widely used on food and drug industries with promising applications in the polymer industry, having a global production of around 346 ktons/year (Martin-Dominguez et al. 2018). This demand is satisfied through a petrochemical process consisting of maleic acid isomerization. Very intensive conditions and the presence of maleic anhydride are managed in this process, entailing a great environmental risk. In an attempt to have fewer intensive requirements, enzymatic routes are currently under study, although their maturity is still limited (Martin-Dominguez

Table 8.6 Fumaric acid production processes from FW

Substrate	Microorganism	Pretreatment	FA yield	Reference
Apple pomace (AP)	*Rhizopus oryzae* 1526	Oven dried	52 g/kg$_{AP}$	Das et al. (2015a)
Cane bagasse	*Rhizopus oryzae* ATCC 20344	Hydrolyzation and activated carbon adsorption	34.2 g/L	Deng and Aita (2018)
Food Waste	*Rhizopus* RH 7-13	Milling, heating Separation of liquid fraction.	31.26 g/L	Liu et al. (2016)
Food Waste	*Rhizopus* RH 7-13-807	Pulverization and hot water extraction	23.94 g/L	Fan et al. (2020)

et al. 2018). Table 8.6 summarizes some fumaric acid production processes using FW as substrate.

In the development of a new fermentative process through the biorefinery concept, several renewable raw materials related with food and agro-food industries have been studied by several authors. In the last decade, many authors have tested different waste types, achieving good production yields using “classical” pre-treatments like drying and enzymatic hydrolysis, very consolidated on lignocellulosic biomass revalorization (Deng and Aita 2018). Also, different kinds of operation have been tested (Das et al. 2015b), such as Solid State Fermentation (SSF), where excellent yields are reached having simpler pre-treatments and process conditions. The direct use of FW has been studied, too, reaching very promising results, mostly requiring easier handling pretreatments (Fan et al. 2020).

IA is employed overall as a very versatile monomer in the chemical industry, particularly in fibres and polymers, also having many other applications in pharma and health industries (Yang et al. 2020). It is known to be a much consolidated bio-product obtained by a fermentative process carried out by *Aspergillus terreus* using glucose or sucrose as the substrates (Huang et al. 2014b).

With a global production of about 407 kton/year, IA would involve a potential market of US$567 million in 2022 (Ramakrishnan et al. 2020). Substrates are responsible for its high production costs; thus, it is necessary to find an alternative raw material to reduce prices (Huang et al. 2014b) and move this process into the green industry cycle. Lignocellulosic biomass has been studied as potential raw material for this process (Yang et al. 2020). As compiled in Table 8.7, very promising production yields are reached using different FW.

8.3.6 Diols

Diols constitute a very versatile family of compounds for the chemical industry. This term refers to compounds containing two alcohol groups that are attractive biorefinery products mainly for their potential as monomers in bio-based polyesters

Table 8.7 Studies focused on itaconic acid production from FW

Substrate	Microorganism	Pretreatment	FA yield	Reference
Corn starch	Modified *Aspergillus terreus*	Enzymatic hydrolysis	80 g/L	Huang et al. (2014a)
Bamboo	*Aspergillus terreus* AtYSZ-38	Alkaline treatment, steam explosion and enzymatic hydrolysis	41.54 g/L	Yang et al. (2020)
Watermelon *(Citrullus lanatus)* rind (CLR)	*Aspergillus japonicas*	Drying, grinding and micro-wave assisted solvent extraction	21.52 g/kg_{CLR}	Ramakrishnan et al. (2020)

Table 8.8 Studies for the production of diols from FW

Substrate	Microorganism	Pretreatment	Diol and yield	Reference
Cooking Oil	Microbial consortium	Raw glycerol from waste cooking-oil-based biodiesel production	1,3-PDO 27.77 g/L	Wang et al. (2019)
Sugar cane	*Enterobacter ludwigii*	Sugar cane molasses provided by industry	2,3-BDO 50.6 g/L	Psaki et al. (2019)
FW	*Bacillus licheniformis* YNP5-TSU	Homogenization	2,3-BDO 6.8 g/L	OHair et al. (2021)
Cardoon	Engineered *Escherichia coli*	Steam explosion and enzymatic hydrolysis	1,4-BDO 0.46 g/$g_{glucose}$	De Bari et al. (2020)

(Sato et al. 2020). Table 8.8 shows some examples of diols produced from FW sources.

One of the most useful diols is 1,3-propanediol (1,3-PDO), whose main application is being a monomer for polytrimethylene terephthalate production (Wang et al. 2019). 1,3-PDO fermentative production is usually through co-production with other diols (Sato et al. 2020) or other bio-based molecules (Wang et al. 2019). Literature on the production of 1,3-PDO from FW is scarce. However, the work by Wang perfectly showcased the concept of biorefinery, using wasted cooking oil to obtain biodiesel and raw glycerol as by-product, which can be ultimately used as substrate for 1,3-PDO production (Wang et al. 2019).

2,3-butanediol (2,3-BDO) is a very promising diol with promising applications in several processes such as polyurethane production (Psaki et al. 2019). Its fermentative production from lignocellulosic biomass is well reported, using standard pretreatments (Psaki et al. 2019). However, there are studies where 2,3-BDO can be produced from direct use of FW in non-sterile conditions (OHair et al. 2021), largely reducing costs due to the pre-treatment.

Finally, 1,4-Butanediol (1,4-BDO), with a global production of 2 million tons/year, is a great building block used in the automotive and fibre (lycra) industries (De Bari et al. 2020). There are some studies confirming the viability of implanting local biorefineries for 1,4-BDO production using different lignocellulosic materials (De Bari et al. 2020).

8.4 Bioingredients and Biomaterials from Food Waste

8.4.1 Biolubricants

Used oils like waste cooking oils are valuable sources of lipids that, under suitable chemical transformations, can lead to obtain valuable chemicals. Specifically, lubricants are an interesting family of compounds essential for tribological science, for they are put to use to reduce overheating and friction in a variety of engines, machinery, turbines and gear. In this sense, biolubricants pose an interesting opportunity due to their superior performance in terms of health and biodegradability considerations. Vegetable oil-based bio-lubricants are recognized to have enhanced lubricity, high viscosity, good anti-wear property, high viscosity index, increased equipment service life, high load carrying ability, low evaporation rate, low emission of metal traces into the atmosphere. To function as lubricants, waste oil must be biologically or chemical processed (Esteban and Ladero 2018; Khodadadi et al. 2020). Table 8.9 presents some examples of the production of biolubricants from FW.

Reactions of biolubricants manufacturing involve hydrolysis, transesterification, epoxidation and oxirane ring-opening reactions (Li and Wang 2015; McNutt and He 2016). Both chemical and biological catalysis are applied. For example, the fatty acid ethyl esters mixture, a fish oil residue obtained after the extraction of omega-3 polyunsaturated fatty esters, has been converted into mixtures of mono-, di-, and triesters of trimethylolpropane by transesterification with a chemical catalyst (Angulo et al. 2018). Many recent examples of the application of biocatalytic reactions for the preparation of biolubricants can be found. In some cases transformations involved enzymatic hydrolysis and chemically catalysed esterification to obtain a maximum yield of biolubricant in minimum time (Chowdhury et al. 2013). Oil can be produced from confectionery and wheat milling side streams. In that case, nutrient-rich fermentation media were produced by a two-step bioprocess involving crude enzyme production by solid state fermentation followed by enzymatic hydrolysis of confectionery industry waste. The extracted microbial oils were enzymatically hydrolysed and the free fatty acids were esterified by Lipomod 34-MDP in a solvent-free system with trimethylolpropane (TMP) and neopentyl glycol (NPG).

Table 8.9 FW valorisation to biolubricants

Substrate	Catalyst	Process	Results	Reference
Fatty acid ethyl esters mixture from a fish oil residue	Sodium ethoxide	Transesterification of mixtures of mono-, di-, and triesters of trimethylolpropane	84% conversion of ethyl esters), enriched in trimethylolpropane triesters (96% selectivity)	Angulo et al. (2018)
Microbial oils obtained from confectionery industry waste	Lipase catalyst. Lipomod 34-MDP	Hydrolysis of oil and esterification in a solvent-free system with trimethylolpropane (TMP) and neopentyl glycol (NPG).	Conversion yields were 88% and 82.7% depending on the source of oil	Papadaki et al. (2018)
Soybean oil	Immobilized lipase from *Candida rugosa*	Esterification with neopentyl glycol (NPG) and trimethylolpropane (TMP) alcohols in a solvent-free medium	90% conversion was achieved after only 6 h	Fernandes et al. (2021)

The highest conversion yields were 88% and 82.7% for NPG esters of *R. toruloides* and *C. curvatus*, respectively (Papadaki et al. 2018).

Enzymatic transformation can be used for the synthesis of biolubricants from by-products of soybean oil processing using the lipase from *Candida rugosa* (CRL) both in free and immobilized forms, to produce biolubricants via their enzymatic esterification with neopentyl glycol (NPG) and trimethylolpropane (TMP) alcohols in a solvent-free medium (Fernandes et al. 2021). Another example is the production of a bio-lubricant, which was obtained through esterification of WCOs free fatty acids with neopentyl glycol by using *Thermomyces lanuginosus lipase* (TL) immobilized on Fe_3O_4-CA (citric acid modified magnetite nanoparticles) catalyst. The immobilized lipase was used for the biolubricant synthesis from WCOs in a solvent-free system (Sarno et al. 2019). Immobilized enzyme catalysts have also been used in esters from branched alcohols and dicarboxylic linear acids (Serrano-Arnaldos et al. 2021). For example, a green and efficient strategy for the preparation of octylated branched biolubricant from waste cooking oil involved hydrolysis and esterification with 2-ethylhexanol employing lipase (Novozym 435) and further epoxidation and activation by a low-cost nucleophilic reagent, octanoic acid, to prepare octylated branched biolubricant using an recyclable ionic liquid, [HMIm][PF6], as catalyst (Zhang et al. 2020).

8.4.2 *Bacterial Cellulose*

Bacterial cellulose (BC) is a homopolymer composed of units of β-D-glucopyranose linked by β (1→4) O-glycosidic bonds, as well as plant cellulose (PC). Cellulose nanofibers are arranged in a ribbon-like structure of 3–4 nm thick and 70–80 nm wide cellulose polymorphism I. Some bacteria genera are BC producers, among all microorganisms *Komagataeibacter* sp. (known before as *Gluconacetobacter*) is the most significant BC producer. Nevertheless, even though BC and PC have the same molecular composition, they differ in their chemical and physical properties. BC has high purity due to the absence of hemicellulose and lignin, high mechanical strength, elevated water holding capacity, biocompatibility and high crystallinity (approx. 90%) make it an interesting material for a wide range of applications.

The most widespread culture medium for BC production is the Hestrin-Schramm medium (HSM). The main drawbacks of HSM are the cost of carbon and nitrogen sources and the requirement of a buffer to avoid the decrease of pH caused by the gluconic acid release (Hussain et al. 2019). Depending on the mixing of culture media, a pellicle in the broth surface can be obtained (most common) if it is statically incubated or sphere-like particles, if submitted to stirring conditions. For BC production, general conditions are 28–30 °C, pH from 4.0 to 8.0 and an incubation period from 3 to 25 days or more, in static conditions (Hussain et al. 2019). Regarding the BC purification process, it involves an alkaline treatment followed by a washing step. From an industrial point of view, BC generation is hindered by both the considerable economic cost of the culture media (approx. 30% of process economics) and productivity. Nowadays, there are companies that produce BC employing coconut water as raw material and use batch reactors (tanks and trays) for the production. Nonetheless, this source is not available worldwide. In the last years, a variety of FW has been tested, reaching among 2.1–10.8 g/L from 3 to 28 days, depending on the raw material and culture condition (Fan et al. 2016; Abdelraof et al. 2019; Kuo et al. 2019; Salari et al. 2019). Furthermore, pretreatment steps are usually employed when FW is used in order to breakdown their polymers, thereby enhancing carbon intake by the microorganisms. This approach shows interesting results if the production of BC with HSM is compared to the higher yield of BC achieved with FW (Table 8.10). The second possible step is to isolate or modify BC producers using all the molecular biology, genetic and microbiology tools available nowadays.

The broad diversity of BC application is caused by its remarkable physicochemical properties added to its classification as GRAS (Generally recognized as safe) by the FDA (Food and drug administration) in 1992. In the medical field, it has been applied for the development of wound dress, dentary prostheses, tissue scaffolds, blood vessel replacements and biosensors. In the food industry, it has been used as packaging material (biopackaging), and a food ingredient like fat substituent, probiotics immobilizer and stabilizing agent (Andriani et al. 2020). In the textile industry, composite manufacturing, 3D printing material and optoelectronics are examples of the extensive utilization list of this biopolymer (Andriani et al. 2020; Hussain et al. 2019; Zhong 2020).

Table 8.10 Production of bacterial cellulose from FLW

Substrate	Microorganism	Pretreatment	Fermentation condition	Production (g/L) Productivity (g/L day)	Reference
Potato peels	*Gluconacetobacter xylinus* ATCC 10245	Nitric acid hydrolysis	Static condition; 28–35 °C, pH 6.0 and 4–6 days	FWM: 4.72/ 0.79 HSM: 1.21/ 0.30	Abdelraof et al. (2019)
Orange peels	*Gluconacetobacter xylinus* BCRC 12334	Enzymatic hydrolysis	Static condition; 28–30 °C, pH 4.8, 8 days	FWM: 3.40/ 0.43 HSM: 0.97/ 0.19	Kuo et al. (2019)
Citrus wastes	*Komagataeibacter xylinus* CICC No.10529	Enzymatic hydrolysis	Static condition; pH 5.0, 28–32 °C, 21 days	FWM: 5.7/ 0.71 HSM: 3.9/ 0.48	Fan et al. (2016)
Beet molasses and cheese whey	*Gluconacetobacter xylinus* PTCC 1734	Beet molasses: acid hydrolysis Cheese whey: Enzymatic hy*drolysis*	Static condition; pH 5.5, 28 °C and 14 days	FWM: 4.56/ 0.32 FWM: 3.55/ 0.25 HSM: 3.26/ 0.23	Salari et al. (2019)

8.4.3 Polyhydroxyalkanoates (PHA)

Polyhydroxyalkanoates (PHAs) are biodegradable polyesters (bioplastics) which constitute an alternative to fossil-derived plastics. They are classified depending on the polymerization units size in short-chain-length PHAs (scl-PHAs, 3–5 carbon atoms) and medium-chain-length PHAs (mcl-PHAs, from 6 to more than 14 carbon atoms) (Sabapathy et al. 2020). PHAs production is widespread among *Bacteria* and *Archaea* domains, whose synthesis takes place under unbalanced growth conditions with an excess of carbon source and they are accumulated inside cells. The most common PHAs are polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and their copolymer polyhydroxybutyrate-co-polyhydroxyvalerate (PHBV) (Anjum et al. 2016). The scl-PHAs have poor mechanical characteristics due to their crystallinity, mcl-PHAs have more suitable ones. That is the reason for the requirement of mixtures of different PHAs and their modification to improve their qualities as a material. Nevertheless, they show significant application potential, because they are biodegradable, biocompatible and they produce low end-of-life environmental problems. In consequence, PHA has wide applicability as biomedical material such as surgical sutures, regeneration materials and prostheses (Grigore et al. 2019). These are biopolymers with interesting perspectives. There are also some applications in biodegradable food packaging and active packaging as well as in agriculture as a substituent of thermoplastics. Furthermore, they are used as composites and 3D printing inks (Grigore et al. 2019).

Table 8.11 Valorisation of FW using PHA production processes

Substrate	Microorganism	Pretreatment	Fermentation condition	Yield (% g CDW) Productivity (g/L day)	Reference
Sunflower used cooking oil	*Burkholderia thailandesis* E264	Non specified	37 °C, pH 7.0, 120 h aeration	60/1.5	Kourmentza et al. (2018)
Organic fraction of the municipal solid waste	Microorganism consortium	Acidogenic fermentation pretreatment	Non controlled temperature (10–30 °C), pH 7.8–8.4, 120 days	55/6.7–11.8	Valentino et al. (2018)
Apple pulp waste	*Pseudomonas chlororaphis* subsp. *aurantiaca* DSM 19603	Dilution and centrifugation pretreatment	30 °C, pH 7.0, 72 h, aireation	49/1.5	Pereira et al. (2021)
Grape pomace	*Cupriavidus necator* H16 CCM 3726	Organic extraction, enzymatic hydrolysis and freeze drying	30 °C, pH 7.0, 29.5 h, aireation	63/4.3	Kovalcik et al. (2020)

At present, PHAs comprise 1.7% of the 2.11 million tons of the global bioplastic market. PHA production takes place using pure microbial cultures and definite fermentation broth, which includes carbon sources such as pure sucrose and glucose, organic acids (from 4 to 10 carbon atoms), alcohols and oils (Anjum et al. 2016). With regards to production at pilot-scale and large-scale processes, to date fed-batch production shows the highest productivities, despite these continuous and semi-continuous reactors have already been tested (Sabapathy et al. 2020). Table 8.11 compiles a few examples of PHA production from FW.

Fermentation process parameters which are crucial in PHAs synthesis are the use of elevated carbon to nitrogen ratio, control of pH and feedstock composition, all together affect the production yield and polymer composition (Anjum et al. 2016). However, the price of raw materials is one of the main disadvantages of current PHAs production methodologies comprising up to 40–50% of the final production cost. FW is an alternative substrate for cost-reduction in PHA production. For PHAs synthesis, carbohydrate-rich or fatty acids-rich residues are adequate for producer microorganisms. Moreover, pretreatments are often needed to enhance substrate access and reduce the possible toxicity via detoxification steps. In that sense FW, for instance, cheese whey (rich in lactose and proteins), cereal residues (e.g. wheat straw and rice straw), sugar industry by-products (e.g. molasses), fat-rich residues (e.g. frying oil and seeds with high oil level) are used to substitute expensive raw materials. Final PHAs production yields obtained with this feedstock exceed 50%

PHA content per dry cell weight, and can reach more than 80% in some cases (Table 8.11).

Another critical drawback in PHAs manufacturing is the accumulation inside the microorganism as mentioned above, generating complex downstream processes which involves cell lysis to extract PHAs. Purification costs can account around 30% of the process economy. These drawbacks result in a high price of PHAs around 5–6 EUR/kg, a disadvantage if compared to 0.8–1.5 EUR/kg for most common petroleum-related plastics (El-Malek et al. 2020; Khatami et al. 2021; Sirohi et al. 2020).

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Part IV
Downstream Processing for Resource Recovery

Chapter 9
Valorisation of Anaerobic Digestate: Towards Value-Added Products

F. Guilayn, J. Jimenez, F. Monlau, and C. Vaneeckhaute

Abstract Anaerobic digestion (AD) is considered an important brick of the circular economy allowing to treat and stabilize organic residues, produce renewable energy and promote the return to soil of organic matter and mineral nutrients. Digestate has been historically seen as a biogas by-product with a fertilizing value while representing a significant cost sector to AD plant operators. A paradigm shift is now necessary as other renewable energy sources with lowering production costs tend to disrupt an AD economic model greatly relying on subsidized biogas valorisation either via electricity or purification to biomethane. This chapter is focused on digestate post-treatments allowing to generate value-added products while closing and enhancing the loop between major agricultural inputs and outputs, the latter being indirectly present in digestates. Several options exist to generate mineral fertilizers, soil amendments, organo-mineral fertilizers, biostimulants, bio-control products, energy and beyond from digestate. Consumer behaviour and regulatory framework evolution are necessary for increasing the demand and enabling a more sustainable agriculture based on biosourced upcycled materials. A major global milestone has been recently achieved as the EU has introduced a new fertilizer regulation (CE 2019/1009) that will tend to boost the commercialisation of digestate-based products within the world's largest common market.

Keywords Biogas · Anaerobic digestion · Circular economy · Biowaste · Organic waste

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Abbreviations

ABP	Animal by-products
AD	Anaerobic digestion
APL	Aqueous pyrolysis liquid
Bt	*Bacillus thuringiensis*
CMC	Component material categories of EU regulation CE 2019/1009
CSTR	Continuous stirred-tank reactor
DM	Dry matter
EU	European Union
LF	Digestate liquid fraction after phase separation
MBT	Mechanical biological treatment
OFMSW	Organic fraction of municipal solid waste (here defined as obtained from mixed-collection after MBT)
OM	Organic matter
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PFC	Product function categories of EU regulation CE 2019/1009
PFR	Plug flow reactor
R&D	Research and development
SF	Digestate solid fraction after phase separation
SHF	Separate hydrolysis and fermentation
SSF	Simultaneous saccharification and fermentation
TAN	Total ammoniacal nitrogen
VFA	Volatile fatty acids
WWTP	Wastewater treatment plant

9.1 Introduction

Improving soil quality and fertility by recycling organic waste products has become a crucial approach to substitute mineral chemicals and to participate in climate change mitigation by promoting carbon storage in soils. (Alburquerque et al. 2012; Gissén et al. 2014; Minasny et al. 2017). In this context anaerobic digestion (AD) should play a crucial through the valorisation of digestate, the digested output. This process is being successfully implemented in Europe as shown by the 18,202 plants recorded in 2018 by the European Biogas Association (EBA 2019).

AD consists of several biological reactions where the organic carbon is converted to its most oxidised state (CO_2) and its most reduced form (CH_4). The methane is an energy vector for directly producing electricity, heat and power or after purification and injection in the natural gas grid. In an energetic and climatic crisis context, AD is considered as an alternative for organic waste valorisation.

Numerous positive aspects of AD as an organic waste treatment can be listed: (1) organic waste stabilisation (Möller et al. 2010; Kothari et al. 2014), (2) carbon and nutrients reuse promoting the conservation of natural resources (Vaneeckhaute et al. 2017), (3) a cost-effective (Kothari et al., 2014), energy-positive and relatively simple process applicable to a wide range of substrates (Appels et al. 2008; Capson-Tojo et al. 2016), and (4) the production of value-added products (biogas and digestate) from high moisture organic waste inputs (Guilayn et al. 2020b).

A paradigm shift is necessary for AD as other renewable energy sources with lowering production costs tend to disrupt an AD economic model greatly relying on biogas valorisation via electricity (usually via combined heat and power) or purification to biomethane. For instance, according to Brémond et al. (2021), solar and onshore wind had an expected leveled cost of electricity of US$5–6/MWh by 2020 while biogas cost reduction only allowed to reach a leveled cost of US$8–9/MWh. In this context, digestate management is one of the key challenges for allowing AD to be a full-sustainable and economic-efficient solution.

Indeed, AD has been mostly considered as an organic waste valorisation for biogas production. In the last decade, interest has been grown for the digestate which tends to be the main final product in terms of mass. The digestate consists of a valuable mix of microbial biomass, minerals and undigested inorganic and organic material (Guilayn et al. 2020b).

Digestates have been successfully used as an alternative fertilizer and can be more effective than using NPK fertilizer in certain cases (Barłóg et al. 2020), reducing agricultural costs while improving soil quality. Indeed, AD is known to conserve P and mineralize N into ammoniacal nitrogen during organic matter biodegradation leading to enhanced P and N recovery (later discussed) (Mazzini et al. 2020).

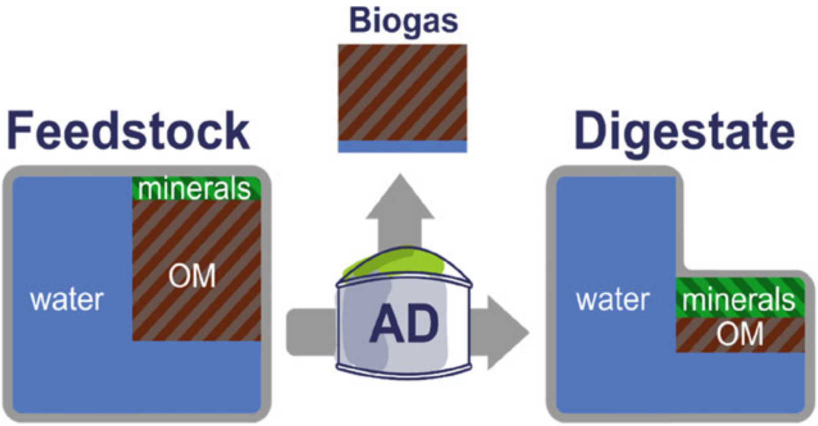
Direct landspreading of raw digestate and/or its mechanical separation fractions is currently the most common digestate management strategy. However, adding to the economic pressure to boost AD economic model (as discussed above), the direct agricultural use of digestates as organic fertilizers is limited by several factors such as transportation costs, organic matter quality, nutrient availability and environmental impacts. Indeed, agricultural use of digestate is strictly controlled by environmental authorities. In some cases, they can be associated with environmental risks as ammonia volatilisation, pathogens, organic micropollutants and heavy metal content, nutrients lixiviation, among other (Nkoa 2014). Furthermore, the biochemical composition of digestate is related to the feedstock nature of AD, the process conditions and the post-treatments (Alburquerque et al. 2012; Guilayn et al. 2019a; Barłóg et al. 2020; Akhiar et al. 2021). There is no one digestate but several types of digestates. This variability could be an advantage by using feedstocks and AD conditions as actuators for dedicated organic fertilizer production being in adequation with the crop and soil needs. In this frame, digestate post-treatments are necessary, especially for public environmental services providers operating regional (centralized) and urban AD facilities treating waste (Guilayn et al. 2020b). However, current options for digestate post-treatments are limited, often costly and with low creation of value.

The use and development of digestate upgrading technologies is crucial and have to take into account several objectives including (1) removing undesired digestate characteristics (e.g. through chemical precipitation, nitrification/denitrification, impurity removal), (2) reaching disposal requirements, (3) reducing logistics costs by concentrating the valuable components (e.g. liquid/solid separation technologies more or less advanced, drying, evapo-concentration); (4) producing high market-value products (e.g. N-stripping, struvite crystallisation, biostimulants, etc.) (5) ensuring homogenous quality over time; and (6) increasing market acceptance and (7) creating new markets (Guilayn et al. 2020b).

In this chapter, an overview of digestates valorisation pathways is provided from full-scale to the most promising approaches under development. First, the effects of AD and the direct agronomical valorisation of digestate are discussed. Then, the most relevant value-added products that can be obtained from digestates, according to the author’s view, are presented and discussed. Finally, insights on the regulatory framework in the EU and in North America are presented.

9.2 Anaerobic Digestion Effects on Digestate Properties

As AD will produce a series of systematic effects on its feedstock, several trends can be generalized regarding the quality of digestates. A simplified overview of AD effet on input is provided in Fig. 9.1.



☐ Most of the biodegradable OM converted to biogas (~ 60:40 CH_4:CO_2) and microbial biomass

☐ Increased concentration of non-biodegradable OM

☐ Most of Organic N converted to mineral N in form of TAN

☐ Variable water loss due to hydrolysis: small but significant

Fig. 9.1 A simplified summary of most notable effects of AD. Areas are proportional to mass and illustrate the case of a feedstock containing about 30% total solids

9.2.1 Mass Reduction

Due majorly to the conversion of OM to biogas and to a lesser extent due to the consumption of water for hydrolysis, digestate mass and volume are always reduced compared to the AD reactor input. As most of this mass loss is the biodegradation of organic particles, the greater the dry matter (DM) content of the input, the more this effect will be noticeable. For instance, full-scale Dry-AD can result in up to 10–25% mass reduction (as 1-input/output) (Bolzonella et al. 2006; Schievano et al. 2011; Banks et al. 2011). However, it is important to consider the overall process line, notably considering AD pre-treatment. As an example, in the case of biowaste wet-AD, the process line might rely on heavy dilution for depackaging and/or hygienisation steps which can increase by two- to threefold the wet volume of AD input compared to the plant feedstock (data from field expertise).

9.2.2 Organic Matter Stability

About 50 to over 90 % of input OM is converted to biogas during AD for typical inputs. Usually, less biodegradable material such as fibrous feedstock (notably from manure, lignified green waste and crop residues) and secondary/biological sludge (i.e. waste activated sludge) will present a conversion rate in the lower range and the opposite for non-fibrous and highly biodegradable feedstock (e.g. food waste and primary sludge). The resulting digestates contain microbial biomass and concentrates the more stable fractions of OM. Beyond that, some authors defend the presence of humification-like processes occurring in AD (microbiological processes resulting in the complexification of the organic matrix) (Brunetti et al. 2012). From the perspective of EU fertilizer regulation (CE 2019/1009), most of the digestates should be conforming to the stability thresholds of 25 mmol O_2/kg OM/h or 250 mL biogas/gOM (Guilayn et al. 2017).

9.2.3 Nitrogen and Phosphorus

The mineralisation of input OM includes the biodegradation of proteins and amino acids, thus the conversion of organic nitrogen into total ammoniacal nitrogen (TAN, present as NH_3 and NH_4^+). Total nitrogen of digestates is usually composed of 50–90% of TAN (Guilayn et al. 2019a), which is readily accessible to plants, meaning that the digestate fertilizing value is greatly enhanced compared to inputs. However, coupled to a neutral to alkaline pH, NH_3-related issues (e.g. odor and toxicity) are increased and must thus be considered for plant design (e.g. air treatment and covered digestate storage) and land spreading (e.g. injecting techniques must be preferred).

Concerning phosphorus (P), during AD, P is theoretically conserved in the digestate. Organic P forms will tend to be mineralized but the solubility and bioacessibility of resulting minerals can be highly variable. Due to the overall mass loss and conservation of P, a concentration increase can be expected. However, some authors indicate low P losses (less than 10% for Schievano et al. 2011) while others observe losses of up to 36% (Marcato et al. 2008). The reason is probably the retention and accumulation of phosphorus in solid form in the reactor following precipitation (Möller and Müller 2012). The AD effect on OM, nitrogen and phosphorus will be further discussed in the next sections of this chapter.

9.2.4 Innocuity

No intrinsic AD mechanism is notable for decreasing AD feedstock innocuity other than increasing ammonia concentration as discussed above. Indeed, the digestate will inherit eventual hazardous characteristics from the feedstock. When hazardous components are not anaerobically biodegradable, a slight concentration reduction (due to loss in the reactor) or a slight concentration increase (due to digestate volume reduction) will be observed (notably heavy metals, inert impurities and some organic micropollutants). On the contrary, several innocuity parameters can be intrinsically improved by AD such as pathogens (c.f. below) and odors (Hjorth et al. 2009). Additionally, AD often enhances waste management practices as any biomethane potential loss is a revenue loss for operators (even animal wellbeing) as shown by Couturier et al. (2019) in a study with 45 French farmers operating AD plants. It is also to be noted that a low quality feedstock might jeopardize digestate quality whose disposal costs are often higher than 80 €/t in Europe.

Regarding pathogens, AD temperature (in the case of thermophilic AD), microbial community acclimation (thus greater competitiveness for substrate) and VFA inhibition can be related as factors promoting partial up to virtually total pathogen kill/inactivation during AD (Jiang et al. 2020). This effect is though highly variable depending on retention time and pathogen family. In certain countries, thermophilic AD is recognized as a hygienising process. However, in the EU, AD alone is not recognized as a standard hygienisation process by the animal by-product (ABP) regulation (CE 1069/1009).

As discussed above, due to mass loss, trace metals can be slightly concentrated. However, its bioaccessibility is often reported to be reduced (Marcato et al. 2009). Regarding organic micropollutants, their decomposition is difficultly generalized, being very compound-dependent (Stasinakis 2012).

Globally, it is widely accepted that AD greatly enhances the fertilizing value of digestates compared to AD inputs. Post-treatment technologies may further increase digestate fertilizing value, as well as enable other market destinations. For many of these advanced technologies, AD can be also seen as a key pre-treatment step (next sections).

9.3 Digestate Typology

Typical AD configurations (i.e. combination of feedstock and process line) arise from a set of local/regional factors including regulation and policies (e.g. for renewable energy, waste (water) collection and treatment, land spreading), economy and market (e.g. types of waste and existing technology providers).

As with any product from an engineered process, the composition of digestates is a result of feedstock composition, process design, operational conditions and the overall resulting process performance. It should thus be the case that the typical AD configurations (input/process) should be linked to typical digestate quality (i.e., resulting in a digestate typology). From an EU point-of-view, the following AD configurations can be highlighted, which had been recently linked to a digestate fertilizing-value typology based on digestate quality database (Guilayn et al. 2019a).

9.3.1 Agricultural Digesters

In the EU, agricultural digesters are the most common, notably in Germany, due to historical support policies. According to the European Biogas Association, there were nearly 18,000 biogas plants in Europe in 2017 (landfills included), about 50% of them being agricultural digesters in Germany. Depending on member state's national policy, typical inputs may vary. For instance, in France, agricultural AD will typically co-digest manure/slurry, crop residues and/or catch crops. In Germany, the legislation historically allowed AD of energy crops as the main crop cultivated specifically for AD. These digesters are usually mesophilic continuous stirred-tank reactors (CSTR) but agricultural dry-AD is also reported, especially for fibrous manure. In Fig. 9.2, they can be related to digestate types 1 and 6. Higher dry matter (>5% in Wet-AD, relating to interquartile ranges), volatile solids (>70% DM) and C/N ratio (5–20) would be related to the more fibrous characteristic of agricultural inputs. Agricultural digestates tend to be easier to commercialize from a regulatory point-of-view. This is the most dominant digestate type as, in Europe, most biogas installations are based on dedicated energy crops (Brémond et al. 2021). This trend tends to continue but probably shift to rotational crops (catch crops) to avoid food production competition while providing side benefits to the main crop (Brémond et al. 2021).

9.3.2 Wastewater Treatment Plants

Wastewater treatment plant (WWTP) digesters are also numerous. Given the low concentration of sewage sludge, they are usually large mesophilic CSTR. As the sludge is conventionally digested prior to dewatering, these AD plants are usually on

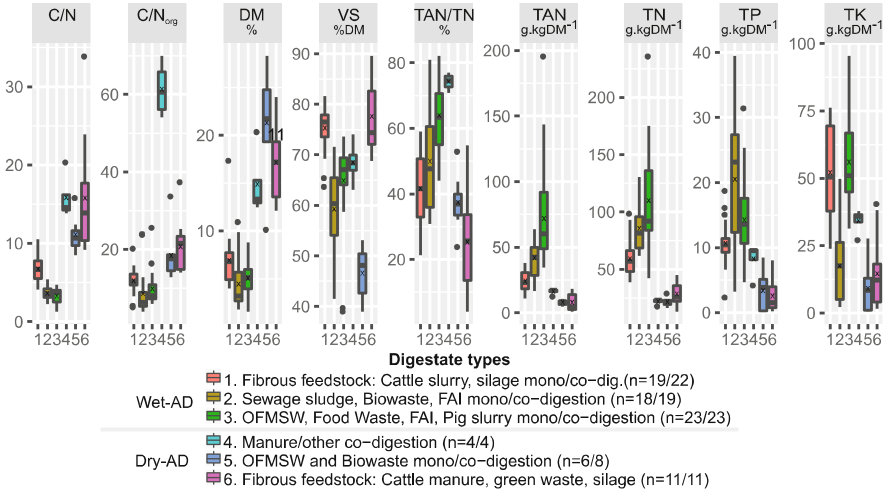


Fig. 9.2 Digestate typology based on a clustering analysis on a database of 91 samples (extracted from Guilayn et al. 2019a)

site. WWTP digesters typically receive a combination of primary (more biodegradable) and secondary (biological) sludge (less biodegradable) and AD plants with free capacity might boost biogas production by accepting external organic waste when allowed. In Europe, co-digestion with source-separated organic waste tends to be limited/forbidden. In Fig. 9.2, they can be related to type 2. It is the cluster with the lower DM range (typically <5%) and high phosphorus (>1% DM) and low potassium (<2.5%) contents characteristics of sewage sludge. In Europe, in the case of land spreading, sewage sludge digestates are usually spread under a waste status and/or national standards. Some countries count with end-of-waste standards for composted sludge (e.g. NF U 44-095 in France). They were not included as inputs for the latest EU regulation on fertilizers (CE 2019/1009), except recently for struvite recovery and ashes after incineration.

9.3.3 Centralized/Regional Digesters

Centralized digesters, also referred to as “regional” or “territorial”, are large-scale biogas facilities (>1–2 MW and >50 kt/year), usually mesophilic CSTR treating a great mixture of organic waste streams from a large area, such as food processing waste, municipal/industrial sludge, household waste, green waste, agricultural waste, among other. Most of these installations are wet-AD because typical pre-treatment for depackaging and hygienisation relies on heavy dilution. Given the very diversified types of inputs and mixtures, they are more difficultly clustered but could be associated mainly to type 3 and to some type 2 and 5 digestates in Fig. 9.2.

9.3.4 Municipal Solid Waste Digesters

The organic fraction of municipal solid waste (OFMSW) is usually treated in large-scale municipal biogas facilities. OFMSW is obtained after a mechanical biological treatment (MBT) of mixed-collection urban waste. MBT of such a stream usually produces a fibrous cellulosic biodegradable material with a structured bulk capacity without needing a structuring co-substrate. MBT is thus often followed by a Dry-AD thermophilic digester.

Another emerging configuration is Dry-AD of biowaste (source-separated) when it contains a significant contribution of green waste serving as structuring material. It is important to mention that some authors will also refer to source-separated biowaste from municipal solid waste collection as OFMSW. In Fig. 9.2, they compose most of type 3 and 5 digestates presenting low nutrient content that can be associated to the typical cellulosic material obtained from MBT. In Europe, on the one hand, the restrictions and end-of-waste scenarios described for sludge digestate apply similarly to MBT digestate from mixed-collection waste. On the other hand, source-separated biowaste digestate is clearly trending to reach more easily "end-of-waste" status. For instance, biowaste (source-separated) was included in the latest EU regulation on fertilizers (CE 2019/1009)

To conclude, even if AD configurations can be somehow generalized, the process/digestate typology is also a result from a limited technical expertise imposing design and operational rules that are being constantly challenged and optimized by research. This process might take a significant time to reach the market, thus the typology can be expected to be constantly evolving.

9.4 AD Operational Strategies for Enhancing Digestate Value: The Case of Residual Organic Matter

As organic matter is the major digestate component (other than moisture), valorizing digestate organic matter is one of the greatest levers for creating value. In the future, a more defined economic value to stabilized carbon is expected through carbon credits. Additionally, an increasing economic value tends to be associated for the beneficial effect of organic matter in agriculture, especially as most soils are being rapidly depleted in OM. In this scenario, optimizing AD for considering not only biogas yield but digestate OM quality and quantity can be crucial. A change of paradigm will be needed. Adapting the process line to enhance final digestate quality while lowering biogas production has already been done to achieve better economic results in one of the largest urban AD facilities in Europe (internal information from SUEZ).

First of all, feedstock quality plays a major role in the proportion of OM degraded during the anaerobic digestion process and during land spreading of the digestate (Guilayn et al. 2019a, 2020b). As previously said, fibers-like feedstock enhance OM in digestate because lignin-like compounds are not biodegraded (i.e., manure, crop residues, straw), whereas biowaste-like feedstock decrease OM in digestate because the OM content is more biodegradable (i.e., OFMSW and biowastes).

All bibliographic sources agree that a fraction of the digestate's OM remains biodegradable once it is incorporated into the soil, making post-treatment interesting by composting to achieve a more stabilized OM. This fraction of biodegradable OM converted into methane and carbon dioxide is dependent on the efficiency of AD performance in particular on parameters such as temperature, organic loading rate and hydraulic residence time. On average, 2/3 of the biodegradable OM introduced into the digester is transformed into biogas (Alburquerque et al. 2012).

In addition to feedstock and process parameters, the technology itself seems to have an impact on the soil amending value of digestates: those resulting from dry-AD seem to contain more OM consisting mainly of carbon chains very difficult to degrade by the microorganisms. AD would not decompose the humic potential of OM because the microorganisms do not break down lignin, complex lipids, steroids and precursor molecules for humus formation (Jimenez et al. 2017). As previously stated, some authors indicate the presence of humification-like processes occurring in AD (Brunetti et al. 2012), but humification is a controversial topic for over a century in soil science. However, a stabilized OM is obtained in the digestate due to the transformation of labile fractions of OM in biogas and the formation of more stable compounds (increased degree of aromaticity, accumulation of longer aliphatic chains) according to Möller (2015).

To conclude, the digestates contain a fraction of residual biodegradable OM and a proportion of stabilized pre-humic matter, which depends on the conditions of the digestion and feedstocks but also on the post-treatment applied to the digestate. These parameters can be used as actuators to control the quality of the digestate.

9.5 Digestate Landspreading: Practices and Limitations

9.5.1 Agronomic Digestate Value

The most classical valorisation of digestates and by-products is the agronomic use in crop soils. Indeed, as previously mentioned, because of the stabilized OM and the mineralized nutrients, digestates are considered as organic fertilizers if they are properly managed. Three types of fertilisation can be obtained using organic residues in crop soils: (1) chemical fertilizing (available nutrients NPK used at short/mid- term to feed the plants), (2) biological fertilizing (labile OM able to feed the soil microorganisms at short term) and (3) physical fertilizing (amendment potential of stabilized OM to improve the soil structure). Several different types of digestates have been demonstrated to be effective replacements for mineral fertilizers while reducing environmental impacts (Walsh et al. 2012; Koszel and Lorencowicz 2015; Panuccio et al. 2019; Verdi et al. 2019). Nevertheless, regulatory constraints, good management and spreading practices are necessary for controlling environmental and health risks as it can be expected for any chemical fertilizers, raw manure and sludge (Nkoa 2014).

Considering chemical fertilisation, mineral elements increase chemical fertility by feeding the plants' nutritional needs. Nitrogen fertilizing is the main target when chemical fertilizer is considered. During AD, ammonia reacts with water in the anaerobic environment to form ammonium found in the digestate. After land spreading, nitrification by soil bacteria transforms ammonium into nitrate, which can be assimilated by the plant, within a period of a few days to a few weeks. Losses in the form of nitrous oxide or nitrogen oxide may occur during this process. However, the total nitrogen stock remains constant compared to the undigested inputs, but the final concentrations are higher, due to the loss of a quantity of carbon in the form of biogas during the AD process (Tambone et al. 2009).

When the digestate is incorporated to the soil, part of the carbon is used as an energy source for the soil microflora and nitrogen is used as a nutrient. A phenomenon of reorganization of mineral nitrogen is often observed: as soon as the digestate is added to the soil, the microbial activity of the soil is reinforced with the production of new cells because its incorporation provides a source of carbon energy. This requires a proportional amount of nitrogen, which is part of the composition of many essential molecules in cells. If the supplied OM does not contain enough of N to meet this demand, microorganisms will take (and therefore immobilize) N soil solution to be able to grow (Reibel and Leclerc 2018).

For raw and liquid digestate, with a lower C to N ratio compared to solid digestate, studies report that the rate of net nitrogen mineralisation is usually positive (Cavalli et al. 2016; Jimenez et al. 2020a). On the other hand, for the solid digestate, net immobilisation of nitrogen, even in the medium term can occur, depending on the digestate typology (Jimenez et al. 2020a). Indeed, the authors showed that the C to N ratio is negatively correlated with soil mineralized N and N recovered in plant tissues. It seems to be a good indicator for the mineralisation potential of organic N and for apparent recovery fraction of N by plants as shown by Jimenez et al. (2020a).

As previously discussed, the nitrogen fertilizing value of digestate depends on: (1) the mineral nitrogen content, which depends on the feedstocks and post-treatments. More than half of the organic nitrogen contained in the raw digested inputs is found as ammonium quickly mobilized by plants, conferring a strong fertilizing potential. (2) The rate of mineralisation of the organic fraction of nitrogen in digestates. The mineralisation kinetics depends on the type of feedstock and the environmental conditions (temperatures and mainly soil moisture). However, the mineralisation of organic nitrogen appears to play a minor role in the fertilizing value. Little organic nitrogen remains in the soil after a growing season, thus reducing the long-term effect of so-called residual nitrogen as well as long-term nitrogen leaching (Reibel and Leclerc 2018). (3) The phenomenon of ammonia volatilisation, which can in some cases reach 100% mineral nitrogen. This phenomenon is also a function of the type of feedstock, post-treatment, storage, spreading and pedoclimatic conditions (Reibel and Leclerc 2018). The spreading conditions have a strong influence on the apparent recovery fraction of N by crops: a liquid digestate applied in surface can lose 35–100% of its ammonia (Nyord et al. 2008;

INRA-CNRS-IRSTEA 2014). Climatic conditions on the day of intake and following the day of intake also seem to be a strong factor explaining the variability observed in certain field trials, because this parameter greatly influences the ammonia volatilisation.

Concerning the N fertilizing potential, post-treatments highly impacts the immediate availability of nitrogen and the digestates can be classified as follows, in terms of the fertilizing value equivalent coefficient to short term (one crop year): Liquid digestates> Raw digestates> Solid digestates> Digestates composted ~ Dried digestate (Reibel and Leclerc 2018).

Concerning P fertilisation, as previously discussed, P is theoretically conserved in the digestate but low to significant losses can be observed due to accumulation in the reactor (Marcato et al. 2008; Schievano et al. 2011; Möller and Müller 2012). Similar to nitrogen, organic P can be converted to inorganic P, but unlike nitrogen, resulting phosphorus is mainly found in a solid form in the raw digestate. It is mainly converted to ortho-phosphates that can be present as salts (such as calcium phosphate and struvite) and/or adsorbed to particles. For example, Zhang et al. (2012) observed on samples of nine digestates of agricultural origin, an average of 70% of phosphorus in solid form, against 30% in interstitial fluid. According to Reibel (2018), the fertilizing value in P of the digestate depends first on the phosphorus content, varying according to the feedstocks with total P contents extremely variable (from 4 to more than 20 g P/kg DM). The highest levels are observed for digestates from wastewater treatment (WWTP) sludge, with up to 21 g P/kg DM. Digestates from pig slurry AD and animal by-products have also high levels of P but slightly lower. In contrast, the lowest contents are associated with digestates from the bio-waste and green waste AD (INRA-CNRS-IRSTEA 2014). However, the total P content is not a sufficient indicator of the P fertilizing value of a digestate. P speciation on availability and the soil physicochemical conditions govern the apparent P recovery by plants. Indeed, Jimenez et al. (2020a) showed that P speciation and post-treatments impact the P chemical availability as well as the P recovery by plants in a calcareous soil where P is the lowest available for plants (i.e. high pH value and carbonates levels).

Digestate post-treatments have also an impact on P speciation and P fertilizing value. According to Reibel (2018) a classification can be made (%DM): P liquid digestate from screw press> raw digestate> P digestate dried> P digestate solid fraction separation by centrifuge> P digestate solid fraction separation by screw press> composted digestate.

Indeed, the liquid phase which contains orthophosphates retains a fertilizing value in phosphorus greater than the solid phase of digestate or compost, with composting breaking down the concentration of P in the digestate. This classification makes it possible to estimate the phosphorus concentration in the digestate. However, in terms of raw matter, a different order is obtained, the products richest in DM allow providing more P (in% raw matter): P dried digestate> P composted digestate> P digestate fraction solid separation by centrifuge> P digestate solid fraction separation by screw press> digestate raw> liquid digestate.

Moreover, contrary to the fate of N, physicochemical reactions govern the P fate in soil. According to Ahmad et al. (2018), more than 80% of the applied P is easily immobilized in soil by adsorption/precipitation reactions or conversion into organic form. P can thus become partially/poorly unavailable for the plants.

Considering biological and physical fertilisation through OM, digestates can provide stable OM to compensate soil humus mineralisation as soil improvers or soil amendments. OM in soil is crucial to feed the microbiological activity, provide bulk capacity which improves soil structure, increases cation exchange, pH buffering and water retention capacities, adsorbs nutrients, among many other effects. In practice, the complete distinction of mineral fertilizers and soil improvers is not always pertinent. Some materials as dried digestates are both rich in OM and nutrients, allowing acting both as organic soil improvers and "slow-release" fertilizers (Guilayn et al. 2020b). Moreover, mineral fertilizers can be used to enrich and balance nutrient content on organic soil improvers such as composts, providing readily available nutrients along with stable OM. In the literature the amending potential of digestates varies from 10 to 354 kg C/t of raw digestate with the following classification: Composted digestate> Solid digestate> Raw digestate> Liquid digestate (Reibel 2018).

9.5.2 Limitations of Digestates Use in Agronomy

AD enhances undoubtedly the N availability for plants growth, but this process can also enhance the potential loss of ammonia by volatilisation during storage (minimized if the storage is covered) and spreading compared to initial materials (Reibel 2018). This increase can be partially offset by the better infiltration capacity of liquid digestates in the soil and by covering actions during storage as well as appropriate practices during spreading such as rapid burial, dry climatic conditions and cool temperatures, non-bare soil, etc. Spreading recommendations are found more suitable for slurries and is not observed for solids, composted and dried digestates.

Greenhouse gases can also be produced during storage and spreading. However, some studies showed that AD decrease CH_4 and N_2O emissions compared with feedstock spreading (Holly et al. 2017; Reibel 2018).

Another limitation of some types of digestates is the metallic trace elements content. AD tends to increase trace mineral concentrations via degradation of the organic matrix with a clearer tendency for sewage sludge and OFMSW. For the digested sewage sludge, speciation of metallic trace elements seems to be evolving towards more stable forms and less available during digestion (Reibel 2018). Concerning organic micropollutants, AD modifies the concentrations of organic contaminants. For example, the anaerobic digestion of urban sludge has demonstrated a potential for degradation of PAH, nonylphenol and PCB (Reibel 2018).

According to Guilayn et al. (2020b), digestate farmland spreading is the mainly digestate management strategy. However, for the non-agricultural digestate providers, several legal and technical bottlenecks are found as follows: (1) digestate spreading regulation tend to be stricter for digestates form non-agricultural AD feedstocks. For example, in the EU fertilisers regulation, digestate is an authorized material but the text excludes some urban feedstocks as sewage sludge, OFMSW and other mixed-stream substrates (CE 2019/1009). Consequently, those digestates follow the waste regulations, requiring high administrative cost procedures for spreading and homologation. (2) The agricultural needs are seasonal while the production of digestates is continuous on a yearly basis. This aspect leads to storing the digestate for a long time or transport to distant regions (King et al. 2013; Gong et al. 2013). (3) The time variability of the digestate composition can occur and is related to the feedstocks variability and performance of AD stability (Zirkler et al. 2014). This aspect can induce quality control issues for spreading and marketing purposes. (4) The quantity of the produced digestate can exceed the capacity of the local available soils for receiving nutrients (Vaneeckhaute et al. 2013; Nkoa 2014) leading to an increase in transport costs. Dahlin et al. (2015) reported that the digestate transport distance is become twice higher in the last years (i.e. 150 km). Moreover, the number of large and centralized facilities had grown because of their higher economic feasibility. However, most of these plants exceed the local nutrient spreading capacity.

Despite the digestate value, its agricultural use as direct spreading is not enough to overcome the digestate challenge, mainly in the cases of large-scale and/or non-agricultural digesters. Adding to that, even for agricultural AD, increasing or creating value for digestate is one of the major levers to balance decreasing subventions on biogas valorisation. New ways of digestate valorisation through upgrading technologies are essential.

9.6 Digestate Phase Separation: A Key Step for Digestate Spreading and Post-treatment

Digestate phase separation (also referred to as dewatering in the wastewater treatment sector) is a key step for enhancing digestate management practices and enabling digestate post-treatment advanced technologies. The most applied technologies are screw press and decanting centrifuge (sometimes combined in this sequence) but vibrating screens and filter presses are also commonly related (Guilayn et al. 2019b; Akhiar et al. 2021). These technologies greatly differ in performance which is a combination of equipment performance and digestate type driving technology choice. As a rule-of-thumb, fibrous agricultural digestates tend to be separated by screw presses, which are poor performing compared to centrifuges (Guilayn et al. 2019b).

The first point to be highlighted is the benefit of (partially) separating moisture from solids. The reduced moisture of the solid fraction (SF) implies a reduced transportation cost thus greater distances and surfaces for spreading. Adding to that, other operational and agricultural benefits are related. The SF is better stackable whereas the LF is better pumpable. The SF might contribute to the soil bulking capacity, whereas the LF has better infiltration in soil. Regarding post-treatment (later detailed), the SF can be post-treated by technologies needing a low-moisture content (notably composting and drying) whereas the LF through technologies needing low-solids and/or presenting clogging issues (notably nitrogen stripping, struvite recovery, (vacuum-)evaporation and membrane filtration).

Adding to this "physical" effect, digestate phase separation enhances nutrient and organic matter management in agriculture. The SF concentrates 30–90% of the OM into 5–50% of the initial mass (Guilayn et al. 2019b). It can thus be better used as a soil amendment (adding to the bulking capacity effect), composted or as constituting growth medium material replacing peat (Nesse et al. 2019). The LF concentrates most of the ammoniacal nitrogen and potassium, while phosphorus tends to follow the organic matter and tends thus to be concentrated in the SF (Guilayn et al. 2019a, b). This nutrient fractioning effect can be used as a strategy for improving nutrient management (e.g. different crops or seasons) and increasing the spreading surface of the fractions by reducing the concentration of the limiting nutrient (usually N or P).

9.7 Value Added Products from Liquid Digestates

Given the benefits described above, digestate post-treatment technologies are classified in this chapter by their applicability concerning digestate rheological state. To the best of the author's knowledge, this process classification has not yet been linked to an actual rheological objective parameter, but the DM content (i.e., total solids) is a usual practical indicator. The techniques described below for liquid digestates are usually applied to LF or wet-AD digestates with less than 5–8% DM. After phase separation, adding to the enhanced physical aspects described in the previous section, it is important to mention that most of the "liquid-state" technologies described below will benefit from an enhanced nutrient content (e.g., N-stripping, microalgae, membrane filtration and evaporation).

9.7.1 Nutrient Fractionation

Nutrient fractionation is considered a mechanism for extracting target nutrients from the liquid digestate stream into different product fractions. This can notably be accomplished using various membrane filtration steps. As such, following the initial phase separation, the liquid fraction could, for example, be further treated through nanofiltration followed by reversed osmosis. In this case, a mineral nitrogen-phosphorus rich fertilizer and nitrogen-potassium rich fertilizer can be produced in sequence, as already implemented at full scale by the company NEREUS (France). The produced water following reversed osmosis typically meets reuse standards. A full-scale system called the Biorek Process has been installed by BIOSCAN (Denmark). Besides reversed osmosis, microfiltration and ultrafiltration units can also be combined with ammonia stripping (Vaneeckhaute et al. 2017). Operating temperatures for membrane filtration typically range between 10 and 40 °C. The pH is typically between 6 and 8. The cost of membrane filtration for manure and digestate treatment was evaluated through a large-scale pilot project conducted at eight installations in the Netherlands. The estimated cost ranged between 9 and 13 €/t of manure or digestate (de Hoop et al. 2011). Potential revenues for the reversed osmosis concentrates were estimated at an average of 6.1 €/t. An important technical issue when using membrane filtration is clogging and fouling of the membrane, which can result in significant costs for the use of cleaning products. In order to mitigate this problem, Vaneeckhaute et al. (2012, 2019) evaluated the performance of vibratory membrane filtration (VSEP technology) for digestate purification at demonstration scale. Although the chemical use was significantly reduced, the energy requirements of this technology are not negligible. The potential pollution of the recovered concentrate flows, for example with heavy metals, also remains an important point of attention.

9.7.2 Concentration and Granulation

As previously discussed, digestate present a pool of valuable compounds notably stabilized organic matter and nutrients. Liquid digestates and LF, however, present a large content of moisture (usually over 90%) thus its valorisation is restricted to landspreading over small distances (about <50 km). Spreading limits can be easily attained, imposing higher transportation costs that would drive the investment on digestate post-treatment.

According to the study of Fuchs and Drosg (2013), digestate evaporation is economically feasible from about a reference transportation distance (no post-treatment) of 80 km. Digestate (vacuum-)evaporation techniques are fully developed and proposed by several companies. Global costs including operation expenditure and capital amortisation are in the range of 15–30 €/t of digestate (Guilayn et al. 2020b, annex material). They can be used as a treatment for simultaneous nitrogen stripping (due to temperature) and recovery as ammonium sulphate as described in the next section. Due to clogging issues, suspended solids must be low and input digestates are often required to present less than 1–3% dry matter. Anyway, scaling issues due to the soluble mineral content have also been observed (industrial expertise from SUEZ). Output concentrates is a dark liquid "syrup" presenting up to 20–25% DM. Adding to that, it might be economically feasible to large-scale facilities to further include a full drying/granulating step after evaporation such as the *ecoDry* process proposed by SwissCombi (Switzerland). In the EU, both strategies could be interesting for achieving end-of-waste status through the regulation CE 2019/1009 as discussed by Guilayn et al. (2019a, b), but authorized post-treatments are not yet clear.

9.7.3 Nutrient Recovery as Pure and Reformulated Products

Several technologies have been developed in the last decades to extract pure and formulated end products from liquid fractions of digestate. Based on a review executed by Vaneeckhaute et al. (2017), the current most implemented technologies at full-scale include struvite precipitation and crystallisation, as well as ammonia stripping and scrubbing.

Struvite precipitation allows to recover soluble phosphorus (ortho-P) from wastewater streams at high phosphorus loads (usually >80 kg P/day) (Vaneeckhaute et al. 2018). It typically requires the addition of a magnesium source (typically MgO, Mg $(OH)_2$ or $MgCl_2$) and caustic soda (NaOH) to increase the pH (8.3–10) and induce precipitation of $MgNH_4PO_4 \cdot 6H_2O$ (struvite). Alternatively, the pH can be increased through stripping of carbon dioxide, without the addition of NaOH. The precipitation-crystallisation reaction usually takes place in a fluidized bed reactor or a completely stirred tank reactor. Important parameters to control include pH, temperature, mixing intensity, and the presence of impurities such as calcium. Struvite can be reused as a valuable slow-release fertilizer product containing the macronutrients N, P and Mg that support plant growth, equivalent to 12% P (28% P_2O_5). Capital costs for producing struvite have been estimated at 0.05 €/day. However, the overall benefits for the treatment plant can reach 0.52 €/day (Vaneeckhaute et al. 2017). The latter is related to chemical savings (conventional Fe/Al-salts), savings from reduced sludge handling and disposal, as well as savings related to the reduced cleaning of uncontrolled struvite deposits. The market value for struvite is variable, with numbers of 45 €/t in Belgium to 250 €/t in Japan (Vaneeckhaute et al. 2017).

Nitrogen stripping and scrubbing allows to recover nitrogen from a variety of wastewater streams at high ammonia (NH_3) nitrogen concentrations (usually >500 mg/L) (Vaneeckhaute et al. 2018). It involves the physical transfer of ammonia from the aqueous phase to the gas phase at increased pH. The ammonia is then absorbed in sulphuric acid by means of an air scrubber to produce liquid ammonium sulphate. Ammonia stripping typically takes place in a packed bed tower or a submerged aeration system. Key advantages of the first is its easy operation and low capital cost, while key advantages of the latter are the absence of packing material (no risk of fouling) and its ability to increase the pH without chemical addition (through CO_2 stripping). Acidic air scrubbing usually takes place in a packed bed tower. Sulphuric acid and air are introduced into the tower in counter-current. Important parameters to control are pH (typically 10–11) and temperature (typically 60–70 °C). The ammonium sulphate concentration in the recovered liquid product ranges from 25 to 40% by weight. It can be valorised as a fertilizer product rich in the macronutrients nitrogen and sulphur. Capital costs for stripping are estimated between 500,000 euros and 1.58 million euros for a packed bed tower, whereas this amounts to 3.5–15 M€ for a submerged aeration system. The operational costs range between 1.4 and 2.5 M€/year (Vaneeckhaute et al. 2017). The market value of the recovered ammonium sulphate solution ranges between 80 and

120 €/t of fresh weight. As such, under optimal process conditions, nitrogen stripping and scrubbing can be viable.

9.7.4 Microalgae and Cyanobacteria Cultivation

The cultivation of microalgae and cyanobacteria has attracted a lot of research attention these last decades as new valorisation routes for liquid digestate valorisation (Franchino et al. 2013; Xia and Murphy 2016; Zuliani et al. 2016). Liquid digestate is mainly composed of soluble compounds, water and nutrients (N and K sources majority) that make it an ideal culture support for microalgae or cyanobacteria (Nkoa 2014; Akhiar et al. 2017, 2021; Guilayn et al. 2019b). Microalgae can be done in open systems (i.e. raceway) or in closed systems called "photobioreactors" (Kirnev et al. 2020). Nonetheless the chemical properties of digestate and especially its high turbidity and high content of ammoniacal nitrogen can limit the microalgae growth (Xia and Murphy 2016). Due to their chemical properties, liquid digestate from urban wastewater or agro-industrial wastes are more appropriate than agricultural ones (Xia and Murphy 2016; Zuliani et al. 2016).

In order to overcome these chemical barriers (turbidity, ammoniacal nitrogen), several treatment options can be implemented such as dilution with fresh water or others agro-effluents with less turbidity (Franchino et al. 2013; Zuliani et al. 2016; Markou et al. 2021). For instance, Franchino et al. (2013) have tested three microalgae strains (*Neochloris oleoabundans, Chlorella vulgaris and Scenedesmus obliquus*) on an agro-zootechnical digestate at different dilution ratios (1:10; 1:15; 1:20: 1:25). Specific growth rate of 0.26, 0.23, 0.49/day were observed for, respectively, *Neochloris oleoabundans, Scenedesmus obliquus and Chlorella vulgaris* by applying a dilution rate of *1:20* (Franchino et al. 2013). Similarly, Jimenez et al. (2020a, b) have investigated at different dilutions (1:20, 1:30, 1:50) the *Monoraphidium* sp. on agricultural liquid digestate in laboratory trials. Optimum dilution factor was 1:50, with a specific growth rate of 0.13/day and a complete nitrogen removal in 25 days. Markou et al. (2021) have also investigated *Spirulina* cultivation in artificial seawater at 2.5%, 5%, 10% or 15% (v/v) of digestate in a fed-batch mode. The highest production was noticed at 5% ($\approx$1300 mg/L dry biomass) but further increases in digestate concentrations lowered biomass accumulation ($\approx 1020-1150$ mg/L dry biomass). Other investigations have investigated alternative pre-treatment methods to avoid dilution including: activated carbon treatment (Marazzi et al. 2017), flocculation-biological contact oxidation (Zhou et al. 2019), aerobic treatment (Wang et al. 2019) and struvite precipitation (Jiang et al. 2018).

The cultivated microalgae can be further used in different applications such as biofuels such as biodiesel (Sialve et al. 2009), bioethanol and biohydrogen (Harun et al. 2010; Yun et al. 2012). The microalgae can be also sent back to the biogas plant for methane production (Sialve et al. 2009; Mussgnug et al. 2010). Other alternatives can be animal feed (Madeira et al. 2017), fertilizers and biostimulants (Hidalgo

2015; Ronga et al. 2019a). Microalgae can also be used for the upgrading of biogas and several studies have been done in the last decades (Tongprawhan et al. 2014; Rodero Raya et al. 2019). Finally, when considering the valuation chains it is important to consider the contamination risks (i.e. pathogens, organic and inorganic contaminants) and biomass safety concerns (Markou et al. 2018) and for this purpose human-consumption applications are often not considered. Up to date, some R&D projects have been implemented in Europe coupling liquid digestate with microalgae cultivation. Among these projects, the AlgaeBiogas project (https://algaebiogas.eu/) has investigated the use of liquid digestate for microalgae cultivation.

9.7.5 Biological Nutrient Recovery Strategies

Liquid digestate and LF can be used more indirectly for the recovery of value-added products by providing nutrients and other compounds (such as phytohormones) for living organisms. This is the case for microalgae recovery (presented previously), but also for a large range of emerging technologies. It can be highlighted (not exhaustive): (1) Nutrient and phytohormone source for hydroponics (Antón et al. 2017; Ronga et al. 2019b; Guilayn et al. 2020a), (2) Macrophytes recovery. A full-scale demonstration plant of duckweed recovery was recently constructed in Europe (Pascual 2016) and (3) Liquid culture medium. For instance, liquid digestates have been successfully used as a culture medium to produce bioplastics (Passanha et al. 2013) and ethanol (Ujor et al. 2020).

9.8 Value Added-Products from Solid Digestates

As introduced during the “liquid-state” valorisation section, the DM content is a usual practical indicator for the feasibility of the technologies described in this section. The techniques described below for solid digestates are usually applied in SF or dry-AD digestates with more than 20–25% DM. Adding to the enhancement of physical properties described for “solid-state” technologies (Sect. 9.6), most “solid-state” technologies will benefit from a greater OM content of SF after phase separation, such as composting, post-fermentation and thermal conversion.

9.8.1 Composting

Composting process consists in an aerobic biological decomposition of biodegradable organic matter into CO_2 and microorganisms. Digestate composting is a commonly used post-treatment in agricultural, urban, and industrial AD plants. Compost of digestate has a good amendment potential compared with raw digestate and solid or liquid phases (Reibel and Leclerc 2018). Due to the more favourable thermodynamics and aerobic conditions, a higher variability of microorganisms (i.e. bacteria, actinomycetes, fungi) can be found both effects allowing a higher OM decomposition than AD (Guilayn et al. 2020b).

Industrial composting can be controlled by several parameters as the retention time (from 3 weeks up to 1 or 2 months), the optimal C to N ratio between 20 and 40, the temperature, the moisture ($> 60\%$), the bulking agent and aeration rate and method (Epstein 2011). Composting is an exothermic process. Temperatures reach more than 70°C within the piles inducing an authorized hygienisation process of digestates in several countries. Temperature, exposure time and the number of turnings are usual regulatory parameters varying from country to country. For example, in Germany, temperatures of 55, 60 and 65 °C are requested for a period of respectively 14, 6 and 3 days (Amlinger and Blytt 2013). Largely due to the self-heat reaction, water loss occurs during composting and decreases transportation costs. Levasseur et al. (2017) reported a mass loss from 30 to 50%. As physical impurities and trace metals are conserved during composting, depending on the mass loss rate and the bulking agent used, these compounds can be either concentrated or diluted (compared to digestate). Besides, bioaccessibility and solubility of heavy metals can be reduced due to their strong bonds to compost organic matter (Smith 2009).

Composting is usually performed on the solid phase of digestates. Besides, some digestates need bulking agents because of (1) the low part of biodegradable OM allowing temperature increase, (2) the physical structure of digestates which do not allow sufficient aeration and (3) the C to N ratio of digestates which are lower the optimal values (Tremier et al. 2014; Zeng et al. 2014, 2015). Common bulking agents are green waste, wood chips, sawdust and compost grinding wastes (Epstein 2011). A recent and new technique for liquid wastes is based on the spreading and the constant turning of the liquid into a saturated support bulking material (Chiumenti 2015; Levasseur et al. 2017).

Composting can convert ammonia to nitrates through nitrification. However, depending on the process operation, ammonia can be largely volatilized, denitrified (under anoxic conditions) and lost as N_2 or even N_2O (a strong greenhouse gas). Zeng et al. (2012) observed 2–43% of total N loss as ammonia and up to 76% including nitrification-denitrification. More recently, the addition of biochar has been used as co-substrate to avoid NH_3 volatilisation due to adsorption and support for nitrifying bacteria (Wu et al. 2017). Researches indicate that industrial composting can be optimized to produce minimal amounts of NH_3 and N_2O ($<1\%$ input N) (Chiumenti 2015), but without a diffcult-to-achieve complete nitrification, an important N_2 emissions still represent a relevant loss in value.

Despite all the advantages of the composting process, composting is not necessarily a low-cost technology. Moreover, the compost producer usually receives a price near to zero or even pays an intermediary distributor. According to Dahlin et al. (2015) and (Guilayn et al. 2020b), composts price goes from under 0 to 7 €/t, way below other value-added products that can be recovered from digestates.

Regarding composting costs, the long retention time and the bulking agent volume induce an installation four times or more larger than the surface needed for AD. Furthermore, providing aeration and the subsequent air treatment for a high surface can be extremely costly. The use of forced aeration and/or mechanical turning is needed. Low-cost passive aeration based only on convection (heat moving up) is usually not allowed for producing certified composts despite its attested effectiveness. Adding to that, composting leachate treatment can be challenging (Roy et al. 2018).

9.8.2 Digestate Drying

Solid digestates and solid fractions can be dried through thermal and solar drying equipment such as those conventionally applied to wastewater sludge for several decades. Drying equipment present a high capital investment (typically over 500 k €), being mostly restricted to large facilities. Commonly related equipment are belt, rotary and disk dryers. Belt driers seem more suited as rotary and disk dryers can be damaged by digestates containing large particles. Fire risk due to self-heating and ignition risk of explosive atmosphere must be considered during design and operation of digestate drying and storage facilities (Guilayn et al. 2020b).

From a fertilisation perspective, thermal drying induces ammoniacal nitrogen loss through volatilisation as NH_3. It can be though recovered as ammonium salt/acidic solution through air collection and treatment (Vaneeckhaute et al. 2017). However, in practice, many operators can be reluctant to operate air treatment equipment (i.e. acid washing towers) in less acidic levels (e.g. pH 5–6), as any emission risk might represent air pollution, neighbourhood complains and penalties. In such cases, the final product can be too acidic for farmers (pH 2–3) and represent a disposal cost superior to 40 €/m^3 in Europe (SUEZ expertise). In the opposite, digestate can be acidified prior to thermal drying to avoid nitrogen loss (Pantelopoulos et al. 2016).

By removing most of digestate moisture, thermal drying can be an effective option for enabling large-scale facilities to export digestate to distant areas, while maintaining product stability over time. Transportation costs can be required to be further reduced by pelletisation, as it increases product bulk weight from 100 to over 600 kg/m^3 (Dahlin et al. 2015).

9.8.3 Growth Media

Digestate can be used as a growth medium for plant seedlings, partially/totally substituting conventional non-renewable materials such as peat. Zhang et al. (2013) successfully used solid digestates as a growth medium for tomato, while reporting a growth biostimulant effect. The solid portion as well as a solid state digestate may be used as growth medium for insects and invertebrates. Some experiences have already been carried out by using either the liquid or the solid fraction of the digestate as obtained from conventionally applied separation techniques (Cesaro 2021). O'Brien et al. (2019) successfully tested solid digestates derived from dairy manure and food waste in the cultivation of the fungal species *Pleurotus ostreatus*.

Waste-based composts have been extensively studied as growth media in hydroponic cultivation, while the use of the digestate is more recent. The potential of the anaerobic digestate has been also explored as growth medium in hydroponic systems (Cesaro 2021). These can be considered as an engineered plant cultivation method, which uses soil-less growth medium and a nutrient solution. Ronga et al. (2019b) evaluated the cultivation of baby leaf lettuce in hydroponic systems, using both the solid and the liquid fraction of digestate as alternative growth medium and nutrient solution, respectively.

Cerda et al. (2019) have proposed a solid-state fermentation (aerobic) technology based on solid food waste digestate as substrate/support medium. They have observed interesting yields for the production of *Bacillus thuringiensis* (Bt), the major biological pesticide in the organic farming market. The final product can be used as a Bt-enriched compost-like product, or, preferentially, an extraction step should be added to produce a further value-added extract for foliar application.

9.8.4 Thermal Conversion

These last decades, a high interest has been brought among the scientific communities to valorise the solid fraction of digestates through thermo-chemical processes (mainly hydrothermal, gasification and pyrolysis) (Freda et al. 2019; Miliotti et al. 2020; Cesaro 2021). Most of the studies were performed on digestate originating from OFMSW, agricultural or WWTP sludges. Among them a specific attention has been paid on the pyrolysis process (Torri and Fabbri 2014; Neumann et al. 2015; Monlau et al. 2015a; Tayibi et al. 2021). Pyrolysis is defined as the thermal decomposition of the organic matrix under non-oxidizing or very low-oxidizing stoichiometric atmospheres, and occurs in the temperature range of 250–1200°C (Bridgwater 2012; Biswas et al. 2017). During pyrolysis, organic matter such as lignin, proteins, cellulose, and hemicelluloses are thermally broken down and rearranged forming three major products (Fig. 9.3): (1) biochar (carbonaceous solid fraction), (2) bio-oil (mainly composed of 15–30% w/w liquid of wide variety of organic components and 85–70% of aqueous pyrolysis liquid (APL)) (Fabbri and Torri 2016), and (3) syngas composed of non-condensable gases (i.e. CO, CO_2, CH_4 and H_2) (Tayibi et al. 2020). Depending on the operating conditions (i.e. temperature, heating rate, residence time) the pyrolysis process can be divided into three main subclasses: slow, fast and flash pyrolysis (Laird et al. 2009).

Syngas can represent an interesting supplementary energy source that can be further converted into heat or heat/electricity alone or mixed with biogas in boilers, engines but also used for methanol production (Gollakota et al. 2016; Giuliano et al.

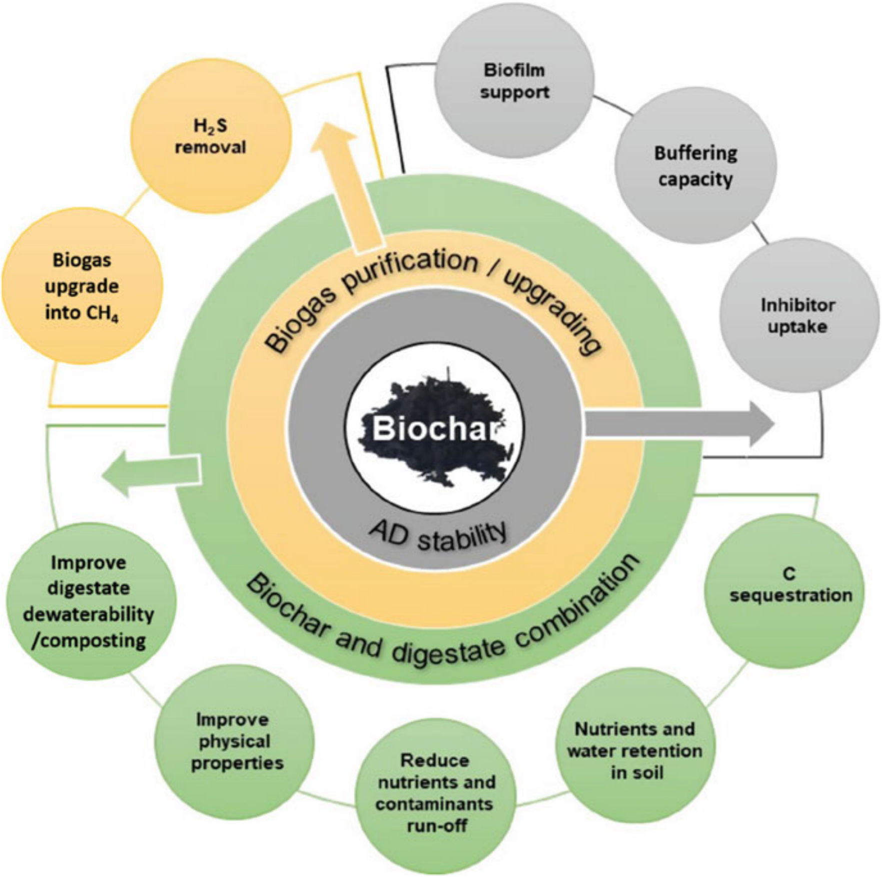


Fig. 9.3 The role of biochar in improving the anaerobic digestion chain

2020). Syngas has also attracted recently the attention as hydrogen source in biological methanation processes (Schwede et al. 2017; Grimalt-Alemany et al. 2018). In parallel, bio-oil is generally separated into an organic and aqueous phase, the first one can be used as a blend with existing transportation fossil fuels or directly used as transportation fuels (Gollakota et al. 2016). On the contrary, the aqueous phase can be used as new feedstock in the AD process in co-digestion with other organic wastes (Torri and Fabbri 2014), but specific attention should be paid to the furans and phenolic compounds present that can inhibit the microbial communities of the AD process (Barakat et al. 2012; Monlau et al. 2014).

Pyrolysis has been applied on solid digestate from OFMSW (Giuliano et al. 2020), agricultural wastes (Feng and Lin 2017; Monlau et al. 2015a; Tayibi et al. 2020), biowastes (Opatokun et al. 2017; Giwa et al. 2019) and wastewater sludges (González-Arias et al. 2020). In most cases, slow pyrolysis was applied with temperatures ranging from 350 to 750 °C (Neumann et al. 2015; Ghysels et al. 2020) with most of the studies operating at 500 °C (Monlau et al. 2015a; Ghysels et al. 2020; Tayibi et al. 2021). Tayibi et al. (2020) have investigated the pyrolysis (500 °C, 10 °C/min, 1 h) of solid digestate treating sludges and agricultural biomasses and reported biochar, bio-oil and syngas yields of 37%wt, 34%wt, 29%wt respectively. Similarly, Karaeva et al. (2021) reported biochar, bio-oil and syngas yields of 41%wt, 31%wt, 28%wt, respectively, after pyrolysis at 550 °C of solid digestate from agricultural wastes. After pyrolysis of solid digestate, syngas energy of 12.9 MJ/Nm^3 (Tayibi et al. 2021), 9.5–15.7 MJ/Nm^3 (Monlau et al. 2015a), 13.1 MJ/Nm^3 (Neumann et al. 2015) were reported. The organic phase of bio-oil generally exhibited energy yields of 23.5 MJ/kg (Tayibi et al. 2021), 28.4 MJ/kg (Monlau et al. 2015a), 33.9 MJ/kg (Neumann et al. 2015), 24.9–32 MJ/kg (Ghysels et al. 2020).

Biochar can be used for several applications especially for improving the stability of composting and AD (Torri and Fabbri 2014; Fagbohungbe et al. 2017; Xiao et al. 2017), in agronomic applications alone or in combination with fertilizers like liquid digestate (Laird et al. 2010; Semida et al. 2019; Guilayn et al. 2021; Tayibi et al. 2021), or for gas treatment like biogas purification and upgrading. A lot of synergies have been identified in the recent years by associating AD and pyrolysis and most of them are using biochar as a central element as shown in Fig. 9.3 (Fabbri and Torri 2016; Fagbohungbe et al. 2017; Luz et al. 2018). Up to date, even if such processes are mature and applied at industrial scale, there is no real example that has been tested at industrial scale for such dual symbiotic approach.

9.8.5 Bioethanol Production

As previously mentioned, the solid digestate from the AD process especially coming from agricultural biogas plants represents a promising perspective for the production of biofuels such as bioethanol (Logan and Visvanathan 2019). Indeed, during the AD process of agricultural residues such as crops and manures, part of the organic matter is not degraded and among them a significant part of cellulose that can be used for bioethanol production in a biorefinery concept (Ruile et al. 2015; Santi et al. 2015). Another approach for bioethanol fermentation commonly consists of two steps: enzymatic hydrolysis and fermentation, which can be realized separately or simultaneously. Two strategies can be generally applied: enzymatic hydrolysis separately from fermentation, as separate hydrolysis and fermentation (SHF), or simultaneously, as simultaneous saccharification and fermentation (SSF). In general, the advantage of SHF is the ability to perform each step (i.e. enzymatic hydrolysis and fermentation) under optimal temperature conditions (40–50 °C for enzymatic hydrolysis and 30 °C for fermentation), whereas SSF offers the opportunities to limit contamination and reduce the size of reactors (Cotana et al. 2015; Sukhang et al. 2020).

Recent studies have focussed on the bioethanol fermentation from solid digestate and obtained a low ethanol yield (Monlau et al. 2015b; Sheets et al. 2015; Sambusiti et al. 2016). Indeed, the solid digestate represents a highly recalcitrant biomass especially due to its high lignin and crystalline cellulose content that can limit its further biodegradation by enzymes during the saccharification process (Santi et al. 2015; Sambusiti et al. 2016). For these purposes, pretreatment technologies can be applied such as mechanical, thermal, thermo-chemical, physical, biological or a combination of them (Cotana et al. 2015; Sambusiti et al. 2016; Carrere et al. 2016). Until now, the pretreatments that have been reported in the literature to enhance bioethanol fermentation from solid digestate are comprised of thermo-acid (Teater et al. 2011; Stoumpou et al. 2020), thermo-alkaline (Yue et al. 2011; Stoumpou et al. 2020), ozone (Wang et al. 2016) or mechanical (Sambusiti et al. 2016) treatment.

For instance, Yue et al. (2011) investigated the impact of the nature of digestates (from CSTR and a plug flow reactor (PFR)) on bioethanol production. Ethanol production of 105 g/kg dry digestate was noticed for the digestate from the CSTR and 85 g/kg dry digestate for the digestate from the PFR. Similarly, Stoumpou et al. (2020) have investigated acid and alkaline pretreatment on solid digestate (from anaerobic digestion of wheat straw) to improve bioethanol production. Acid pretreatment led to low bioethanol production probably due to the production of inhibitors. In parallel, ethanol fermentation presented yields up to 65% from alkaline pretreated digestate and all the available glucose was consumed, implying that no inhibitory factors were present (Stoumpou et al. 2020).

From an industrial point of view, it is important that pretreatment technologies of solid digestate take into account the ease of implementation, their cost and the potential production of inhibitors (i.e. furans, polyphenols) (Barakat et al. 2012; Jönsson and Martín 2016; Sukhang et al. 2020). Up to date, to our knowledge, there is no industrial plant producing second-generation bioethanol from solid digestate. In general, second-generation bioethanol is struggling to find industrial profitability even if some units are already operational or under construction, most of them in Europe and the United States. Although the first industrial-scale units appeared in the United States (DuPont, Abengoa, Ineosbio, KiOR and Poet), some initiatives are also existing in Europe such as the demonstrative Futurol platform (180,000 L/year) in France and the Beta Renewables (approx. 80,000 m^3/year) plant in Italy (Crescentino).

9.8.6 Nutrient Recovery from Incineration Ashes

Nutrients can be extracted from the remaining ashes after combustion of biodegradable wastes. Since phosphorus and potassium are non-volatile, these macronutrients are concentrated in the ashes (Schoumans et al. 2010). Nevertheless, these ashes can also be rich in heavy metals, including for example cupper (Cu), cadmium (Cd) and zinc (Zn). The available process to extract phosphorus from ashes are generally classified as thermochemical and wet-chemical technologies. An example of the first class is the process developed by Outotec (Finland), where alkaline reagents are added to the ashes at a temperature of 1000 °C, thereby gasifying the heavy metals (Hermann and Schaaf 2018). Phosphorus is bound and recovered as $CaHPO_4$, which can be sold as mineral fertilizer. An example of the second class is the process developed by the company EcoPhos (Belgium), where hydrogen chloride (HCl) is added to the ashes to chemically extract the phosphorus (Bolland 1996; Takhim et al. 2018). Phosphorus recovery efficiencies higher than 90% have been achieved as such (Saerens 2017; Schoumans et al. 2010; Takhim et al. 2018). Nevertheless, currently, few full-scale installations exist for digestate treatment due to the relatively high costs for combustion (up to 10 euros per ton of fresh weight) and the need for a thorough flue gas cleaning system (Vaneeckhaute et al. 2017).

9.9 Regulatory Framework in EU and North America

Quality management of digestate and its (by-/co-)products involves a wide range of permits and quality standards to ensure its safety and effectiveness. Strict local regulation usually applies for spreading these products under a waste status in law. End-of-waste schemes may vary regionally, and they tend to impose both product quality/innocuity parameters, process design/operation criteria and good practices. Such regional/international differences are a strong barrier for developing true markets around digestate (by-/co-)products.

The EU has recently enforced a new Fertiliser Regulation allowing a homogenous definition of quality and process criteria applicable to several types of materials including digestates (CE 2019/1009). More broadly, this regulation represents a huge international milestone as it promotes the trade of biosourced fertilisers obtained from organic waste streams within the largest common market in the world. It establishes 11 Component Material Categories (CMCs) to produce different CE-labeled fertilising products. Concerning digestates, two CMC are related: CMC 4 for fresh crop digestate and CMC 5—Digestate other than fresh crop digestate. Different CMCs can be used to constitute a wide range of so-called Product Function Categories (PFC), as detailed in the Annex I to the EU Regulation. Several PFCs can be related to products coming from digestates (PFC 1 Fertiliser, PFC 3, Soil Improver, PFC 4, growing medium, PFC 6 Plant Biostimulant). More recently, phosphate salts (such as struvite), ashes from incineration and biochar were included in the regulation as three new CMC. These categories represent even further a new milestone as phosphate salts and incineration ashes coming from WWTP sludge will be accepted. In the future, more CMC can be included as new recycled products become scientifically proven to be effective and safe. It could be the case, for example, for ammonium sulphate from acid scrubbing, recently added to a French standard (NF U42-001-1 A1)

The most generic regulation currently in place in North America includes the US Environmental Protection Agency (EPA) Classes of biosolids, which applies to products derived from sewage sludge. The EPA issued a 40 CFR Rule (Part 503) that categorizes biosolids as Class A, Class A EQ (Exceptional Quality) or Class B, depending on the level of pathogens and the ability of the material to meet or exceed Vector Attraction Reduction (VAR) requirements. Hereby, for Class A biosolids, pathogens must be reduced to virtually non-detectable levels and the material must also comply with strict standards regarding metals, odors and VAR. Class A EQ is used to describe a biosolids product that not only meets, but exceeds, all Class A pathogen reduction, metals and VAR requirements. Finally, Class B biosolids contain higher levels of detectable pathogens than Class A biosolids and may require a permit from the EPA with conditions on land application, crop harvesting and public access. Additional state, provincial or local regulations may apply and are currently under development for digestate and digestate-derived products.

9.10 Perspective

AD is a fully industrial, trending and politically encouraged technology. It is expected to play a crucial role for achieving a circular economy while fighting climate change. Digestate is traditionally seen as a by-product of AD as a renewable energy technology that produces biogas or biomethane. However, it is usually the major AD product in terms of mass. It represents nowadays a major cost centre for most of industrial operators while presenting valuable compounds that can be concentrated, fractionated and/or chemically/biologically transformed to generate value-added products described in this chapter.

Today, full-scale post-treatment processes such as composting, drying and N/P-recovery generate negative to moderate net value, but can effectively enable and enhance digestate return to soil. Increasing demand for these products could increase their price in the future, while emerging technologies such as microalgae and thermal conversion could start true biorefineries from digestates, presenting significant potential for creating value.

Adding to technological bottlenecks, all these options need a trusted end-of-waste regulatory status that can be different interdependently according to AD feedstock category, local regulation and public/consumer acceptance. Fortunately, this situation is evolving fast along with the urgency to reshape the economy. The EU has provided an example and a global milestone with the new and still evolving regulation on fertilizers (CE 2019/1009). It allows the commercialization in the world's largest common market of several product categories that can be derived directly or after post-treatment of several types of digestate and digestate by-products.

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Chapter 10
Biochar Produced from Organic Waste Digestate and Its Potential Utilization for Soil Remediation: An Overview

Suchanya Wongrod, Gilles Guibaud, Stephane Simon, Piet N. L. Lens, David Huguenot, Yoan Pechaud, and Eric D. van Hullebusch

Abstract Contamination of metal(loid)s and organic pollutants in soils has caused detrimental effects to the environment, so that there is a need to develop appropriate treatment approaches to resolve the soil pollution. In recent years, biochar produced from biowaste material has been widely used as a potential adsorbent in remediating

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organic and inorganic pollutants in soils. This review aims to overview the production technologies and characterization of biochars derived from sewage sludge digestate (SSD) and the organic fraction of municipal solid waste digestate (OFMSWD) and their applications for soil treatment. Critical discussions on the sorption mechanism, important factors influencing contaminant retention in soils, bioavailability of trace elements with biochar addition, and potential effects of biochar application to soils are summarized. The interaction mechanisms involved between the SSD and OFMSWD-derived biochars and contaminants, the main factors influencing the biochars' sorption efficiency and possible effects to the environment are discussed in this review.

Keywords Biochar · Sewage sludge · Municipal solid waste · Heavy metal removal · Organic pollutants removal · Soil amendment

10.1 Introduction

The increment of food supply for human beings, rapid expansion of industrial production and intensive agricultural activities are raising concerns. There are many negative impacts on the environment, e.g. discharges of metal laden wastewaters into rivers, spills of petroleum hydrocarbons to soils, transportation of veterinary pharmaceuticals from animal manures into surface runoff and soil leachate on farmland. Thus, water and soil ecosystems are prone to biomagnification and bioaccumulation of toxic chemicals into living organisms through the food chain. Soil contamination requires risk assessment studies and remediation to increase environmental safety by reducing the mobility and toxicity of pollutants.

Several treatment technologies have been sought to minimize pollution (Beesley and Marmiroli 2011), e.g. excavation, solidification and stabilization, soil washing, phytoremediation and bioremediation (El Sawwaf and Nazir 2012; Iturbe and López 2015). However, these conventional technologies are often expensive for in situ treatment and may lead to nutrient losses in soils (Beesley et al. 2011). Supplementation of biochar to soil is an alternative to promote environmental sustainability by converting organic waste by-products, for instance, the solid digestate from biogas plants, into a value-added product, i.e. biochar (Meng et al. 2013; Tan et al. 2015).

Solid digestate is an organic by-product generated by wastewater treatment plants. Their treatment before a final disposal is required to decrease volume and reduce unpleasant odors. Moreover, these solid digestates are considered as hazardous waste due to the remaining pathogens that can possibly be transferred to the soil (Al Seadi and Lukehurst 2012). Therefore, sludge management with environmental-friendly and cost-effective technologies are required. Conventional technologies to dispose sludge such as landfilling or direct use in agriculture may be restricted, respectively, due to limited landfill site availability and possible transportation of pollutants to the farmland (Devi and Saroha 2016). Therefore, the valorization of digested sludge arises as an interesting approach to treat solid digestate and consequently produce biochar.

Biochar is a black solid char derived from thermal conversion technologies (e.g. pyrolysis, hydrothermal carbonization, and gasification) of biowaste materials in a limiting oxygen environment (Inyang et al. 2016). Pyrolysis produces biochar as a main product, and bio-oils and syngas as by-products. There are extensive studies on the use of biochars derived from agricultural residues (e.g. rice straw, pine chips, and bamboo) and animal manures (e.g. swine solid, dairy manure, and poultry litter) for soil and wastewater treatment (Ahmad et al. 2014; Ok et al. 2015; Sohi et al. 2010; Tan et al. 2015). Only a few studies focused, however, on the use of biochar produced from organic waste digestate. The solid digestates such as sewage sludge digestate (SSD) and the organic fraction of the municipal solid waste digestate (OFMSWD) are considered as alternative materials for biochar production (Neumann et al. 2014; Pituello et al. 2014; Wongrod et al. 2018a, b).

Solid digestate-derived biochars have been increasingly used for soil remediation due to its improved properties after pyrolysis, for instance, more available oxygen-containing functional groups (e.g. carboxyl or hydroxyl), and surface properties (e.g. surface charge and hydrophobicity). For example, Zielińska et al. (2015) reported the increase of specific surface area (2–4 times), macro- and micronutrient content, and aromaticity in sewage sludge biochar, compared to its origin feedstock, particularly at higher pyrolysis temperature (500–700 °C). The biochar also provide several benefits to the soil, e.g. immobilize toxic pollutants, increase nutrient retention to enhance crop yields, and provide longer carbon sequestration in soils (Lehmann and Joseph 2009).

Biochars are applied in four main areas: carbon sequestration, soil fertility enhancement, bioenergy production and contaminant remediation. This chapter describes recent findings on the characterization and application of biochars derived from SSD and OFMSWD for remediating organic and inorganic contaminants in soils. The interaction mechanisms involved between biochars and contaminants, the main factors influencing the biochars' sorption efficiency and possible effects to the environment are discussed in detail.

10.2 Biochar Production from Organic Waste Digestates

10.2.1 Biochar Production Technologies

Figure 10.1 shows various thermal conversion processes to produce biochar including slow pyrolysis, fast pyrolysis, gasification, and hydrothermal carbonization (HTC). Prior to pyrolysis or gasification, drying of the digestate to reduce the moisture content to less than 10% is required, while no dehydration is needed for HTC. Under slow pyrolysis, biochar is produced at low heating rates (10–30 °C/min) and long residence times (5 min–12 h) at temperatures ranging from 300 to 650 °C (Kambo and Dutta 2015). In general, higher temperatures result in lower biochar yields due to partial degradation of lignin and cellulose (Kambo and Dutta 2015).

Table 10.1 presents the production conditions and yields of bioproducts of the different thermal conversion technologies. The biochar produced under slow

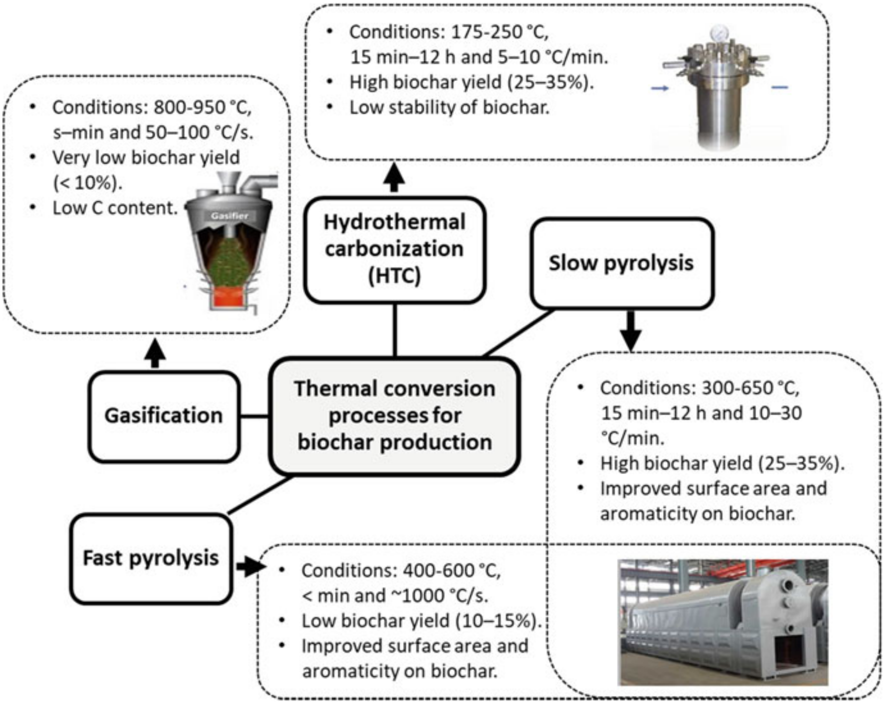

Fig. 10.1 Thermal conversion processes for biochar production. Adapted from Kambo and Dutta (2015); Novotny et al. (2015); Sohi et al. (2010)

Table 10.1 Production conditions and yields of solid, liquid and gas products from thermal conversion processes

Mode	Production conditions (operating temperature, heating rate, residence time)	Gas (syngas) (%)	Liquid (bio-oil) (%)	Solid (biochar) (%)
Fast pyrolysis	400–900 °C, 100–1000 °C/s, s–min	~13	~75	~12
Slow pyrolysis	250–700 °C, 10–30 °C/min, 15 min–2 h	~35	~30	~35
Hydrothermal carbonization (HTC)	180–260 °C, 5–10 °C/min, 15 min–2 h	~5	~25	~70
Gasification	800–950 °C, 50–100 °C/s, 10–20 s	~85	~5	~10

Adapted from Belcher and Masek (2013); Duku et al. (2011); Iwasaki et al. (2014); Kambo and Dutta (2015); Sohi et al. (2010)

pyrolysis provides high biochar yields (25–35%) and oxygen-contained functional groups such as hydroxyl and carboxyl on the biochar surface (Kambo and Dutta 2015), influencing the sorption capacity of the biochar. Fast pyrolysis is a process in which biofuel (bio-oil) is produced as a main product, and biochar and syngas are generated as by-products. Under fast pyrolysis, the process performs at 400–700 °C with a very high heating rate (~1000 °C/s) and short residence time (< min) (Mohan et al. 2014). High bio-oil (75%) and low biochar (10–15%) yields are often achieved in fast pyrolysis (Table 10.1). In order to obtain homogenous biochar, pretreatment of the feedstock, e.g. sieving to a small particle size (<2 mm) and drying (65–80 °C) to reduce the moisture to less than 10% are required (Pituello et al. 2014). Due to lower biochar yields and higher operation costs from fast pyrolysis, the slow pyrolysis is a more favorable option to produce biochar.

Gasification is a combination of thermal and chemical processes which is mainly for fuel-gas production (Novotny et al. 2015). The fuel gases are mainly composed of hydrogen (H_2) and carbon monoxide (CO) that can be further used as renewable energy sources for internal engine and power supply in industries (Novotny et al. 2015). Nevertheless, due to very high operating temperatures (800–950 °C) during gasification, the obtained biochars are relatively small, thus less desirable for biochar production (Table 10.1). In addition, biochar produced from a hydrothermal carbonization process shows low stability, i.e. high O/C ratio, whereas biochar produced under slow pyrolysis acts as an effective sorbent due to its physicochemical properties.

Biochar yields vary mainly depending on the operating temperature, which strongly influences the biochar properties (Singh et al. 2010). For instance, at increasing pyrolysis temperature (from 300 to 700 °C) of SSD, a higher surface area (from 11 to 26 m^2/g) and ash content (66–87%) but lower biochar yields (from 83 to 65%) and O/C ratio (from 0.56 to 0.05; implied higher biochar stability) were obtained (Yuan et al. 2015). In addition, the origin of feedstock also plays a role in the biochar properties. Agrafioti et al. (2014) reported that rice husk contains lower volatile matter (%) than sewage sludge and organic solid waste, which resulted in its lower biochar yield.

10.2.2 Organic Waste Digestates and Their Derived Biochars

The solid sludge by-product (solid digestate) obtained from anaerobic digestion can be used as substrate for biochar production using pyrolysis technology (Fig. 10.2). By coupling anaerobic digestion with the pyrolysis process, more energy recovery and sustainability of the digestion plant were found since the bioenergy could be used to dry the solid digestate prior to pyrolysis (Monlau et al. 2015). This chapter focuses on two types of solid digestates: sewage sludge digestate (SSD) and organic fraction of the municipal solid waste digestate (OFMSWD).

10.2.2.1 Sewage Sludge Digestate

Sewage sludge digestate (SSD) is the organic residue remaining after the anaerobic treatment of wastewater and waste activated sludge. The management of SSD is currently a big concern because of the large quantities of solid digestate generated at the wastewater treatment sites. The valorization of the solid digestate is an

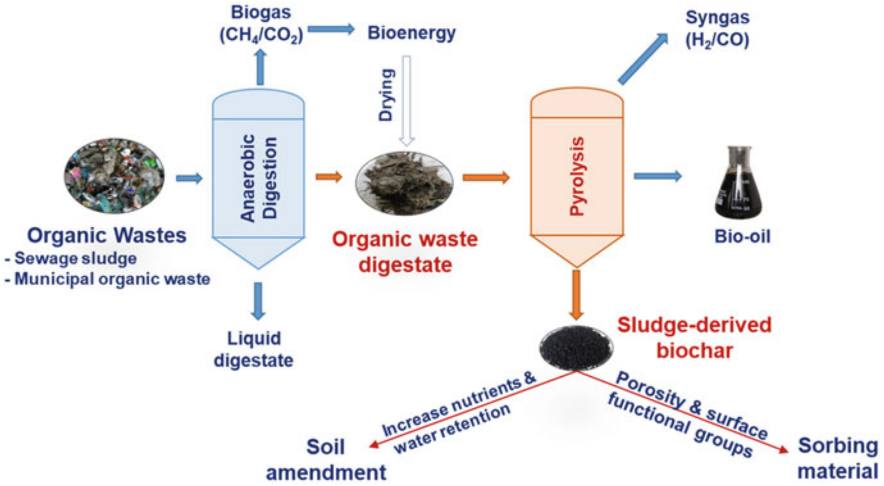

Fig. 10.2 Biochar production from organic waste digestate and its applications in soil bioremediation

alternative to reduce the volume and eliminate organic pollutants in the digestate. Waqas et al. (2014) reported a significant reduction of the polycyclic aromatic hydrocarbons (PAHs) concentration after the conversion of sewage sludge into sewage sludge-derived biochar.

Table 10.2 represents the composition of biochar derived from sewage sludge. From Table 10.2, the SSD is rich in Cu, Cr, Pb and Zn (Pituello et al. 2014) as well as Fe and P (Yuan et al. 2015) due to the addition of $FeCl_3$ for phosphate precipitation during the wastewater treatment. Moreover, the SSD biochar is rich in minerals compared to biochars produced from biomass residues. This may result from the diversity and complexity of sewage sludge (Zielińska et al. 2015). Sewage sludge (59%) and its derived biochar (72%) have a high ash content, corresponding to the dominant mineral fractions (such as SiO_2, $CaSO_4{\cdot}2H_2O$ and $CaCO_3$) contained in the sludge (Zielińska et al. 2015). In addition, the SSD may contain undigested organic compounds (such as carbohydrates, lipids and proteins) preliminarily from the wastewater, inorganic elements from soils and synthetic materials from the substrates (Devi and Saroha 2016).

10.2.2.2 Organic Fraction of the Municipal Solid Waste Digestate

The organic fraction of municipal solid waste digestate (OFMSWD) is a by-product after anaerobic biological treatment of municipal solid waste. Municipal solid waste in Europe often comprises of a large organic fraction (30–40%) with high moisture content and biodegradability (Cesaro et al. 2019). This is due to the large content of organic waste, food waste and leftovers from residences, restaurants, factories and markets (Peng and Pivato 2017). The specific location and collecting time play a

Table 10.2 Properties of biochars derived from sewage sludge digestate

Process for biochar production	Experimental conditions T_p[a], RT[b], HR[c]	Yield (%)	pH	Ash (%)	C (%)	H (%)	O (%)	N (%)	S (%)	P (% or g/kg)	Surface area (m^2/g)	Reference
HTC	225, 16, NA[d]	50	NA	NA	38	NA	NA	NA	NA	6%	NA	Huang et al. (2018)
Slow pyrolysis	250, 4, 3.3	69	NA	NA	36	NA	NA	NA	NA	4%	NA	Huang et al. (2018)
Slow pyrolysis	250, 1, 16–19	NA	6.9	48	28	NA	NA	3	0.8	17 g/kg	0.8	Pituello et al. (2014)
Slow pyrolysis	300, NA, 10	72	5.3	52	32	2	8	3	4	NA	NA	Hossain et al. (2011)
Slow pyrolysis	300, 0.5, 17	62	6.0	NA	39	4	NA	7	NA	NA	4	Agrafioti et al. (2013)
Slow pyrolysis	400, NA, 10	63	4.9	63	20	1	4	2	4	NA	NA	Hossain et al. (2011)
Slow pyrolysis	450, 1, 16–19	NA	7.2	67	22	NA	NA	2	0.6	21 g/kg	7	Pituello et al. (2014)
Slow pyrolysis	450, 4, 3.3	47	NA	NA	29	NA	NA	NA	NA	7%	NA	Huang et al. (2018)
Slow pyrolysis	500, 25	54	7.1	73	18	0.7	4	2	3	5%	31	Zielińska et al. (2015)
Fast pyrolysis	500, NA	28	9.0	65	19	1	8	4	0.2	NA	NA	Arazo et al. (2017)
Slow pyrolysis	600, 25	51	11.0	77	18	0.4	1	2	4	5%	24	Zielińska et al. (2015)
Slow pyrolysis	700, 25	48	12.2	79	18	0.2	0.7	1	4	6%	54	Zielińska et al. (2015)
Slow pyrolysis	700, NA, 10	52	12.0	72	20	0.5	NA	1	6	NA	NA	Hossain et al. (2011)

(continued)

Table 10.2 (continued)

Process for biochar production	Experimental conditions T_p[a], RT[b], HR[c]	Yield (%)	pH	Ash (%)	C (%)	H (%)	O (%)	N (%)	S (%)	P (% or g/kg)	Surface area (m^2/g)	Reference
Gasification	850, 0.57, NA	36	NA	74	21	0.5	NA	1	NA	NA	NA	Freda et al. (2018)
Fast pyrolysis	900, 0.033, NA	13	NA	52	33	NA	27	NA	1	3%	27	Deng et al. (2017)

[a] T_p refers to pyrolysis temperature (°C)
[b] RT refers to residence time (h)
[c] HR refers to heating rate (°C/min)
[d] NA refers to not available

significant role in the variability of the OFMSWD (Alibardi and Cossu 2015). In contrast, Davidsson et al. (2007) showed minor effects in chemical composition of the OFMSWD collected from different origins.

Table 10.3 shows the chemical and physical composition of biochar produced from different OFMSWD at various production temperatures. The OFMSWD is usually rich in Cu and Zn (Pituello et al. 2014), which further concentrate after the anaerobic digestion of the organic waste (Tampio et al. 2016). Direct use of this OFMSWD sludge in the field may be restricted by the presence of odors, mainly volatile organic compounds (VOCs), and potential soil contamination by leachate (Cesaro et al. 2019). Hence, a digestate treatment to stabilize the OFMSWD via thermal processes (e.g. pyrolysis and gasification) (Garlapalli et al. 2016) is often performed to eliminate the organic compounds, reduce the sludge quantities and obtain valuable bioproducts (i.e. biochar, bio-oil and syngas).

10.3 Characterization of Organic Waste Digestate-Derived Biochars

10.3.1 Physicochemical Properties

Biochar derived from different bio-sources and pyrolyzed under several conditions shows a wide range in chemical compositions, e.g. carbon, hydrogen, nitrogen, ash, and metal content. The nature of the feedstock and the pyrolysis temperature are the two most important parameters that strongly influence the chemical properties of biochar. Low temperature biochars (300–400 °C) contain several oxygen functional groups that can interact with inorganic or polar organic chemicals through electrostatic forces and precipitation, whilst biochars produced at high temperature (500–900 °C) show high hydrophobicity which is likely to bind with organic contaminants (Ahmad et al. 2014).

The main components of organic materials are water, hydrocarbons (HCs), and tars (condensed polyaromatic compounds). Antal et al. (2003) demonstrated that C, H and O contained in biochar tends to vaporize into H_2O, H_2, CO and CO_2 with increasing temperature. Typically, C and N are volatilized during pyrolysis, and higher C:N ratios in biochar than in feedstocks are observed (Karaj et al. 2011; Nartey and Zhao 2014; Yuan et al. 2015). In general, the volatilization of N and K occurs at low temperatures, while P, S, Ca and Mg tend to mobilize at higher temperature, and metal elements like Fe and Mn are likely to remain in the biochars (Rodriguez 2010).

Biochar produced from SSD and OFMSWD have higher ash contents than biochar obtained from wood and crop residues (de la Rosa et al. 2014; Pituello et al. 2014). High ash contents in biochars can result from large mineral fractions contained in the feedstock. de la Rosa et al. (2014) demonstrated that 69.5% of ash was found in sewage sludge-derived biochar, whilst biochar made from wood

Table 10.3 Properties of biochars derived from the organic fraction of municipal solid waste digestate

Process for biochar production	Experimental conditions Tp[a], RT[b], HR[c]	Yield (%)	pH	Ash (%)	C (%)	H (%)	O (%)	N (%)	S (%)	P (% or g/kg)	Surface area (m^2/g)	Reference
Slow pyrolysis	250, 1, 16–19	NA[d]	7.2	37	33	NA	NA	4	1	17 g/kg	0.7	Pituello et al. (2014)
Slow pyrolysis (mixed material)	300, 2, NA	92	7.8	12	40	5	53	0.3	NA	0.08 g/kg	NA	Rehrah et al. (2015)
Slow pyrolysis	350, 1, 16–19	NA	7.6	44	34	NA	NA	4	0.9	20 g/kg	5	Pituello et al. (2014)
Slow pyrolysis	400, 0.33, NA	NA	8.0	6	48	12	31	1	0.1	NA	20	Jin et al. (2014)
Slow pyrolysis	450, 1, 16–19	NA	7.4	55	29	NA	NA	3	0.8	24 g/kg	27	Pituello et al. (2014)
Slow pyrolysis	500, 0.33, NA	NA	8.5	9	59	9	20	1	0	NA	29	Jin et al. (2014)
Slow pyrolysis	550, 1, 16–19	NA	7.1	61	26	NA	NA	2	0.6	26 g/kg	77	Pituello et al. (2014)
Slow pyrolysis	600, 0.33, NA	NA	9.0	6	70	8	13	1	0.1	NA	29	Jin et al. (2014)

[a] T_p refers to pyrolysis temperature (°C)
[b] RT refers to residence time (h)
[c] HR refers to heating rate (°C/min)
[d] NA refers to not available

contained an approximately 6 times (10.6%) lower ash content. The main composition of ash is alkaline salts of Na, K, Ca and Mg (de la Rosa et al. 2014). Many studies showed that the percentages of ash in biochars increased along with higher temperature, this may result from the higher organic matter volatilization with increasing temperatures (Cantrell et al. 2012; Tsai et al. 2012; Zielińska et al. 2015). Additionally, the presence of Ca, Fe and Al oxides on the biochar solid matrix can be attributed to the precipitation of target pollutants on the biochar surface. The studies of Agrafioti et al. (2014) showed that biochars produced from sewage sludge and the organic fraction of municipal solid waste contained much higher mineral fractions (i.e. CaO, Fe_2O_3 and Al_2O_3) than biochar produced from rice husk (<1.3% *w/w*). CaO was found in both SS (17% *w/w*) and OFMSW (50% *w/w*) biochars, whereas Fe_2O_3 and Al_2O_3 were mainly found in the SS biochar (13% and 5% *w/w*, respectively), but were negligible in the OFMSW biochar (< 1.5 % *w/w*) (Agrafioti et al. 2014).

The physical characteristics of biochar, such as BET (Brunauer, Emmett and Teller) specific surface area (S_{BET}) and the crystallographic structure, also play a role in adsorption of contaminants as well as retention of water and nutrients. Rodriguez (2010) stated that biochars have a relatively large S_{BET} and high porosity, which vary depending on the type of organic material and the production conditions. Typically, micropores enhance the sorption capacity of contaminants while mesopores are mostly related to adsorption between solid and liquid phases, whereas macropores are significant for the bulk soil structure and aeration in soils. However, a higher S_{BET} may not always corresponds to a better sorption for metal elements. Agrafioti et al. (2014) showed that biochar produced from organic digestates have a higher sorption efficiency for As(V) and Cr(III) than rice husk-derived biochar even they have a much lower S_{BET} (10–30 times) than the latter. This suggests that the sorption mechanism of trace elements onto these biochars is predominated by electrostatic interactions (i.e. anionic and cationic trace elements attraction) rather than physical adsorption. Nevertheless, a high S_{BET} and pore volume can enhance a faster mass transfer between contaminants and biochar pores (Agrafioti et al. 2014).

10.3.2 Modification of Biochars

Biochars are recently applied as media for retention of organic and inorganic contaminants in soils. However, a low sorption capacity has been found in certain conventional biochars and thus a modification post-treatment to improve the sorption efficiency for target pollutants becomes necessary. Several pretreatment methods aiming to improve the surface charges of biochar can be applied, such as treatments with acidic or basic chemicals, steam activation, magnetization, and surfactant modifications (Rajapaksha et al. 2016). The selection of the treatment method for biochar depends on the type of contaminants such as hydrocarbons compounds, metal(loid) elements, anionic and cationic ions and the hydrophobicity and polarity of the biochar (Rajapaksha et al. 2016).

Activation of biochar with steam was found to have higher nutrient retention times available for plants than the raw biochar and activated biochar showed almost doubled positive effects on the soil than non-activated biochar (Borchard et al. 2012). Regarding the difficulty in removing powdered biochars from aqueous solution after the treatment, magnetic modification of biochar is an interesting technique. Devi and Saroha (2014) found that zero valent iron (ZVI) impregnated biochar composites, synthesized by $FeSO_4 \cdot 7H_2O$ as a chemical reagent and $NaBH_4$ as a reducing agent, provided simultaneous adsorption and dechlorination of pentachlorophenol.

Chemical modifications of biochars can be carried out by treatment with acidic chemicals such as phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4) and nitric acid (HNO_3), an oxidizing agent such alkaline chemicals such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) (Rajapaksha et al. 2016). H_3PO_4 is one of the common reagents used to modify chemical structures of adsorbents (Kang et al. 2011). Treating with H_3PO_4 helps to break down lignocellulose, aliphatic and aromatic biomass and further forming phosphate and polyphosphate to avoid contraction during the development of pores (Yang et al. 2011). H_2O_2, as an oxidant, has been used to modify biochar and induce more oxygen-containing functional groups, particularly carboxylic groups, on its surface (Gao et al. 2012). In addition, KOH was found to induce higher S_{BET} and more available functional groups on the biochar surface (Jin et al. 2014). Moreover, biochar treated with urea had more available N functional groups and surface basicity (Stavropoulos et al. 2008).

Regarding the improved properties of biochars after modification, the sorption capacity of the modified biochars towards both inorganic and organic pollutants have been investigated. The Pb sorption capacity was enhanced from 0.88 mg/g (raw biochar) to 22.82 mg/g on H_2O_2-modified biochar, in accordance with more carboxylic groups available on the biochar surface (Gao et al. 2012). Modification of municipal solid waste-derived biochar with KOH was found to enhance the sorption efficiency of As(V) 1.3 times, in agreement with its higher S_{BET} and more available surface functional groups (Jin et al. 2014). Rajapaksha et al. (2014) stated that removal of organic pollutants could be improved by the π-π electron donor interactions of biochar with the aromatic rings of organic pollutants. Biochar treated with urea was also found to have higher uptake rates of phenol due to better π-π dispersion interactions (Stavropoulos et al. 2008).

10.4 Applications

Biochar derived from organic waste digestate is currently considered as an effective amendment for fertilization in agriculture. According to the high carbon content in biochar, it acts as a good conditioner for soils to enhance their physical, biological and chemical properties (Ahmad et al. 2014). Biochar can retain up to 18% of water in soils, provide a nutrient sink for plants and a habitat for living organisms, thus improving soil structure and enhancing crop yields (Verheijen et al. 2010).

Apart from application of biochar as a soil amendment, it also plays a role as an active medium for pollution sinks in soils. Soil contaminants can be classified into two main groups: organic and inorganic. The most common organic pollutants are PAHs, petroleum hydrocarbons, pesticides, industrial organic solvents, pharmaceuticals (e.g. carbamazepine and diclofenac), and antibiotics (e.g. sulfamethoxazole) (Jung et al. 2013; Qiu et al. 2009; Williams et al. 2015; Xu et al. 2011; Zheng et al. 2013). The main sources of organic pollutants in soils are inappropriate anthropogenic activities such as mineral extraction, waste disposal, and spreading of fertilizer on soils (Ahmad et al. 2014; Wang et al. 2016; Zhang et al. 2015; Zheng et al. 2013).

Potential toxic metals such as Pb, Zn, Cu, Cd and Cr, and metalloids like As and Se are well-known inorganic pollutants which are non-biodegradable and persistent in the environment. Toxicity mainly involves the dissolved and bioavailable fraction of the metals, since they can be taken up by organisms (Florence et al. 1992). The release of dissolved metals to the environment can result in their transfer, bioaccumulation (i.e. accumulated in the tissue of organisms) and biomagnification (i.e. increased concentration in animals higher in the food chain) (Wuana and Okieimen 2011). Generally, the bioaccumulation of metals in ecosystems results from anthropogenic sources such as direct use of digested organic sludge as fertilizer on soils, use of pesticides in agriculture, discharge of high-metal contaminated wastewater into rivers as well as irrigation using industrial or metal mining wastewater (Tan et al. 2015; Zhang et al. 2013).

Because of the large specific surface area, high porosity and the presence of metal oxides on sludge-derived biochar, metal ions can be sorbed or precipitated onto the biochar, leading to lower concentrations of pollutants in soils and water runoff. Most organic pollutants are hydrophobic and are, therefore, preferentially retained by biochar. In addition, non-carbonized fractions on the surface of sludge-based biochar contain oxygen functional groups such as –OH, –COOH and C=O, which can effectively enhance the sorption ability for the PAHs (Waqas et al. 2014; Zielińska and Oleszczuk 2016).

10.4.1 Sorption Mechanisms

Figure 10.3 shows the main mechanisms of sorption for organic and inorganic pollutants onto the biochar surface. The main mechanisms between biochar and organic pollutants are electrostatic forces, active binding of oxygen functional groups on biochar pores with polar organic compounds and bonding of non-polar organic compounds on hydrophobic sites of biochar (Fig. 10.3). In general, organic waste-derived biochar produced at high pyrolysis temperatures possesses a higher sorption ability for hydrocarbon compounds due to their large S_{BET}, high porosity and high hydrophobicity on the biochar surface.

Sorption mechanisms between biochar and metal elements include ion exchange between these elements and Na, Ca or K present on the biochar surface, electrostatic attractions with the available surface functional groups (e.g. carboxyl and hydroxyl)

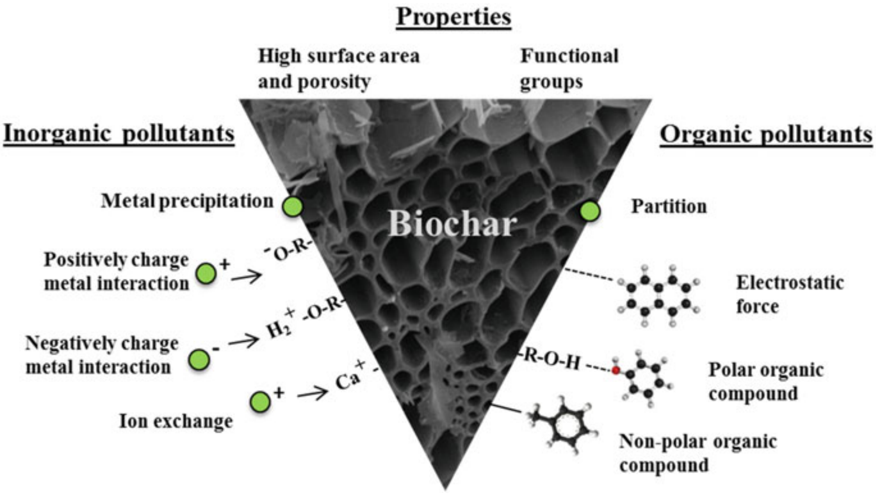

Fig. 10.3 Interactions of biochar with positively and negatively charged pollutants

and co-precipitation of metals with oxide groups of biochar and humic substances (Ahmad et al. 2014; Inyang et al. 2016; Zhang et al. 2013).

10.4.2 Environmental Factors Influencing Contaminant Retention in Soils

Zhang et al. (2013) stated that degradation of organic pollutants is significantly influenced by hydrolysis reactions, which can be enhanced by the initial solution pH, contact time, temperature and initial pollutant concentration. In addition, the presence of mineral fractions and metal oxides on sludge-based biochar surfaces also affects the sorption efficiency of organic pollutants.

The initial solution pH plays an important role in the sorption interactions between biochar and pollutants. The adsorption capacity of methylene blue on municipal sewage sludge-derived biochar was enhanced when the pH was increased from 3 to 8 (Fan et al. 2016). This indicates that alkaline conditions (at high pH conditions) favored the sorption of methyl blue on the biochar via electrostatic interactions. Similarly, Oh and Seo (2016) reported significant increases of the sorption efficiency of biosolid-derived biochar for halogenated phenols (e.g. triclosan) or pharmaceuticals (e.g. ibuprofen) when the pH was adjusted from 4 to 7. In addition, they found that the sorption of halogenated phenols is clearly related to the chemical and physical properties of the biochar (i.e. carbon content and specific surface area) and properties of the halogenated phenols (i.e. hydrophobicity) (Oh and Seo 2016).

The adsorption and partitioning of organic pollutants in soils are also affected by the clay minerals and the organic carbon content present in the native soil (Ahmad et al. 2014; Zhang et al. 2015). Zielińska and Oleszczuk (2016) found that the presence of dissolved organic carbon (DOC) and clay minerals in the soil play also a role in reducing the sorption ability of phenanthrene and pyrene by sewage sludge-derived biochar. Zhang et al. (2015) investigated that with the same biochar content, a low organic carbon content in the soil exhibited a 10 times higher adsorption coefficient (K_f) than soil with a high organic carbon content, and 98 times higher compared to the control soil. This shows that biochar enhances more the sorption ability of soils with a low organic carbon content.

Table 10.4 shows the sorption characteristics of organic waste digestate-derived biochar for organic and inorganic contaminants. With different composition in the feedstock, biochar can behave differently in the sorption interaction (Table 10.4). The mobility of Cu is significantly affected by the organic carbon content in biochar (Beesley et al. 2010). Yang et al. (2016) studied the effect of coexisting Al on P sorption in acidic polluted soils upon the addition of biochar made from sewage sludge. Al was shown to reduce the on the biochar via pH buffering against biochar alkalinity (Yang et al. 2016). They also reported the enhancement of Pb-K co-precipitation at lower pH and coexisting Al, whilst the co-precipitation of Pb-P on sewage sludge biochar was the dominant Pb sorption mechanism at higher pH (Yang et al. 2016).

10.4.3 Effect of Production Temperature on Biochar Properties

By varying the production temperatures, unequal effects on physicochemical properties of organic sludge-based biochar have been observed (Pituello et al. 2014). Generally, the pH value increases along higher pyrolysis temperatures due to the volatilization of some acidic functional groups during the pyrolysis (Laghari et al. 2016). The pH of digested organic waste biochar ranges from 7 to 11 in most cases. Pituello et al. (2014) found almost neutral pH on both municipal organic waste and sewage sludge digestate-derived biochars at production temperatures between 250 and 550 °C, whereas Zielińska et al. (2015) reported a higher pH of around 11–12 on sewage sludge biochar at pyrolysis temperatures from 600 to 700 °C (Table 10.2). In addition, biochars produced at higher temperatures possess higher specific surface areas, while biochar yields decrease along higher operation temperatures (Tables 10.2 and 10.3). Kim et al. (2013) reported large increases in pH and BET surface area (S_{BET}) at pyrolysis temperatures from 400 to 600 °C, leading to an enhancement of cadmium (Cd) sorption onto biochar. However, opposite results have been observed by Ding et al. (2014) as the sorption of lead (Pb) was reduced from 21 to 6.1 mg/g when the pyrolysis temperature increased from 250 to 600 °C.

Table 10.4 Sorption characteristics for organic and inorganic contaminants on biochar produced from organic waste digestate

Biochar feedstock	Pollutant	pH	CR[a], contact time	Isotherm/ kinetic models	Adsorption capacity	Main mechanisms	Reference
Municipal solid waste digestate (500 °C)	As(V)	6.0	5–400 mg/L, 30 h	Langmuir/ PSO[b]	24.49 mg/g	Surface complexation with O-contained functional groups (e.g. carboxylic and phenolic); physical sorption via surface area and pore volume of biochar	Jin et al. (2014)
Municipal solid waste digestate + KOH (500 °C)	As(V)	6.0	5–400 mg/L, 30 h	Langmuir/ PSO	30.98 mg/g		
Municipal organic waste digestate (300 °C)	As(V)	6.0–7.7	90 μg/L, 72 h	Freundlich/ PSO	3.54 μg/g	Adsorption of As(V) with mineral fractions of biochar (i.e. CaO, Fe_2O_3 and Al_2O_3); electrostatic interactions between negative surface charge of biochar and Cr(III) cations	Agrafioti et al. (2014)
	Cr(III)	7.0–9.5	170 μg/L, 72 h	Freundlich/ PSO	42.37 μg/g		
Sewage sludge (300 °C)	As(V)	6.0–7.7	90 μg/L, 72 h	Freundlich/ PSO	4.25 μg/g		
	Cr(III)	7.0–9.5	170 μg/L, 72 h	Freundlich/ PSO	30.12 μg/g		
Waste-art-paper digestate (300 °C)	Pb	5.0	20–400 mg/L, 24 h	Langmuir/ PSO	51.2 mg/g	Precipitation of Pb with carbonate to form $PbCO_3$ and $Pb_2(OH)_2CO_3$ on biochar surfaces	Xu et al. (2017)
Municipal sewage sludge + tea waste (300 °C)	Methylene blue	2.0–11.0	50–150 mg/L, 24 h	Langmuir/ PSO	12.58 mg/g	Endothermic adsorption; electrostatic interaction; ion exchange; surface complexation	Fan et al. (2016)
Paper mill sludge (800 °C)	Tricaine methanesulfonate	7.0–7.5	10–500 mg/L, 500 min	Freundlich/ PSO	87.4 mg/g	The p–p interactions between aromatic structure of tetracycline and graphite-like sheets of biochar	Ferreira et al. (2017)

[a] CR refers to concentration range

[b] PSO refers to pseudo-second-order

This can be attributed to the loss of oxygen-containing functional groups at higher pyrolysis temperatures.

During pyrolysis, the organic materials degrade to volatile matter, resulting in mass reduction and shrinkage when converted into biochars (Rodriguez 2010). In addition, lower volatilization rates of the C content than the O, N and H contents were observed at higher operating temperatures, leading to a decrease in the H/C, O/C and (O+N)/C ratios. The H/C ratio represents the degree of carbonization of biochars as H is primarily associated with organic substances within biomass: the lower H/C ratio results in a higher carbonized biochar (Tan et al. 2015). The lower O/C ratio of biochar demonstrates the higher aromaticity and hydrophobicity on its surface, whereas the reduction of biochar polarity is affected by a low (O+N)/C ratio due to a decrease of polar functional groups at higher pyrolysis temperatures (Chen and Zhou 2008; Chun et al. 2004).

The structural modifications of organic sludge-based biochars start from 350 to 550 °C due to the decomposition of macromolecules (i.e. proteins and carbohydrates), resulting in the disappearance of amines and carboxyl groups and the formation of amorphous carbon (Pituello et al. 2014). Moreover, Pituello et al. (2014) stated that C is rearranged into more complex structures of amorphous and aromatic rings, leading to a higher biochar stability than its raw feedstock. In addition, the aromatic C with a variety of functional groups predominates in biochar produced at 350 °C (Pituello et al. 2014), which may induce sorption interactions between the biochar and target contaminants. Zielińska and Oleszczuk (2016) reported higher retention of phenanthrene and pyrene in soil amended with sewage sludge-derived biochar produced at higher pyrolysis temperatures (i.e. from 500 to 700 °C). On the other hand, Oh and Seo (2016) found that the adsorption efficiency of halogenated phenols or pharmaceuticals was not influenced by the pyrolysis temperature of the biochar.

10.4.4 Remediation of Organic and Inorganic Contaminants in Soils

10.4.4.1 Remediation of Organic Contaminants

In recent studies, biochar produced from digested organic sludge has been recognized as a potential tool for the sorption of organic pollutants in soils (Khan et al. 2013; Waqas et al. 2014; Zielińska and Oleszczuk 2015). The presence of micropores and mesopores on the biochar surface as well as aromatic structures and functional groups help to retain toxic contaminants like PAHs, atrazine and sulfamethazine in soils (Cao et al. 2011; Rajapaksha et al. 2014; Vithanage et al. 2014). Soil amended with biochar reduced the dissolved concentrations of phenanthrene and pyrene compared to soils without biochar addition (Zielińska and Oleszczuk 2016). Addition of 5% w/w sewage sludge-derived biochar to soil enhanced the sorption capacity of phenanthrene from 8.3 to 20.3% (Zielińska and

Oleszczuk 2016). Also, the sorption of pyrene in soil amended with sewage sludge-derived biochar was increased from 14.5 to 31.7% with respect to control soil (Zielińska and Oleszczuk 2016). Mukherjee et al. (2016) investigated the potential adsorption-desorption of pesticides (i.e. bentazone, boscalid and pyrimethanil) using digestates from a biogas plant (i.e. maize silage, manures and urine) in a loamy sand soil. The partition coefficient (K_{oc}) values of the pesticide boscalid were approximately 5 times higher in soil mixed with 30% digestate and 5% biochar compared to the control soil.

Application of sewage sludge and its derived biochar to soils significantly decreased the available PAHs concentration (Waqas et al. 2014). Also, supplementation of sludge and sludge-based biochar decreased the bioaccumulation of PAHs into *Cucumis sativa* L. by 44–57% with biochar amendment and 20–36% with sewage sludge amendment (Waqas et al. 2014). These results show that biochar promotes a higher efficiency in the immobilization of PAHs than the raw sewage sludge digestate during soil remediation. However, a higher uptake rate of terbuthylazine in biochar amended in low organic carbon soil was found compared to soil with a high organic carbon content. This suggests that the presence of dissolved organic carbon in soil may block the biochar pores, resulting in lower accessibility of pesticides to biochar (Ahmad et al. 2014).

10.4.4.2 Remediation of Inorganic Contaminants

In situ treatment of metals by addition of alkaline chemicals (i.e. lime) or natural organic waste materials as soil amendments has been noticed to stabilize metal elements in soils (Gadepalle et al. 2007; Kumpiene 2010). Biochar can be used as a tool to immobilize metals in contaminated soils through several interactions as illustrated in Fig. 10.3. Extensive studies on biochar applications as carbonaceous materials for the stabilization of inorganic pollutants in soil have been performed (Ahmad et al. 2014; Mohan et al. 2014; Zhang et al. 2013).

Table 10.5 shows the application of organic waste digestate-derived biochar for organic and inorganic contaminant remediation. From Table 10.5, Méndez et al. (2012) showed that the application of sewage sludge-derived biochar increases the environmental safety of soils. Lower metal leaching of Cu, Ni and Zn from biochar-soil amendment than soil mixed with raw sewage sludge digestate occurred after 200 days of incubation (Méndez et al. 2012). In addition, sewage sludge-derived biochar has also been reported to increase soil respiration with respect to the control soil (Méndez et al. 2012). Conversely, Khan et al. (2013) showed that sewage sludge-derived biochars facilitate adsorption of As, Cr and Pb in soils. However, Cu, Zn and Cd tended to mobilize due to higher availability of these elements in biochars (Table 10.3). Thus, the supplement of sludge-based biochar to soils should be verified before field applications.

Table 10.5 Application of organic waste digestate-derived biochar for organic and inorganic contaminant remediation

Inorganic contaminant	Biochar feedstock	Pyrolysis temperature (°C)	Effect	Reference
As, Cd, Cr, Co, Cu, Ni, Pb and Zn	SSD	500–550	Immobilization of As, Cr, Co, Ni and Pb (rise in pH) but mobilization of Cu, Zn, and Cd in soils	Khan et al. (2013)
Cu, Cd, Ni, Zn and Pb	SSD	500	Biochar increased soil respiration compared to control soil but lower rate than soil with SSD. Lower leaching of Cu, Ni and Zn in soil-biochar amendment than in soil amended with SSD	Méndez et al. (2012)
Cu, Pb, Zn, Cd and Cr	SSD	450	Biochar enhanced soil fertility and crop productions. Reduction of metals availability for plant which decrease the toxicity in contaminated soil	Liu et al. (2014)
As, Cd, Cu, Pb and Zn	SSD	550	Soil + SSD biochar: significantly decreases of As, Cu and Pb concentrations Soil + SSD amendment: increases in metal concentrations	Waqas et al. (2014)
Phenanthrene (PHE) and pyrene (PYR)	SSD	500 and 700	Application of 5% *w/w* biochar enhanced 2.4- and 2.2-times higher sorption capacity for PHE and PYR, respectively in soils. The sorption increased with biochar produced at higher temperature. DOC and clay minerals present in the soils reduced the efficiency of PHE and PYR sorption by biochar	Zielińska and Oleszczuk (2016)
Polycyclic aromatic hydrocarbons (PAHs)	SSD	550	PAH concentrations in biochar significantly decreased after pyrolysis. Biochar addition to soil reduced availability and bioaccumulation of PAHs into *Cucumis sativa* L.	Waqas et al. (2014)
Halogenated phenols	OFMSWD	400	The sorption efficiency of biochar effectively increased at pH 4 or 7. Surface area and carbon content of biochar and hydrophobicity of halogenated phenols mainly affect the phenol sorption	Oh and Seo (2016)
Pharmaceuticals (i.e. ibuprofen)	OFMSWD	400	pH significantly affected the sorption capacities of biochar for ibuprofen due to the point of zero charge (PZC) of sorbents and deprotonation of the pharmaceutical	Oh and Seo (2016)

10.4.5 Bioavailability of Trace Elements with Biochar Addition

The mobility and fate of metals in contaminated soil amended with biochar have been widely studied (Beesley et al. 2014; Houben et al. 2013; Kargar et al. 2015; Nartey and Zhao 2014). The effects on metal bioavailability in soils vary depending on the nature of the biochar feedstock and type of metal (Zhang et al. 2013).

Addition of organic wastes as soil amendments to contaminated soils can increase the bioavailability of metal(loid)s (Nartey and Zhao 2014). Tampio et al. (2016) reported that plants had a higher metal contents and lower N bioavailability upon amendment of a soil with a mixture of vegetable waste digestate and activated-sludge. However, addition of biogas digestate from food waste and the organic fraction of municipal solid waste to the soil showed positive outcomes as they provided more bioavailable nutrients in the soil (Tampio et al. 2016).

Biochar produced from municipal wastewater treatment sludge contains mineral oxides and a carbonized organic fraction which serves as a good sorbent for metals (Zhang et al. 2016). The precipitation of metal (Pb and Zn) phosphate and more available sorption sites were observed after aging of biochar for 30 days, ensuring durability of metal immobilization in sludge-derived biochar during soil amendment (Zhang et al. 2016). Campos and De la Rosa (2020) reported that Cu and Pb were effectively immobilized in soils amended with biochar, which affirmed the promising potential of biochar to recover land polluted with heavy metals. It is important to understand that one type of biochar cannot be representatively used as sorbent to remediate all types of metals. Hence, the use of solid digestate-derived biochar in soils should be verified for each particular biochar type to ensure the environmental safety for field application.

10.5 Potential Effects of the Application of Sludge-Derived Biochars to Soils

10.5.1 Stability and Durability Effect of Biochars in Soils

It is important to understand the stability of biochar in a soil environment to quantify its persistence in soils and to be able to manage its fate in the environment in a long term, e.g. for soil nutrient supplementation and enhancement of the water holding capacity. Biochar can be degraded by biotic (e.g. microbial incorporation or oxidation in carbon respiration) and abiotic (e.g. chemical oxidation or solubilization) processes (Kuppusamy et al. 2016). The degradation of digestate derived biochar is influenced by the available functional groups on the biochar surface and the aromaticity of the adsorbent (Kuppusamy et al. 2016).

The molar ratio of oxygen to carbon (O:C) indicates the stability of biochar in which black carbon is present (Spokas 2010). The stability of biochar increases with lower O:C ratio and biochar with an O:C ratio lower than 0.2 shows a half-life of more than a thousand year, whilst a reduction of the biochar half-life to less than a hundred year has been observed with an O:C ratio higher than 0.6 (Kuppusamy et al. 2016). Also, the pyrolysis temperature and feedstock source are two main parameters affecting the O and C content of a biochar (Spokas 2010). The O:C ratio is likely to provide a strong indicator of biochar stability in soil rather than solely the operation conditions or feedstock type (Spokas 2010). In addition, the biochar persistence in soil can be predicted from the fraction of aromatic rings and non-aromatic compounds present in the biochar (Singh et al. 2012). Hernandez-Soriano et al. (2016) observed that addition of biochar to loamy soil slowed down the soil respiration rate compared to soils amended with raw organic residues during 237 days of incubation. These results showed that the carbon metabolism in soil amended with biochar enhanced the carbon stability in the soil (Hernandez-Soriano et al. 2016). After 4 years of soil-biochar incubation in a field experiment, a significant increase of the C:N ratio of the microbial biomass was found in biochar-amended soil (Zhang et al. 2014). Additionally, they suggested that biochar can reduce the variability of the environmental conditions for microorganisms and thus decrease the temporary fluctuations in C and N dynamics.

Apart from the biochar applications as soil amendments, the use of biochar as active sorbent to retain contaminants in soils in a long term has also been reported. Liu et al. (2019) found that after 240 days of sorption equilibration of lincomycin (an antibiotic) by biochar, about 75% of sorbed lincomycin on the biochars could not be extracted anymore with acetonitrile/methanol extractant. This suggests that biochar has a great potential to retain antibiotics in a long term. Moreover, Stefaniuk et al. (2017) found a significant decrease in the PAHs concentrations after a long-term incubation of sewage sludge and/or biochar in the soil (1.5 years), which were reduced by 19% upon the addition of sewage sludge and by 35% with the addition (5.0%) of sewage sludge and biochar. He et al. (2019) found that a soil incubation with sewage sludge derived biochar can immobilize Pb and Cu in a long term (2 years).

10.5.2 Biological Assessment

Table 10.6 shows possible effects of sludge-derived biochar addition to soils. The possible effects of soil biota upon addition of sludge-derived biochar to contaminated soils can be determined in batch sorption tests and soil incubations. In general, the biological assessment is performed to illustrate the biochar efficiency to reduce the contaminant levels using plants, earthworms or bacteria as test organisms because these are primary producers and consumers in the food chain and can transfer pollutants contained in fatty tissues to predators or humans.

Generally, contaminated land sites are poorly fertilized soils which have little or no cover of the vegetation on the top soil (Beesley et al. 2011). Application of biochar on these polluted sites can reduce the concentration of pollutants in the soil

Table 10.6 Possible effects of the application of sludge-derived biochar to soils

Material	Dosage/soil type	Effect		Reference
		Positive	Adverse	
Sewage sludge (SS) and its derived biochar sewage sludge (BSS)	1:0.3 *w/w* (21 kg SS + 6 kg woodchips) + 8% BSS / SS and BSS	Increased numbers of cocoons by 213% after 4 weeks, and earthworms by 11 times before composting and 5 times after composting. Reduced bioavailability of Cd and Zn to *E. fetida*	Increased bioavailability of Cr to *E. fetida*	Malińska et al. (2017)
Wastewater sludge biochar	0.907 kg/m^2 / Agricultural soils (chromosol)	Increased cherry tomatoes yield by 64% and increased P and N available in soils Metal bioavailable in biochar below the Australian limit level for food	Not reported	Hossain et al. (2010)
Sewage sludge (SS) and its derived biochar (BSS)	1.36 kg/m^2 (7.5 t/ha SS + 0.68 kg/m^2 BSS) / Tropical clay soil	Increased maize growth and total biomass by 49% and 329%, respectively. Decreased Pb, Cu and Zn concentrations in maize by 22% compared to SS treatment alone	Not reported	Gwenzi et al. (2016)
Sewage sludge biochar, *Miscanthus* and pine wood biochar	3% *w/w* / Tropical soils (Acrisol and Ferralsol) planted with proso millet (*Panicum miliaceum* L.)	Increased fungi to bacteria ratio in soils amended with sewage sludge biochar	Unchanged ratio of fungi to bacteria in soils treated with biochar	Paz-Ferreiro et al. (2015)

pore water (Beesley et al. 2011). Biochar added in agricultural soils can provide positive impacts on plant growth such as maize (Agegnehu et al. 2016; Gwenzi et al. 2016) due to the liming effect and a longer nutrient retention time in the soils (Sohi et al. 2010). Conversely, adverse effects on plant growth were found by van Zwieten et al. (2010) since biochar-soil amendment induced reduction of biomass production by wheat and radish.

Earthworms serve as ecosystem engineers as they play important roles in soils, i.e. they accelerate organic matter degradation, increase nutrient availability to plants and nutrient recycling in ecological systems (Beesley et al. 2011). Therefore, earthworms are considered as vital soil animals for which a reduction of contaminants becomes significant to avoid an over-uptake (Sizmur et al. 2015). From Table 10.6, addition of sewage sludge-derived biochar in a mixture of sewage sludge and wood chips integrated with vermicomposting showed 11- and 5-times higher amounts of juvenile earthworms, respectively, before and after composting (Malińska et al. 2017). Also, the concentrations of Cd and Zn bioavailable to *E. fetida* was reduced with biochar application in the pre-composting of sewage sludge (Malińska et al. 2017). However, increased Cr concentrations were observed during biochar-vermicompost treatment (Malińska et al. 2017).

10.5.3 Agronomic Benefits of Organic Waste Digestate-Derived Biochars

Soil quality deterioration is a worldwide problem and has been particularly observed in agricultural areas. Addition of organic amendments to soils may be beneficial to restore the soil quality. Addition of labile organic materials to soil can provide bioavailable nutrients for crops and soil microbiota like microbes and fungi. However, a low nitrogen content in the organic substrates can limit the plant growth (Sohi et al. 2010). Supplementation of alkaline biochar to acidic soils can enhance crop yields through increasing soil pH and reducing acidity constraints which inhibit the plant productivity (Ahmad et al. 2014). The efficiency of biochar amendment depends on the biochar buffering capacity that varies with the nature of feedstock and the pyrolytic temperature (Ahmad et al. 2014; Tables 10.2 and 10.3).

The use of biochar, compost and their combination in a tropical agricultural soil has been studied: significant increases in total N, available P, nitrate nitrogen and ammonium nitrogen in biochar-compost-soil systems compared to the control were found (Agegnehu et al. 2016). Besides, biochar mixed with compost increased crop biomass by 10–29% and helped to reduce N_2O emissions compared to other treatments (Agegnehu et al. 2016). Gwenzi et al. (2016) reported that with the application of sewage sludge mixed with its derived biochar (15 or 7.5 t/ha of each organic amendment) on tropical clay soil showed a 47% enhancement of maize growth and was comparable to inorganic fertilizer (49%). Additionally, adding biochar and sewage sludge in the tropical clay soil reduced Pb, Cu and Zn uptake by the maize plants by 22% with respect to the presence of sludge alone during the treatment (Gwenzi et al. 2016).

Supplementation of 12% biochar significantly reduced total nitrogen losses and GHGs emissions, i.e. CH_4, N_2O and NH_3, respectively by 92.85, 95.14 and 58.03% during sewage sludge composting (Awasthi et al. 2016). However, low dosage (2–6%) of biochar added to compost released more CH_4 and N_2O than the control treatment (Awasthi et al. 2016). In addition, the humic (42%) and fulvic (28%) acid concentrations increased during biochar-compost treatment with 12% biochar addition (Awasthi et al. 2016). van Zwieten et al. (2010) applied paper mill waste sludge-derived biochar in two different agricultural soils, i.e. a ferrosol (high agricultural potential) and calcarosol (low-moderate agricultural potential) in a greenhouse study. The results showed high N uptake rates by wheat crops in biochar-ferrosol amended soil and 250% increases in biomass production of soybean and radish compared to the control (van Zwieten et al. 2010). However, the calcarosol showed varied results, i.e. increases in soybean biomass but decreases of wheat and radish biomass (van Zwieten et al. 2010).

10.5.4 Possible Adverse Effects

Biochar application to soil can alter microbial activities since the degradation of soil organic carbon provides energy for microbes, with addition of hardly degradable carbon (i.e. biochar) to the soil. Thus, possible adverse effects on the microbial community in soil can occur, generally depending on the types of organic residues as feedstock, biochar dosage and time interval of its application (Sohi et al. 2010). Weyers and Spokas (2011) reported a reduction of earthworm biomass when organic sludge-derived biochars were added to soils.

It is also important to consider priming effects when biochar is applied to soil. The priming effect is a phenomenon occurring when higher rates of soil organic carbon decomposition take place corresponding to more organic materials supplemented to the soil. This enhances the activity of the microbial population due to the release of energy during the decomposition of organic substrates, which accelerates the mineralization of soil organic carbon (Fontaine et al. 2003). Positive priming effects were observed by faster decomposition rates of soil carbon when amended with biochar, resulting in microbial activity enhancement and more hydrolysis reactions, which effectively increase with higher soil pH (Ahmad et al. 2014; Kuzyakov et al. 2009). In contrast, a negative priming effect can occur when biochar adsorbs dissolved organic carbon in soils, which lowers the decomposition rates and subsequently reduces the microbial population.

10.6 Future Challenge

Short-term experiments (less than a few years) confirm the potential use of organic sludge biochars as soil amendments and sorbing materials in the environment. However, based on pot experiments in small scale, more studies on field sites are necessary to confirm if similar outcomes are achieved. Also, long-term studies of sludge biochar application in soils are lacking and yet to be further developed. The studies on the longevity of microbial activities in soil-biochar systems and the durability effect of organic sludge biochar in the long-term should be further achieved as well as the regeneration of aged biochar.

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Part V
Integration of AD in Biorefineries

Chapter 11
Integration of Bio-electrochemical Systems with Anaerobic Digestion

M. M. Ghangrekar, S. M. Sathe, and C. N. Khuman

Abstract Anaerobic digestion is a well versed technology for treating organic waste and converting the organic matter into biogas to be subsequently used as fuel or converted into electricity. Over the years, anaerobic digestion has been widely used for the treatment of industrial and domestic wastewaters as well as organic solid waste, while simultaneously generating biogas. On the other hand, bio-electrochemical systems (BES) are one of the prominent and upcoming ways of harnessing organic matter into bioelectricity and industrially valuable products, such as hydrogen, methane, biofuels, and hydrogen peroxide. This chapter reviews the hybridization of BES and anaerobic digestion for enhanced pollutant removal and pollutant monitoring in the form of nutrient removal and recovery, polishing of anaerobically treated effluent, biogas upgrading, application of biosensors, and merger of BES in anaerobic digestion for emerging contaminant removal. Additionally, a brief discussion on the future prospect of the synergy of these two technologies has also been highlighted.

Keywords Anaerobic digestion · Bio-electrochemical systems · Bioenergy · Microbial fuel cell · Resource recovery

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11.1 Introduction

The urge of finding alternative and sustainable energy sources to replace ever-depleting fossil fuels is a major global issue for sustainable development. The use of fossil fuels is not environmentally friendly due to the emission of harmful gases into the atmosphere. Therefore, the use of renewable energy sources such as solar, wind, geothermal, and tidal are becoming increasingly popular now-a-days (Jingura and Matengaifa 2009). Organic waste or biomass is also one of the promising renewable energy sources, which is considered as an environmentally friendly approach (Berndes et al. 2003; Lin et al. 2018; Stephen and Periyasamy 2018). It is estimated that 1 kg of carbohydrates represents 1.06 kg of chemical oxygen demand (COD), equivalent to 4.41 kWh of energy (Rabaey and Verstraete 2005).

Anaerobic digestion (AD) is one of the efficient and proven methods for the treatment of organic matter present in solid waste and wastewater. It is specifically preferred for the treatment of high strength waste in terms of COD due to its low sludge generation, low energy requirement, and formation of valuable methane as end product (Chen et al. 2008; Kiyasudeen et al. 2016). The AD of organic matter takes place via hydrolysis, acidogenesis, acetogenesis, and methanogenesis, resulting in the generation of biogas, which comprises of CH_4 and CO_2 and other gases such as H_2S, H_2 and N_2 (Gujer and Zehnder 1983; Zhang et al. 2014a). Methane generated from the process can be either used as fuel or converted into electricity. AD is a complex process involving a plethora of microorganisms, in which the end-products of the initial bacterial reaction are often the substrate for subsequent bioconversion. Hence, a balance between the microbial population and the substrate concentration is vital for the stable operation of AD. In the initial three stages (hydrolysis, acidogenesis, and acetogenesis), the organic matter is broken down into smaller molecules via the formation of long chain volatile fatty acids (VFAs) to finally short chain VFA and acetic acid; whereas, in the final stage (methanogenesis), methane is produced by the methanogens (acetoclastic and hydrogenotropic) (Gavala et al. 2003; Gude 2018).

The process of AD is vastly affected by variation in temperature, substrate pH, hydraulic retention time (HRT), organic loading rate (OLR), and C/N ratio (Mao et al. 2015). Apart from this, the failure of AD is often linked to toxic effects induced by inhibitory substances. The presence of ammonia, sulfur, heavy metals, other ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}), and organic compounds (such as alkyl benzenes, chlorophenols, surfactants, and alkanes) beyond the threshold limit can cause an imbalance in the AD (Chen et al. 2008). Any imbalance in the process can be related to reduced CH_4 generation and deteriorated organic matter removal efficiency (Chen et al. 2008). This necessitates the requirement of pre-treatments to make the waste fit for treatment in AD.

Bio-electrochemical systems (BES) are a new generation of wastewater treatment techniques capable of recovery of valuables and/or bioenergy production. In the anodic and cathodic chambers of a BES, respectively oxidation and reduction takes place. The organic matter from the waste is oxidized in the anodic chamber using microorganisms; whereas, oxygen is reduced at the cathode to generate H_2O or H_2O_2 (Logan et al. 2006; Fu et al. 2010). The BES in various forms is capable of removing the nutrients and other organic compounds, which cannot be removed in AD. For the industrial wastewaters that contain a high concentration of the aforementioned pollutants, BES can be used as a pre-treatment prior to AD to reduce the concentration of pollutants, while for domestic wastewater BES can be used as a post treatment to AD (Vrieze et al. 2018). Although, BES have been successfully applied in lab scale investigations, upscaling a single reactor volume for field scale operation is not a feasible option owing to a high mass transfer loss and possible scavenging action by the anaerobic anodic microorganisms. Hence, from the view of upscaling, stacking of multiple BES can be considered as a way forward.

11.2 Bio-electrochemical Systems

During AD, microorganisms decompose the organic matter into simpler molecules with the release of energy in the form of electrons and protons. This energy can be harvested using a novel technology known as BES. Compared to AD, the BES is a recent technology that is capable of converting dissolved organic matter from wastewater into bioelectricity or bioenergy. Though the first instance of electricity generation using microorganisms was demonstrated by Potter in 1911 (Potter 1911), the subsequent in depth research and widespread applications were initiated only in the late twentieth century. Owing to the capability of one-step bioelectricity production, BES become an attractive option for the conversion of biomass/organic matter to electrical energy or by applying small external potential other value-added products can be recovered.

A BES is an electrochemical system catalysed by the action of microorganisms for the treatment of polluted soil and wastewater, while harvesting bioenergy or synthesizing value-added products such as biofuels, H_2O_2, H_2 and CH_4. Additionally, they have also been applied for the sequestration of CO_2 with the concurrent production of biochemical and biofuels in microbial electrosynthesis cells (Liu et al. 2005; Jeremiasse et al. 2010; Das et al. 2020). Majorly, BES may be *galvanic* as in the case of microbial fuel cells (MFCs), which allow the conversion of chemical energy of organic matter into electricity or *electrolytic* as in the case of microbial electrolytic cells (MECs), where electricity is externally supplied to the system to facilitate recovery of industrially valuable products (biohydrogen, biomethane, and hydrogen peroxide).

In a nutshell, BES consists of a single pair of electrodes or multiple pairs of electrodes, an ion exchange membrane (may not be necessary for a membrane-less BES configuration), an external load (in case of MFC), or an external power supply (in case of MEC), and microorganisms especially electrogens (Logan et al. 2006). The electrogens are capable of electron transfer to the electrodes from their cell (known as exoelectrogens) and from the electrodes into their cell (known as endoelectrogens or electrotrophs) (Semenec and Franks 2015; Kang et al. 2021).

11.2.1 Microbial Fuel Cell (or Galvanic Bioelectrochemical System)

In a typical double chamber MFC, the anode is dipped inside wastewater, while the cathode is placed in air-saturated water (aqueous cathode) or exposed to air (air cathode). The anode and the cathode are connected to an external load. The anolyte (wastewater) and the catholyte (air-saturated water or air) are separated by a proton exchange membrane (PEM) or cation exchange membrane (Fig. 11.1a). Oxidation of the organic matter occurs in the anodic chamber under anaerobic conditions using microorganisms, thereby releasing electrons, protons, and CO_2. The presence of terminal electron acceptors (generally oxygen) in the catholyte attracts the electrons towards the cathodic compartment. However, the PEM allows only the passage of protons and prohibits the flow of electrons and organic matter towards the cathode. The electrons flow towards the cathode through the external circuit and create a charge imbalance between the anolyte and the catholyte. To maintain charge equilibrium the protons flow through the PEM towards the cathode to combine with O_2 and electrons forming H_2O or H_2O_2 (Eqs. 11.1 and 11.2). Thus, electricity is harvested due to the flow of electrons through the external circuit (Kim et al. 2004; Liu et al. 2005).

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\ (E' = 0.805\ \text{V, vs.standard hydrogen electrode, SHE at pH of 7}) \tag{11.1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2\ (E' = 0.328\ \text{V, vs.SHE at pH of 7}) \tag{11.2}$$

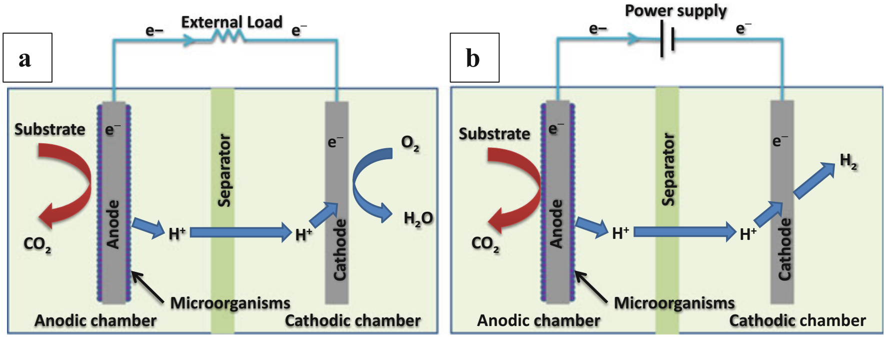

Fig. 11.1 (**a**) Typical dual-chambered microbial fuel cell and (**b**) dual-chambered microbial electrolysis cell

11.2.2 Microbial Electrolysis Cell (or Electrolytic Bioelectrochemical System)

In contrast to MFC, electrical power is externally supplied into the electrolytic BES (Fig. 11.1b). At the anode, oxidation of organic matter catalysed by microorganisms and water hydrolysis takes place. The electrons flow toward the cathode through the external power circuit, while the protons migrate to the cathode through the PEM, similar to that of MFC. The MECs are capable of producing industrial valuable products, such as H_2, H_2O_2 and organic acids, in cathodic chamber along with simultaneous removal of organic matter from wastewater in anodic chamber (Jeremiasse et al. 2010; Jafary et al. 2015). However, the energy required for bioconversion of organic matter into industrial valuable products is lesser in MEC than what is required in conventional electrochemical methods due to the availability of electrons and protons released during microbial decomposition of organic matter (Zhang et al. 2014b; Kuntke et al. 2018).

11.3 Integration of Anaerobic Digestion with Bio-electrochemical Systems

11.3.1 Integrating Bio-electrochemical System with Anaerobic Digestion for Nutrient Removal

BES have been widely explored for the removal and recovery of nutrients (nitrogen, phosphorus, sulfur) from the wastewater that cannot be completely removed using AD. These nutrients have agricultural use and since the recovery of nutrients is possible from the waste source; the BES perfectly fits into the concept of waste to wealth.

11.3.1.1 Nitrogen Removal Techniques

The presence of nutrients and common elements is vital for AD and depending on the particular concentration it can benefit or harm the digestion process. In some of the high strength waste streams in terms of COD, such as concentrate from wastewater sludge, food waste, and leachate, the concentration of total ammonia nitrogen is often considerably higher than that detected in the domestic wastewater. It was observed that a high concentration of total ammonia causes excessive inhibition of methanogenesis (Sheng et al. 2013). The digestion process in the anaerobic digester is most commonly disturbed by the sudden high ammoniacal nitrogen concentration in the influent waste. High ammonia concentrations in the influent cause a considerable increase in the VFA production resulting into reduced methane production (Borja et al. 1996). With the rapidly increasing VFA, the digester might not have enough buffering capacity to maintain the pH in the working range of 6.8–7.2 that is required for the methanogens, and can thus lead to the failure of AD. In such cases (high ammoniacal nitrogen in the influent), instead of removal of ammonia in the form of N_2 gas, its recovery (as fertilizer) can be a beneficial option, considering the valuable applications of the recovered products (ammonium sulfate, ammonium bicarbonate) in the agricultural sector.

For such wastes, the application of a specific pre-treatment technique prior to AD, which is targeted for ammonia removal, might be the best option (Kim et al. 2015a). Over the years, several techniques for the removal of nitrogen from the wastewater have been developed and implemented, which include nitrification and denitrification, anammox process, chemical precipitation, and ion exchange (Peng and Zhu 2006; Zhang et al. 2009b; Lin et al. 2016; Ma et al. 2016). For the wastes that have high nitrogen content, recovery instead of removal can be a feasible option to utilize the nitrogen for beneficial uses. In this regard, BES offers an advantage of nitrogen recovery from the waste at a lower operating cost compared with conventional systems (Zamora et al. 2017).

In the cathodic chamber of BES, the formation of hydroxyl results in an increase in pH. The transfer of NH_3 and NH_4^+ through the cation exchange membrane to the cathodic chamber of BES is due to diffusion and migration, respectively, wherein increased pH causes conversion of NH_4^+ to NH_3 in the cathodic chamber (Kim et al. 2015b). In this way, NH_4^+ ions are removed from the anolyte (waste stream). The formed NH_3 can be successively recovered in the form of ammonium sulfate or ammonium bicarbonate that can be used as a fertilizer. The ammonium sulfate can be obtained via passing gaseous NH_3 through sulfuric acid; whereas the catholyte can be further concentrated via the use of a tri-chambered system with cation and anion exchange membranes to obtain solid ammonium bicarbonate (Nancharaiah et al. 2016; Jermakka et al. 2018). The BES have been used for nitrogen removal and its successive recovery from various wastewater sources, such as urine (Kuntke et al. 2012), landfill leachate (Qin et al. 2016), effluent of sludge dewatering process (Wu and Modin 2013), and the liquid fraction of pig slurry (Sotres et al. 2015). The ammonia recovery depends on the imposed electrical potential and it was observed that under the applied potential (MEC mode), ammonia recovery is higher. Though the supplemented external energy increases the operation cost, it is still lower than electrochemical ammonia recovery methods.

In a scaled-up MEC system operated with urine as anolyte (2.6 L of each catholyte and anolyte), 31% of the total ammonia nitrogen recovery was achieved under the applied potential of + 0.5 V (against Ag/AgCl reference). The electrical energy required for the total ammonia nitrogen recovery in the aforementioned investigation was 4.9 MJ kg N^{-1} (Zamora et al. 2017). On the other hand, considering only the running electricity and fossil energy requirements, the conventional biological nitrification and denitrification process requires about 45 MJ kg N^{-1} of energy in wastewater treatment plants (Maurer et al. 2003). Though complete removal of the nitrogen fraction is not possible using BES, it can reduce the nitrogen concentration so that the effluent can be suitable for AD, without negatively affecting the digestion process.

In one of the investigations, MFC was implemented along with AD for NH_4^+ removal. In between the recirculation loop of AD, a MFC was installed with Nafion as a separator. Substrate with 77–124.4 mg of N g^{-1} of total solids was used as a feed for anaerobic digester. The MFC resulted in a reduction of the NH_4^+ concentration from 654 to 436 mg L^{-1}. The addition of a MFC caused an increase in methane yield from 136 to 173 mL CH_4 L^{-1} day^{-1}. The reduced NH_4^+ might have improved the stability of methanogenic consortia leading to an increased methane yield (Inglesby and Fisher 2012). This shows that integration of BES with AD could reduce the nutrient load thus it can be a feasible solution to prevent the failure of anaerobic digestion.

11.3.1.2 Phosphorus Removal Techniques

Phosphate removal from wastewater is accomplished commonly via chemical precipitation or biological treatment processes. The use of BES gives an edge over other biological processes due to the capability of BES to recover phosphate via the struvite precipitation at the cathode. The struvite precipitation on the cathode is possible due to a high localized pH near the cathode. Using a MFC, iron sulfate from dried sludge was reduced to orthophosphate in the cathodic chamber. Stoichiometrically calculated amounts for magnesium chloride and ammonium hydroxide were externally added to the catholyte, which results in precipitation of struvite at the cathode (Fischer et al. 2011). In another investigation, an air cathode MFC was capable of simultaneous wastewater treatment (COD removal of 76–91%) and 70–82% of phosphorus removal while attaining the maximum power density of 1–2.3 W m^{-2}. The precipitate on the aqueous side of the cathode was struvite, as confirmed by X-ray diffraction analysis. The results confirmed the capability of MFC to simultaneously treat wastewater while attaining the removal and recovery of phosphorus in the form of struvite (Ichihashi and Hirooka 2012). However, in a follow-up investigation the same research group observed that the electricity generation in MFC deteriorated with an increase in struvite precipitation on the cathode. The reduced electrical output might be attributed to the mass transfer limitation at the cathode, caused by a layer of struvite precipitates (Hirooka and Ichihashi 2013). A possible solution for this issue can be the operation of a two-stage system comprising of a separate chamber for struvite precipitation, in order to prevent the deteriorated electrical performance of BES in the long run (Jain and He 2018).

In a different investigation, the effluent from an anaerobic digester was used as a substrate for a MEC with a fluidized cathode electrode for nutrient recovery. With an applied voltage of 1 V, the total phosphorus concentration was reduced to 13 mg L^{-1} compared with 46 mg L^{-1} in the open circuit condition. The phosphorus removal was due to struvite precipitation in the cathodic chamber of MEC (Cusick et al. 2014). A BES developed by Zhang et al. (2014b) showed a capability of 83.4% and 52.4% removal of ammonium nitrogen and phosphate, respectively, under the applied voltage of 0.8 V. The removal was observed to be considerably higher compared with open circuit conditions, which contributed in 3.6 and 21.1% removal of ammonium nitrogen and phosphate, respectively. This confirmed that the current generation is important for nutrient removal and higher current due to externally applied voltage can improve the nutrient removal efficiency in BES (Zhang et al. 2014b).

11.3.1.3 Sulfur Removal Techniques

Many of the industrial wastewaters are the prime source of sulfate. Chemical precipitation, membrane filtration and biological treatments using sulfate reducing bacteria are a common way for the removal of sulfate from sulfate laden wastewater.

Although domestic wastewater has a low sulfate concentration, the converted sulfide remains dissolved in the anaerobically digested effluent that lowers the overall performance. Hence, a post treatment is also essential to eliminate the sulfide from the wastewater. Although sulfate in low concentrations does not contribute to toxicity, a high concentration of sulfate can impart salinization of freshwater bodies (Lens et al. 1998; Sharma and Kumar 2020). During the AD of wastewater, sulfate is reduced to sulfide by sulfate reducing bacteria. The generated sulfide can be inhibitory to the methane producing bacteria, which reduces the rate of methanogenesis, and decreases the methane yield by competing with the available carbon and/or hydrogen (McCartney and Oleszkiewicz 1991). Hence, the sulfate concentration in the influent wastewater needs to be controlled to prevent the inhibitory effect on AD. The BES have been considered as among the promising technologies for the removal of sulfate.

For the removal and recovery of sulfur in MFC, the sulfate reducing bacteria should work along with electrogens in the anodic chamber. The sulfate present in the wastewater is reduced to sulfide by sulfate reducing bacteria and it is subsequently oxidized by sulfide oxidising bacteria to form elemental sulfur (Lee et al. 2014). This has been demonstrated for the first time by Rabaey et al. (2006) using a MFC while simultaneously harvesting a power output of 101 mW L^{-1} volume of net anodic compartment. Granular deposits containing 190 mg of sulfur, corresponding to about 9% of sulfide dose, were observed on the anode. When the same setup of MFC was coupled with an up-flow anaerobic sludge blanket (UASB) reactor, a total of 98% sulfide removal was achieved (Rabaey et al. 2006). The coupling of MFC shows that sulfide can be successfully removed from the anaerobically treated effluent, thus accomplishing a polishing treatment to the effluent. Another investigation showed that the performance of a MFC deteriorated when the COD:sulfate ratio was dropped to less than 0.8. The maximum COD removal efficiency of 79% at a power density of 1136.8 mW m^{-3} was demonstrated using MFC at a COD: sulfate ratio of 0.8 (Ghangrekar et al. 2010).

Chatterjee et al. (2017) used a dual chamber MFC fed with sulfate (200 mg L^{-1}) along with acetate as a carbon source. In the anodic chamber of a MFC, sulfate was reduced to sulfide, which was observed via an increase in sulfide concentration from 0 to 55 mg L^{-1} at an HRT of 48 h. However, after an additional 24 h, the sulfide concentration dropped to 3 mg L^{-1}. In the absence of oxygen and with reducing sulfate concentration, it was concluded that sulfate was reduced to sulfide, which was subsequently oxidized to elementary sulfur. Energy dispersive X-ray spectroscopy confirmed the presence of elemental sulfur on the anode with a weight percentage of 27.45% of the entire surface area (Chatterjee et al. 2017). In the same investigation, Co_3O_4 nano-octahedron was used as a cathode catalyst, whereas a separate MFC without catalyst was operated under the same operating conditions, to analyse the effect of improved electrical performance and reduced oxygen reduction reaction overpotential of the sulfide removal. However, it was observed that except for increased power density and coulombic efficiency, the cathode catalyst had no significant role in improving the sulfide oxidation (Chatterjee et al. 2017).

In a recent investigation, a tri-chamber MFC comprising of an oxic cathode and anoxic cathode sharing the same anode was used for nitrogen and sulfate removal. The system achieved total nitrogen and sulfide removal at rates of 10.0 g N m^{-3} day^{-1} and 206.5 g S m^{-3} day^{-1}, respectively (Zhang et al. 2018). The available investigations confirm the efficacy of BES for the removal of sulfate from wastewater, which can be coupled with AD to aid in the overall treatment process. In the conventional aerobic biological processes, sulfide is oxidized to sulfate; however, in the secondary clarifier due to the oxygen depleting environment, the sulfate can again be reduced to sulfide. On the other hand, using MFC, sulfide is converted to elemental sulfur, thus offering a better way of addressing sulfide removal (Chatterjee et al. 2017).

The use of BES in MFC or MEC mode had demonstrated promising results in terms of removal and recovery of nutrients from the wastewater. The inability of AD to eliminate nutrients creates need for coupling AD with suitable nutrient removal techniques. Hence, integration of BES with AD can be a low-cost solution, which can not only improve the performance of AD, but also be an effective way of nutrient recovery.

11.3.2 Biogas Upgrading

The biogas produced from AD mainly consists of CH_4 (55–75%) and CO_2 (30–45%). Besides these, other gases such as H_2S, N_2, H_2 along with H_2O (moisture) can also be present in the biogas (Igoni et al. 2008). However, CH_4 is the only component of interest in biogas as a source of fuel. The presence of CO_2, H_2S, and H_2O leads to a lower calorific value of biogas. Hence, biogas needs to be processed before utilising it as a fuel source. Biogas processing is done in two broad processes, viz. biogas cleaning (removal of impurities such as H_2O and H_2S) and biogas upgrading (removal or transformation of CO_2 into CH_4 to increase the CH_4 content in the biogas) (Angelidaki et al. 2018; Fu et al. 2020).

Biogas upgrading is more concerning than cleaning as CO_2 contributes a large percentage of the total biogas generated. Biogas can be upgraded through physical absorption, chemical absorption, cryogenic separation, and membrane separation (Miltner et al. 2017; Rafiee et al. 2021). Biological methods of biogas upgrading such as chemoautotrophic biogas upgrading, photosynthetic biogas upgrading, and use of BES have recently gained considerable interest. Depending on the configurations of the upgrading system, the bioconversion process of CO_2 to CH_4 may be either in-situ or ex-situ.

In-situ bioconversion of CO_2 to CH_4 occurs via three pathways namely: (1) direct hydrogenotrophic methanogenesis, where methanogenic archaea reduce CO_2 into CH_4 using externally injected H_2 as electron donor; (2) indirect (acetoclatic methanogenesis) pathway, where CO_2 is converted into acetate by homoacetogenic bacteria, and the acetate is converted into CH_4 by acetoclastic methanogens and (3) direct electron transfer (DET) pathway, where CO_2 is reduced at the cathode of BES operated in electrolytic mode (Angelidaki et al. 2018; Fu et al. 2020). Ex-situ bioconversion may also be achieved by mixing compressed biogas and H_2 in an external digester containing methanogens (preferably hydrogenotrophic methanogens to exhibit direct methanogenesis) or by feeding the biogas into an independent microbial electrosynthesis unit operated in electrolytic mode. Either way, H_2 is necessary for the bioconversion of CO_2 into CH_4. It has to be supplied from an external source into the upgrading system itself (in-situ method) or mixed with CO_2 in a completely independent external digester (ex-situ method), which is a costly approach. Further, it might not be practical for large scale setups to use an external supply of H_2 for the bioconversion of CO_2 into CH_4, because the heating value of hydrogen is more than methane (Lay et al. 2019). The external power supply in electrolytic BES serves as the source of electrons. Moreover, the abiotically produced H_2 (or H^+ ions) from water hydrolysis may present as an excellent replacement for the H_2, which is externally injected in other in-situ or ex-situ methods (Cheng et al. 2009; Xu et al. 2014). Hence, in-situ biogas upgrading using BES is a more sustainable approach compared to other biological methods.

Xu et al. (2014) performed both in-situ and ex-situ biogas upgrading using MFC. It was observed that in-situ biogas upgrading was more effective than ex-situ biogas upgrading although in both cases the CO_2 content was kept below 10% of the total upgraded biogas in batch as well as continuous operations (Xu et al. 2014). In-situ upgrading is more advantageous than ex-situ upgrading, because CO_2 formation and reduction takes place simultaneously in the cathodic chamber; while in the ex-situ method, CO_2 reduction into CH_4 is limited by gas-liquid transfer of CO_2 into the cathodic chamber. Jin et al. (2017) conducted an ex-situ biogas upgrading experiment using an innovative three-chambered microbial electrolytic capture, separation, and regeneration cell to facilitate simultaneous biogas upgrading, CO_2 recovery, and wastewater treatment. Synthetic biogas (60% CH_4 and 40% CO_2) was supplied into the cathodic chamber using a column diffuser at a flow rate of 19.6 mL h^{-1}. The CH_4 content in the upgraded biogas was raised to 97.0 ($\pm$0.20)% within a gas retention time of 5.1 h, while the CO_2 content was below 5%. Additionally, without the use of external voltage (control), the CH_4 content was 85.5 ($\pm$0.3)% indicating a substantial increment in the biogas quality in MFC mode (Jin et al. 2017).

In a different investigation, a MEC with −500 mV (vs. SHE) of applied potential caused $>$ 90% CH_4 upgrading from 70%; in addition to 8.2% CO_2 conversion into CH_4. It was observed that the *Methanothrix* and *Azonexus* species were enriched on the cathode. Further, the transcriptomic analysis revealed that *Methanothrix* uses the CO_2 reduction pathway that stimulates direct electron transfer in MEC for enhancing the CH_4 content of biogas (Liu et al. 2019). These investigations showed that BES presents a potentially sustainable means for in-situ or ex-situ biogas upgrading.

11.3.3 Post Treatment to the Effluent of Anaerobic Digestion Using Bio-electrochemical Systems

11.3.3.1 Polishing Treatment to Anaerobic Digestion

The AD as a sole unit cannot be used as a stand-alone treatment for wastewater. For high strength waste in terms of COD, the effluent of AD still contains a considerable amount of residual organic matter, thus requiring the need for a second stage of treatment. BES can be used in such cases as a follow-up treatment for organic matter removal and energy recovery. On the other hand, for low strength wastewater in terms of COD, the effluent contains nutrients and pathogens; thus, BES can be used as an add-on secondary treatment unit or as a polishing treatment unit or both for the effluent of AD.

Zhang et al. (2012a) reported treatment of organic matter and sulfate in an UASB reactor and MFC. The combined system of UASB followed by MFC achieved 69.9 and 81.8% of COD and sulfate removal, respectively. The MFC harvested a maximum power density of 989.6 mW m^{-2} at a COD/sulfate ratio of 2.3 and HRT of 54.3 h (Zhang et al. 2012a). In another investigation, four MFCs in series were used as a polishing treatment for the biohydrogen and biomethanation process. The MFCs were operated with varied OLR of 0.036–6.149 g COD L^{-1} day^{-1}, resulting in a COD removal efficiency of 35.1–4.4%. The highest coulombic efficiency of 60% was attained at an OLR of 0.572 g COD L^{-1} day^{-1} simultaneously producing a maximum power density of 3.1 W m^{-3} (Fradler et al. 2014).

In another combination, an UASB-MFC-biological aerated filter was developed for the molasses wastewater treatment. The UASB reactor was used for COD removal and the MFC for generating bioelectricity simultaneously degrading COD as well as oxidation of the generated sulfide; whereas the colour removal and phenol degradation was accomplished in the biological aerated filter. The overall removal efficiency of 53.2, 52.7, and 41.1% for COD, sulfate, and colour, respectively, was achieved in the combined system. The MFC in this combined system produced a maximum power density of 1410.2 mW m^{-2} (Zhang et al. 2009a). Various combinations have been tried to integrate BES as downstream treatment to AD in order to meet the discharge norms for the disposal of the treated effluent. Additionally, the harvested bioelectricity from the MFCs can be used for on-site applications. The follow-up treatment in BES also offers an advantage for not only the removal of carbonaceous organic matter but also nutrient removal and recovery as explained in Sect. 11.3.1.

11.3.3.2 Emerging Contaminants Removal

Even after secondary biological treatment targeted for the removal of carbonaceous organic matter and nutrients from the wastewater, pathogens and emerging contaminants (ECs) persist in the effluent. The BES can be implemented to eliminate these pollutants from the secondary or tertiary treated effluents. The role of downstream BES-based technology is of paramount importance because AD is incapable of eliminating the ECs, which could result in discharge of ECs into the receiving water bodies. Pharmaceuticals, dyes, personal care products, estrogens, aromatic hydrocarbons, surfactants, and pesticides are amongst the ECs that have been successfully removed using BES (Chakraborty et al. 2020; Wu et al. 2020). Three different possible approaches for degrading the ECs from the wastewater using BES are: (1) anodic degradation; (2) cathodic degradation; and (3) anodic followed by cathodic degradation.

The ECs can be used as a co-substrate by the anodic microbial consortia along with organic matter. However, for the low concentration of ECs (generally detected in the domestic wastewater), cathodic degradation is considered as an attractive option (Fig. 11.2); wherein, the degradation is achieved using in-situ generated H_2O_2 or $^{\bullet}OH$. In an air-cathode MFC when penicillin (50 mg L^{-1}) was used with glucose (1000 mg L^{-1}) as a feed, a maximum power density of 101.2 W m^{-3} was generated. The MFC achieved 98% penicillin removal in 24 h of operation. The maximum power generated was 6.8-fold higher than that of MFC operated using solely glucose (1000 mg L^{-1}) as a feed. This might be due to the direct electron transfer from the bacterial cell to the anode by increasing the electron permeability of the bacterial cell membrane (Wen et al. 2011b). Similarly, the addition of ceftriaxone and Tween-80 in the anodic chamber caused an increase in the electrical performance of MFC,

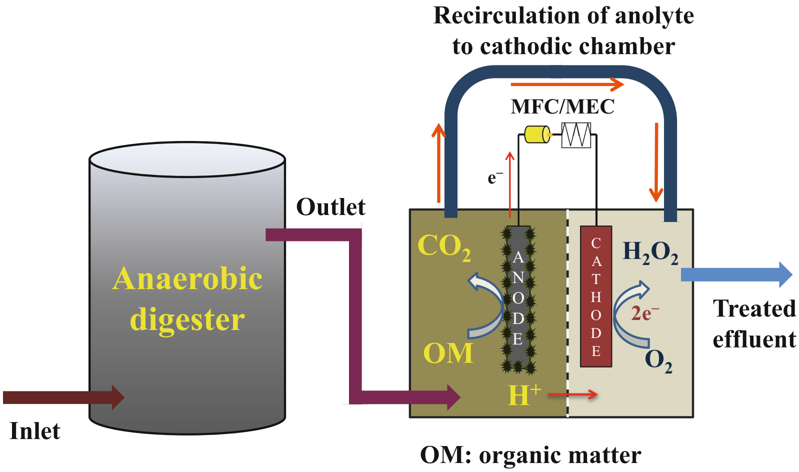

Fig. 11.2 Bio-electrochemical system as post treatment to anaerobic digester (second stage biological treatment followed by tertiary treatment in cathodic chamber)

simultaneously achieving its removal (Wen et al. 2011a, c). However, not all ECs showed a positive correlation with power generation. The addition of metronidazole (10 mg L^{-1}) as feed along with glucose caused a reduction in the maximum power density from 141.94 to 99.23 mW m^{-2} in a dual chamber MFC. However, the MFC demonstrated 85.4% of metronidazole removal in 24 h (Song et al. 2013).

Due to complexity, the ECs require advanced treatment processes for their elimination from the wastewater. In the cathodic chamber of BES, the advanced oxidation processes can be initiated for the removal of ECs. In BES, the Fenton reaction can be carried via in-situ H_2O_2 synthesis supplemented with the use of ferric ions. The first instance of the cathodic Fenton reaction in BES was undertaken by Zhu and Ni (2009) for the degradation of *p*-nitrophenol using scrap iron as Fe source. At a retention time of 12 h, 85% of TOC was removed simultaneously generating 143 mW m^{-2} of maximum power density (Zhu and Ni 2009). In another investigation, sulfamethoxazole was removed in the anodic chamber followed by cathodic treatment in a MFC. The combined process demonstrated 94.66% of sulfamethoxazole removal in 48 h, in which 56.28% removal was in the anodic chamber and remaining in the cathodic chamber due to Fenton oxidation achieved from carbon nanotubes, stainless steel mesh, and γ-FeOOH cathode (Li et al. 2020). The bio-electro-Fenton has been used for the degradation of dyes, antibiotics, pharmaceuticals, and estrogens (Kahoush et al. 2018). It can be used as a polishing treatment to effluents from an anaerobic digester for the removal of ECs, which cannot be removed by the AD.

11.3.3.3 Hybridizing Anaerobic Digestion with Bioelectrochemical Systems

The BES has an edge over conventional AD for the removal of ECs due to the presence of the anode, which acts as an inexhaustible electron sink. Therefore, the merger of BES in an anaerobic digester might be one of the options for bioremediation of recalcitrant contaminants from wastewater. In experiments conducted by Liu et al. (2011b), a zero valent iron bed with graphite plate electrodes was embedded in an anaerobic reactor. With the increase in applied voltage, the COD and colour removal was improved. The bacteriological analysis confirmed the occurrence of azo dye degrading microbes in the anaerobic reactor (Liu et al. 2011b). Similar observations of improved COD and azo dye removal were reported in an anaerobic reactor packed with a pair of Fe-graphite plate electrodes. With 83.4% of COD and 84.7% dye removal, the Fe-graphite electrode embedded anaerobic reactor outperformed the sole anaerobic reactor, in which the COD and dye removal efficiency was 76.4 and 50.7%, respectively (Zhang et al. 2012b).

More recently, Shen et al. (2014) tried integration of BES in a UASB reactor for removal of *p*-nitrophenol in which a graphite felt cathode and anode were horizontally placed inside the UASB reactor. The results demonstrated that the *p*-nitrophenol removal rate in the BES-UASB setup (6.77 M m^{-3} day^{-1}) was higher compared to the UASB reactor only. Also the *p*-aminophenol (final degradation product of *p*-nitrophenol) formation efficiency was reduced from 99.1 to 90.2% in BES-UASB compared to reduction from 98.9 to 53.2% in the sole UASB reactor when the *p*-nitrophenol loading rate was increased from 1 to 6.8 M m^{-3} day^{-1} (Shen et al. 2014). A follow-up study was conducted for the degradation of 2, 4-dinitrochlorobenzene, which demonstrated the ability of BES-UASB to handle shock loads in a better way compared to the UASB solely. At an applied voltage of 1.4 V, 95.78% of 2, 4-dinitrochlorobenzene removal was achieved in the BES-UASB reactor. The enhanced pollutant removal was mainly attributed to the diverse microbial community and presence of electroactive species (Jiang et al. 2016). These lab-scaled investigations validated that the integration of BES into AD might be an innovation hybridization for simultaneous removal of organic matter and ECs in a single setup.

11.3.3.4 Pathogen Removal/Disinfection

Apart from the removal of ECs, the cathodic chamber of BES has been used for disinfection as well. In an investigation conducted by Jadhav et al. (2014), anolyte was circulated in the cathodic chamber of the MFC; wherein sodium hypochlorite in different dosage (0.67–3 g L^{-1}) was used as catholyte to facilitate disinfection. Irrespective of the sodium hypochlorite dose, about 99.5% of disinfection was achieved with the initial bacterial count of 2.8×10^6 colony-forming units per 100 mL of wastewater. The addition of sodium hypochlorite in 3 g L^{-1} dose achieved a 85% increase in sustainable power density (80 mW m^{-2}) compared to the 0.67 g L^{-1} dose of sodium hypochlorite. This states that the addition of chemicals (such as disinfectants) with high redox potential in the catholyte not only achieved disinfection but also increased the power output of MFC (Jadhav et al. 2014).

Instead of externally adding the disinfectant, the cathodic disinfection can be achieved in BES via in-situ synthesis of H_2O_2 at the cathode. Using oxygen as a terminal electron acceptor, the cathodic reaction can be progressed via $2e^-$ or $4e^-$ based on the cathode material and/or cathode catalyst. Although the $4e^-$ pathway is preferred in BES in terms of electrical performance, the $2e^-$ pathway has the advantage of in-situ H_2O_2 synthesis at the cathode. The treated anolyte of BES can be circulated into the cathodic chamber for disinfection or catholyte (high concentration of H_2O_2) and treated anolyte can be transferred to a separate offline chamber for disinfection. Of these, the second option of offline disinfection is better, as direct circulation of the anolyte into the cathodic chamber can lead to biofouling on the cathode. The biofouling on the cathode reduces the availability of dissolved oxygen for the cathodic reaction, thereby increasing the overpotential losses and reducing the electrical performance (Noori et al. 2019). Nevertheless, while targeting the two electron pathway of ORR the power produced from the MFC will reduce due to a lower redox potential of this ORR, however it will offer the advantage of improved wastewater treatment.

For the in-situ cathodic H_2O_2 synthesis different carbon-based cathodes such as carbon felt (Liu et al. 2011a), graphite plate (Li et al. 2017), graphite (Sim et al. 2015), nitrogen-doped graphitic carbon (Asghar et al. 2017) have been implemented. Additionally, different metal-based and metallic nanoparticles ranging from Pd/C (Wang and Wang 2007), Au-Pd (Edwards and Hutchings 2008), and Ni-Pd (Gupta et al. 2020) have also been successful for cathodic synthesis of H_2O_2 in BES. The H_2O_2 production can be achieved in MFC as well as MEC. However, MEC has an edge over MFC in terms of the rate of H_2O_2 generation (Chung et al. 2020).

Over the years, several researchers have tried altering the operating conditions, such as pH, catholyte, anolyte, imposed potential and cathode catalysts in BES to maximize the yield of H_2O_2 in the cathodic chamber (Fu et al. 2010; Sim et al. 2015; Gupta et al. 2020). Arends et al. (2014) developed a wastewater treatment system comprising of a wetland with a BES, capable of synthesizing cathodic H_2O_2. It was observed that after 1 h of contact time, the produced H_2O_2 of 0.1% strength was able to reduce the total coliforms to less than <75 CFU per mL (Arends et al. 2014). In one of the investigations, Zhou et al. (2018) used bio-electro-Fenton for disinfection of wastewater in the cathodic chamber and monitoring was performed in terms of *E. coli* inactivation. The disinfection capability was optimized by varying the applied voltage, iron concentration, and catholyte pH. Under acidic conditions (pH of 3), 4-log scale removal of *E. coli* was achieved at an applied voltage of 0.2 V (against SHE) and Fe^{2+} concentration of 0.3 mM. The production of $^{\bullet}OH$ caused microbial cell membrane destruction, which was identified as a prime reason for the inactivation of *E. coli* (Zhou et al. 2018).

In another investigation, when Ni-Pd was used as cathode catalyst in a dual chamber MEC, the highest H_2O_2 yield of 233 mg L^{-1} day^{-1} was observed at an imposed potential of -0.8 V (against SHE). When treated anolyte with the most probable number of 5.2×10^6 ($\pm 9.3 \times 10^4$) per 100 mL was circulated into the cathodic chamber, 5 (± 1) log-scale bacterial removal was achieved in 3 days of contact time (Gupta et al. 2020). These investigations showed that the secondary and tertiary treatment of wastewater can be achieved using BES by removing organic matter in the anodic chamber and pathogens in the cathodic chamber. Presently considerable lab-scaled investigations have been conducted on in-situ H_2O_2 synthesis in the cathodic chamber of BES. However, it was reported that for upscaling, the H_2O_2 production rates were significantly lower than lab-scaled investigations. It might be due to the overpotential losses as well as H_2O_2 decomposition, which should be addressed in upcoming research. Also, reactor design aspects ranging from cathode size, electrode spacing, catholyte, and anolyte volume need to be optimized for H_2O_2 generation and a complete downstream treatment scheme for anaerobically treated effluent needs to be taken up (Sim et al. 2018; Chung et al. 2020).

11.3.4 Bioelectrochemical System as a Biosensor to Monitor the Anaerobic Digestion Process

The process of AD is interdependent on the interaction of a few microorganisms and the products formed because of microbial interaction. Any imbalance caused in the system due to induced toxicity should ideally be detected within a shorter time to prevent the malfunction of the digester. Factors such as ammonia, hydrogen sulfide, heavy metals, long chains fatty acids, and VFA have an inhibitory effect on digestion. Of these, VFA is one of the factors resulting in the instability of digestion, if not in suitable concentrations (Chen et al. 2008). The conventional lab-based off-line protocols (gas chromatography, high-performance liquid chromatography) of VFA monitoring are tedious and time consuming. Hence, the installation of in-situ real-time sensors could be a useful strategy to monitor VFAs during AD (Fig. 11.3).

MFCs have been used as a biosensor for the detection and monitoring of pollutants from the wastewater including VFAs (Sevda et al. 2020). In an investigation conducted by Kaur et al. (2013), the correlation between the VFA concentration and the resulting current/voltage response was estimated using MFC. It was observed that cyclic voltammetry showed a linear correlation between the VFA concentration and peak current up to a concentration of 40 mg L^{-1} in a response time of 1–2 min (Kaur et al. 2013). A three-chamber microbial desalination cell (MDC) system was used as biosensor, in which VFAs produced from anaerobic digester were dosed in the central chamber separated by an anion and cation exchange membrane on either side. The VFAs in the central chamber could pass through the anion exchange membrane to the anodic chamber, wherein they can be utilized by exoelectrogens on the anode for producing electrons. Two distinct linear relationships were observed for VFA concentrations of 1–30 mM and 30–200 mM against the current densities of 0.04–8.50 mA m^{-2} and 8.50 mA m^{-2} to 10.80 mA m^{-2},

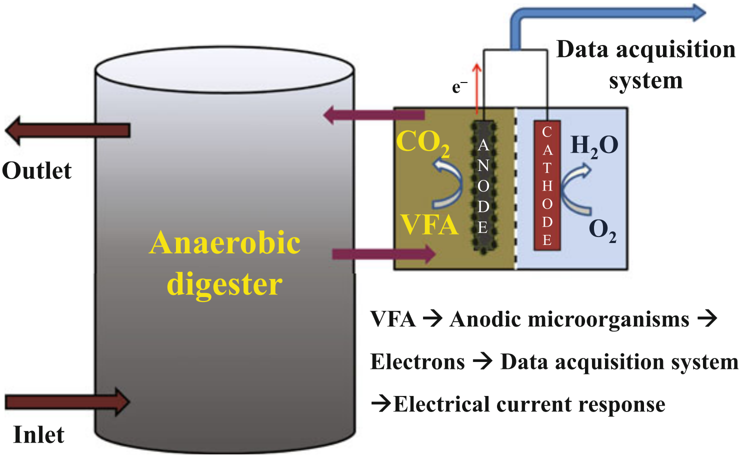

Fig. 11.3 Bio-electrochemical system-based biosensor for volatile fatty acids monitoring

respectively after 5 h of contact time. Further, the VFA quantification by the MDC-based biosensor showed no significant difference when compared with VFA quantification based on gas chromatography, thus showing the accuracy of the system for real time monitoring (Jin et al. 2016).

A single chamber air cathode membrane-less MFC was demonstrated by Schievano et al. (2018) for monitoring the VFA, produced from the anaerobic digester using four substrates (cheese whey, kitchen waste, citrus pulp, and fishery waste). Although the electrical signals of MFC were not proportional to the VFA concentrations up to 1000 mg L^{-1}, the negative peaks of current for VFA concentrations above 4000 mg L^{-1} can be used as early-warning shock-sensors (Schievano et al. 2018). The BES-based biosensors showed promising results for monitoring the VFA production in the AD. In this way, BES can be integrated with anaerobic digester to monitor the digestion process. Such integrations can be a quicker and cheaper alternative compared with off-line monitoring. However, further research is necessary for monitoring the long-term operability and capability of real time monitoring of these BES-based biosensors.

11.4 Future Scope

AD is one of the most proven and proficient techniques of energy recovery from the waste; whereas, BES is a relatively newer concept and offers an advantage of one-step bioelectricity recovery when used as MFC. The process of AD is susceptible to various factors such as pH, VFA, and ammonia concentration. The BES can be effectively used for the recovery of nutrients and removal of ECs or it can be integrated with AD as biosensor for better process control. Unlike AD, for BES a single large reactor is not suitable due to deteriorated electrical performance. Instead, stacking of multiple smaller BES have been recommended and used by the researchers for the wastewater treatment at field scale (Feng et al. 2014; Walter et al. 2018).

The cost is yet another governing factor for the integration of AD and BES. Typically in BES, more than 60% of the overall cost is associated with the electrodes and separator (Rozendal et al. 2008). Metal electrodes have higher conductivity; however, they are susceptible to corrosion in anaerobic conditions. Additionally, metal electrodes lack high surface area and can be potentially toxic to few microorganisms (Noori et al. 2020). For the pilot-scale and field-scale applications, low-cost electrodes and separators need to be developed and integrated into the hybrid system. At the same time, these components should be effective and durable for long term operations. For the use as a separator, ceramic-based membranes show better mechanical and structural properties than polymeric membranes at much reduced cost; hence it can be an ideal choice for separators to be used in scaled up BES (Ghadge and Ghangrekar 2015; Ieropoulos et al. 2015).

The application of BES also needs to be explored in the field-scale setups, augmented with already operated anaerobic digesters to assess the potential of

BES in real life scenarios in the upcoming research to help in confirming the feasibility of the integration. Furthermore, for the integrated systems, the environmental impact in terms of energy balance as well as material balance also needs to be quantified via the use of life cycle analysis tools that will aid in considering the environmental viability of the integrated system. As discussed earlier, BES have an immense potential to complement AD for improving wastewater treatment efficiency. However, more experience is to be gained by operating real life systems to evaluate the efficacy of this integration and to come up with suitable medications in system configurations to gain real advantage of this integration.

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Chapter 12
Use of Biogas for Electricity-Driven Appliances

Afshin Davarpanah

Abstract Biogas can be considered as one of the primary renewable energy sources to generate electricity regarding the grid connection and feed-in tariffs in industrial plants. The present study is focused on introducing biogas systems on electricity production and what environmental policies should be assessed to minimize the air's biogas component emission. Micro-gas turbine (MGT) systems, combined heat and power (CHP) systems, solid oxide fuel cells (SOFC), and organic Rankine cycle (ORC) systems are the most applicable renewable energy systems that can utilize biogas. Combinations of technologies as a hybrid and novel system give the engineers chance to optimize the biogas conversion to electricity for specified industrial purposes. Moreover, environmental features of biogas emissions from industrial plants were discussed and explained.

Keywords Biogas · Electricity Generation · Environmental Features · Full Cells

12.1 Introduction

Due to approaching depletion of the fossil fuels and out dependence on them in recent decades, it is recommended to move towards renewable energy and green technologies. Electricity generation is essential for industrial purposes and generation of electricity from green energy sources such as solar and wind energy should be considered (Andalib-Bin-Karim et al. 2017; Hu et al. 2020; Ardebili 2020). Generating electricity from green energy sources is economically and environmentally beneficial. Bioenergy resources are considered one of the preferable renewable power generation resources due to their sustainable and productive clean electric power (Chang and Zhao 2012; Effah and Boampong 2015; Qadrdan et al. 2018). Right now, the electric power generation from renewable sources is about 8% and

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this should be improved by implementing novel and efficient techniques to generate electricity from bioenergy resources (REN21 2018).

Biogas technology is the combustible gas generation that can be supplied from the anaerobic digestion of biomass. Therefore, to move towards green energy implementation, most of the industrialized countries have intended to convert biogas to electricity for their industrial purposes (Abbasi and Abbasi 2010; Balsora et al. 2017; Inayat et al. 2019). This is advantageous due to the lower operational performance expenditures and the need for minimal energy investment in the industrial sectors. Municipal solid waste, organic waste from industrial sources, and housing (domestic) residual wastes are considered as the common substrates to produce biogas (Pöschl et al. 2010; Kiran et al. 2016; Wu et al. 2016). Nowadays, biomethane that is the upgraded biogas administered in petrochemical plants as a feedstock, especially in gas pipelines (Arthurson 2009).

The biogas composition consists of 50–75% methane, 25–45% CO_2, and 2–8% of water vapor. Other components such as hydrogen sulfide, ammonia, and siloxane that are present in biogas, considered as hazardous materials for the environment and should be treated carefully to reduce the environmental impact (Abatzoglou and Boivin 2009). In theory, fuel cells can be used to convert the biogas to electricity. However, this process needs expensive instrumental setup and extremely clean gas. Proper design and implementation of electric generators is considered as one of the most important factor for converting biogas to electricity (Liu et al. 2012; Makareviciene et al. 2013; Mao et al. 2015).

12.2 Electrical Power Generation from Biogas

The environmental friendly features of biogas in comparison to fossil fuels is the main argument for its use for electricity generation which can revolutionize industrial plants worldwide. Electricity production from biogas systems can be in the range of 8–54% energy conversion efficiency from biogas processed through biogas upgrading and methane reformation. Therefore, the main procedure of biogas utilization would be related to combined heat and power units. The methods below are the most well-known techniques for converting biogas to electricity (Chen et al. 2017; Barzegaravval et al. 2018).

Solid oxide fuel cell coupled with anaerobic digestion is one of the hybrid conversion systems studied by Saadabadi et al. (2019). A high AD temperature condition is applied to enhance the biogas production volume. In this hybrid system, an external pre-reformer is applied in the system to enhance the electricity generation's total efficiency. This procedure is schematically depicted in Fig. 12.1 (Baldinelli et al. 2017; Saadabadi et al. 2019).

A combined heat and power system was used by Kang et al. (2014) to economically evaluate the biogas conversion to electricity efficiency by implementing a micro-gas turbine (MGT) (Fig. 12.2). The feedstock for this system was biogas or natural gas. They concluded that the use of natural gas increased the cost of heat and

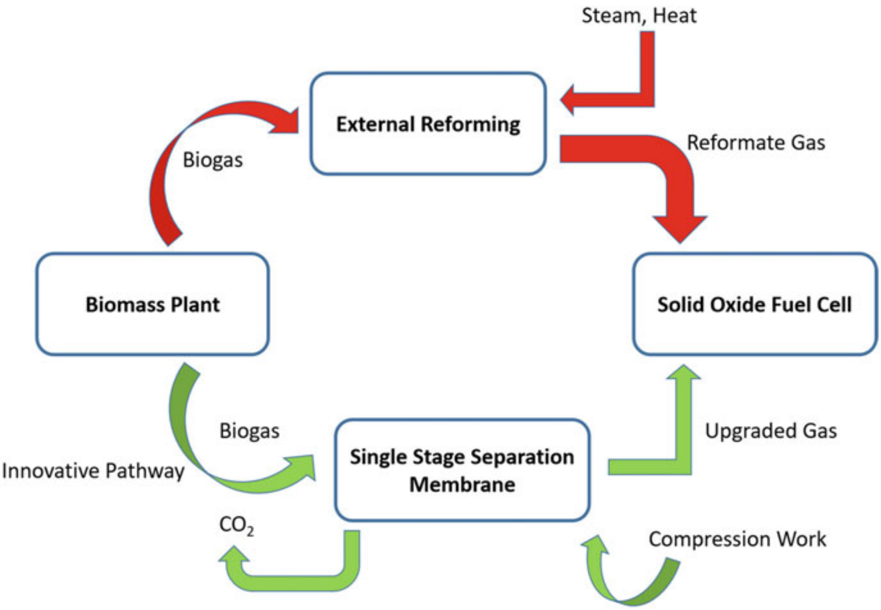

Fig. 12.1 Solid oxide fuel cells for the conversion of biogas to electricity (Baldinelli et al. 2017)

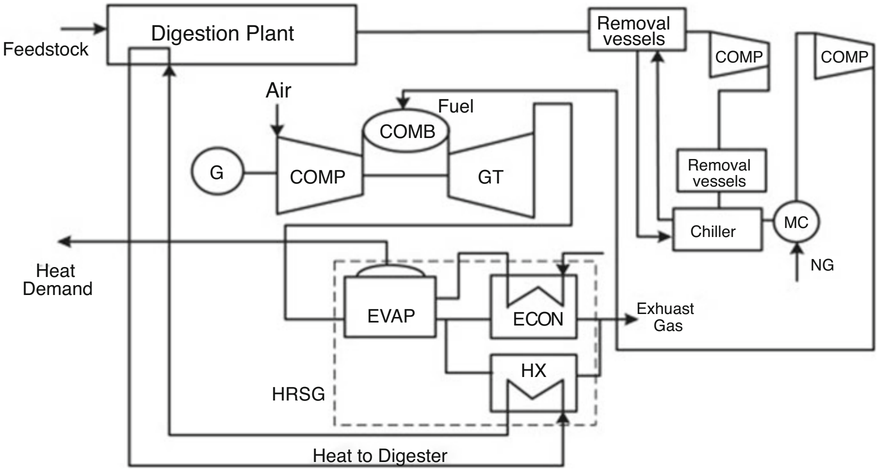

Fig. 12.2 Micro-gas turbine (MGT) system for converting biogas to electricity (Kang et al. 2014)

electricity production. Therefore, the electricity and heat price was 0.1436 $/kWh and 0.0738 $/kWh (Kang et al. 2014). Moreover, according to Kim et al. (2017), electricity and heat production is estimated at 7.4 MWh/year and 8.5 MWh/year for MGT systems in combined heat and power (CHP) and organic rankine cycle (ORC)

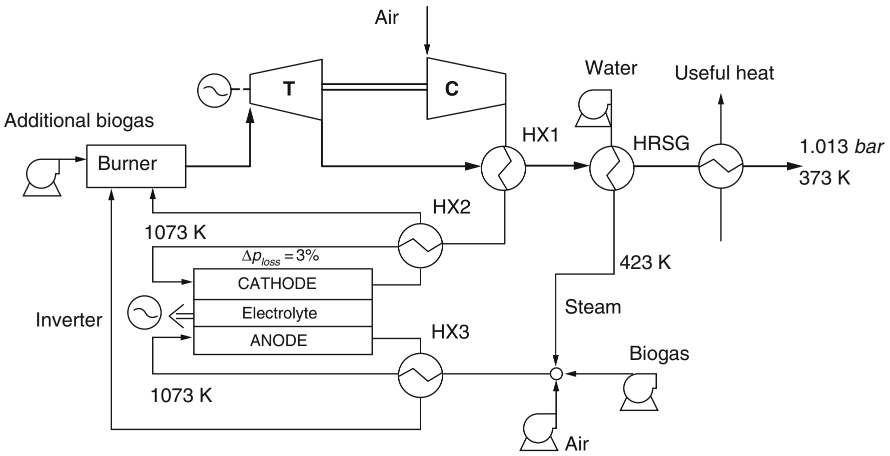

Fig. 12.3 Solid oxide fuel cells coupled with micro gas turbine and combined heat and power system for the conversion of biogas to electricity (Wongchanapai et al. 2013)

systems. Combining the MGT and ORC systems has provided better results than the MGT-CHP system (Kim et al. 2017).

Wongchanapai et al. (2013) developed a novel hybrid system containing solid oxide fuel cells, micro gas turbine, and a combined heat and power system to convert biogas to electricity (Fig. 12.3). In this hybrid system, an internal reformation unit was implemented to convert the methane to hydrogen.

12.3 Environmental Features of Biogas Conversion to Electricity

As biogas is considered as renewable energy resources to manage the energy wastes such as disposal wastes, farming wastes, and landfill processes. Environmental features of biogas conversion in operational processes should be taken into consideration in every industrial procedure. These environmental aspects considered in engineering designation include hazardous materials, wastewater treatment, CO_2 emissions, and maintenance procedures. To implement engineering consideration for biogas conversion, this process's advantages and disadvantages should be explicitly distinguished before any operational performance. The primary utilization of biogas conversion has been done for industrial purposes. Its disadvantages contained extreme noise levels during the operations, air pollution due to the release of CO_2 in the plant, and machines rapture through the separators.

In contrast, biogas to electricity has some advantages that should be preferred to implement its utilization. As the process has been continued throughout the system, more novel systems could be added and replaced, or in some conditions, they can be combined to increase the power generation efficiency. Thereby, waste gases have been removed through the system circulation, and there are less hazardous emissions. According to the measurements of biogas emissions, CO_2 emissions range from 0.1 to 0.4 kg CO_2/kWh. Another biogas emission gas is NO_x, which depends on the nitrogen content of the produced biogas. One of the crucial factors in environmental conservation is the leakage of hazardous materials that increase global warming. As AD of waste has fugitive ammonia and greenhouse emissions, efficient controlling methods to avoid leakages need to be designed (Sommer 1997; Börjesson and Berglund 2006; Karapidakis et al. 2010; Senbayram et al. 2014; Carreras-Sospedra et al. 2016).

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Chapter 13
Syngas Fermentation for Bioenergy Production: Advances in Bioreactor Systems

Arindam Sinharoy, Kannan Pakshirajan, and Piet N. L. Lens

Abstract Renewable energy resources, particularly biofuels, are gradually replacing the fossil fuel sources for energy. This will eventually enable an energy platform with reduced environmental pollution and greenhouse gas emissions. The present technologies and raw materials available for biofuel production have, however, not yet reached commercial scale due to high costs and other economic constraints. In this context, gasification of waste resources to syngas and its subsequent bioconversion to a wide range of useful products, including biofuels, could provide significant advantages over conventional systems. A large number of acetogens have been isolated that are capable of utilizing syngas as the substrate. However, relatively poor gas-liquid mass transfer, CO toxicity to microorganisms and low product yield are some major drawbacks of syngas fermentation. This chapter reviews the literature of syngas fermentation with specific focus on different bioreactor systems available for overcoming the limitations of syngas bioconversions.

Keywords Bioreactors · Biofuel production · Synthesis gas · Syngas fermentation · Biorefinery

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13.1 Introduction

The majority of today's energy demand is fulfilled by energy supplied from fossil fuel resources, as the population and industrial growth progresses, the demand for energy is going to increase furthermore (Johnsson et al. 2019; Sinharoy et al. 2020a). This is one of the main reason for the exhaustion of fossil fuel reserve, which have created many global problems and can potentially leads to future energy crisis (Roy et al. 2016). Apart from that, environmental problems associated with fossil fuel burning and their effect on human health have created worldwide concern and have generated demand for clean energy (Chen et al. 2017). These factors combined with the awareness about global warming have shifted our focus towards safeguarding the environment and creating a more sustainable society by fulfilling our energy demands from renewable sources.

The use of renewable energy sources can provide an alternative to the fossil fuel and simultaneously avoid the environmental degradation associated with fossil fuel to a larger extent (Soeiro and Dias 2020; Jurasz et al. 2020; Sinsel et al. 2020). Biofuels, such a renewable energy source, have received a lot of attention during the recent years. Biofuels are available mainly in liquid form, such as bioethanol, biobutanol and biodiesel, or in gaseous form, such as biogas (mainly methane) and biohydrogen (Bórawski et al. 2019). These fuels are mainly derived from biomass as the raw material or produced via biological or biochemical conversion processes (Sinharoy et al. 2020a). Due to the conflict with food crops, limited availability of agricultural land and large water requirements for production of first generation biofuels, the recent focus is towards the production of biofuels utilizing waste resources (Bhatia et al. 2017). Solid as well as liquid wastes such as municipal solid waste, lignocellulosic biomass, agricultural and forest residues and different industrial wastewaters have been used for production of various types of biofuels (Hassan et al. 2019). In contrast, the potential of gaseous industrial wastes for production of biofuel or other useful products has not yet been fully explored. In this context, the use of synthesis gas or syngas as a low cost substrate for the production of biofuel or other value added products is attractive. This gas fermentation approach is another way of producing second generation biofuels from waste biomass.

Synthesis gas is a mixture of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), nitrogen (N_2) and some higher hydrocarbons. The CO concentration in syngas ranges from 5 to 60%. CO can be steam reformed to enrich the H_2 content of the syngas (Couto et al. 2013). Biomass gasification, which is the main route for syngas production, is an endothermic process and requires heat energy as an input as is carried out at 750–800 °C (Molino et al. 2016). Lignocellulosic biomass and even municipal solid waste can be feedstocks for biomass gasification (Ahmad et al. 2016). For an efficient gasifier operation, a certain amount of feedstock homogeneity should be maintained. If the feedstock is heterogeneous then the product composition may vary widely (Sikarwar et al. 2016). To overcome this bottleneck, pre-treatment and post-treatment steps are included in the gasification process, which increase the operation cost of the process (Cheah et al. 2016). Homogeneous lignocellulosic materials, such as timber industry waste, paper mill waste and agricultural residues can be used as feedstock for biomass gasification (Sikarwar et al. 2016; Burra and Gupta 2018). Although, municipal solid waste can be a suitable substrate for biomass gasification as well, it is still under consideration as it also contains a variety of other (non-combustible) materials (Zheng et al. 2018).

Syngas can be used as the substrate for production of liquid fuel either by the thermochemical catalytic route with a metallic catalyst or by the biochemical route with acetogenic microorganisms (Griffin and Schultz 2012). A number of thermochemical catalytic processes such as Fischer–Tropsch (FT) synthesis and the water gas shift reaction have been applied for converting syngas to valuable products. These operate at high temperature and pressure, and require costly metal catalysts (Subramani and Gangwal 2008). Though the thermo-catalytic process has been commercialized and works successfully in installed plants, it has several disadvantages such as high operating costs, limited choice of metallic catalysts, perishable nature of the catalyst, huge requirement of heat energy and environmental concerns (Griffin and Schultz 2012). Furthermore, these catalyst based processes are often prone to catalyst poisoning due to the emanation of unwanted gases, mainly hydrogen sulfide and other inhibitory substances (Subramani and Gangwal 2008). These disadvantages have resulted in the need for alternative technologies, including biochemical conversion of syngas. Biological methods offer certain advantages such as high tolerance to trace contaminants, high product specificity, in addition to being sustainable, environmental friendly and cost effective (Henstra et al. 2007).

13.2 Syngas Fermentation

13.2.1 Alcohol and Acetate Production

Some acetogens are capable of producing alcohols along with volatile fatty acids from syngas (Table 13.1). These bacteria are obligate anaerobes and can utilize CO/CO_2 as the carbon and energy source (Henstra et al. 2007; Mohammadi et al. 2011). Examples of these solventogenic bacteria are *Clostridium ljungdahlii, Clostridium carboxidivorans, Clostridium autoethanogenum, Clostridium ragsdalei, Alkalibaculum bacchi, Eubacterium limosum, Butyribacterium methylotrophicum*, *Clostridium thermoaceticum* and *Clostridium formicoaceticum* (Mohammadi et al. 2011; Bengelsdorf et al. 2013). Most of these microorganisms can grow on multiple carbon sources, but their potential to utilize gaseous substrates such as CO, CO_2 and H_2 and to produce useful products is commercially attractive. Some strains such as *Clostridium ragsdalei* and *Clostridium propionicum* produce propanol from syngas (Isom et al. 2015). The biochemical pathway used by these bacteria for the production of ethanol is the reductive acetyl-CoA pathway or Wood-Ljungdahl pathway (Mohammadi et al. 2011). This pathway is present in several organisms including acetogenic bacteria (Schuchmann and Müller 2016) and methanogenic archaea

Table 13.1 Alcohol production from syngas in different bioreactor systems

Microorganism	Reactor	Temp °C	pH	Agitation (rpm)	Feed gas composition	Any other carbon substrate	Ethanol concentration /yield	Other products	Reference
Clostridium ljungdahlii	CSTR	37	NR	450	10% CO_2, 15% Ar, 20% H_2, 55% CO	Fructose	NR	Acetic acid	Aghbashlo et al. (2016)
Clostridium carboxidivorans P7	Batch stirred reactor	37	6.15	120	80% CO, 20% CO_2	NR	2.6 g/g of cells	Acetic acid	Hurst and Lewis (2010)
Clostridium carboxidivorans P7	Monolithic biofilm reactor	37	6.0	NA	20% CO, 5% H_2, 15% CO_2, 60% N_2	Fructose	0.17 mole/ mole of CO	Acetic acid	Shen et al. (2014b)
Clostridium carboxidivorans P7	HRPBR	37	6.0	NR	20% CO, 5% H_2, 15% CO_2, 60% N_2	Fructose	7 g/L and 6.7 g/L/day	Acetic acid	Shen et al. (2017)
Clostridium carboxidivorans P7	BCR	37	6.0	NR	25% CO, 15% CO_2, 60% N_2	NR	0.15 mole/ mole of CO	Butanol and acetic acid	Rajagopalan et al. (2002)
Clostridium autoethanogenum	CSTR	30	6.0	250	100% CO	Xylose (under mixotrophic condition)	7.143 g/L	Acetic acid	Abubackar et al. (2016)
Clostridium autoethanogenum	CSTR	30	6.0	250	30% CO, 10% CO_2, 20% H_2, 40% N_2	NR	2.22 g/L	Acetic acid and 2,3-butanediol	Lagoa-Costa et al. (2017)
Clostridium autoethanogenum	CSTR	30	6.0	250	100% CO	NR	907.72 mg/L	Acetic acid	Abubackar et al. (2015)
Clostridium ragsdalei	Two stage CSTR	32	6.0	NR	40% CO, 30% H_2, 30% CO_2	NR	14.74 g/g of cells	Acetic acid	Kundiyana et al. (2011)

Clostridium ragsdalei	CSTR	37	6.1	150	20% CO, 5% H_2, 15% CO_2, 60% N_2	NR	9.6 g/L	Acetic acid	Maddipati et al. (2011)
Clostridium ragsdalei	TBR	37	5.8	NR	38% CO, 28.5% CO_2, 28.5% H_2, 5% N_2	NR	5.7 g/L	Acetic acid	Devarapalli et al. (2016)
Clostridium ragsdalei	CSTR (pilot scale 100L)	37	6.0	150	20% CO, 5% H_2, 15% CO_2, 60% N_2	NR	25.26 g/L	2-propanol, Acetic acid, 1-butanol	Kundiyana et al. (2010)
Alkalibaculum bacchi	BSB—fed batch mode	37	8.0–8.5	150	20% CO, 15% CO_2, 5% H_2, 60% N_2 and 40% CO, 30% CO_2, 30% H_2	NR	1.75 g/L	Acetic acid	Liu et al. (2012)
Alkalibaculum bacchi	CSTR	37	8.0	NR	20% CO, 5% H_2, 15% CO_2, 60% N_2	Corn steep liquor	8 g/L	Acetic acid, n-propanol and n-butanol	Liu et al. (2014)
Anaerobic mixed consortium	BSB	37	6.0	100	$P_{CO} = 2$ kg/cm^2	NR	2.2 g/L	Acetic acid	Singla et al. (2014)

NR, not reported; NA, not applicable; BSB, batch serum bottle; CSTR, continuous stirred tank reactor; HRPBR, horizontal rotating packed bed reactor; BCR, bubble column rector; TBR, trickle bed reactor

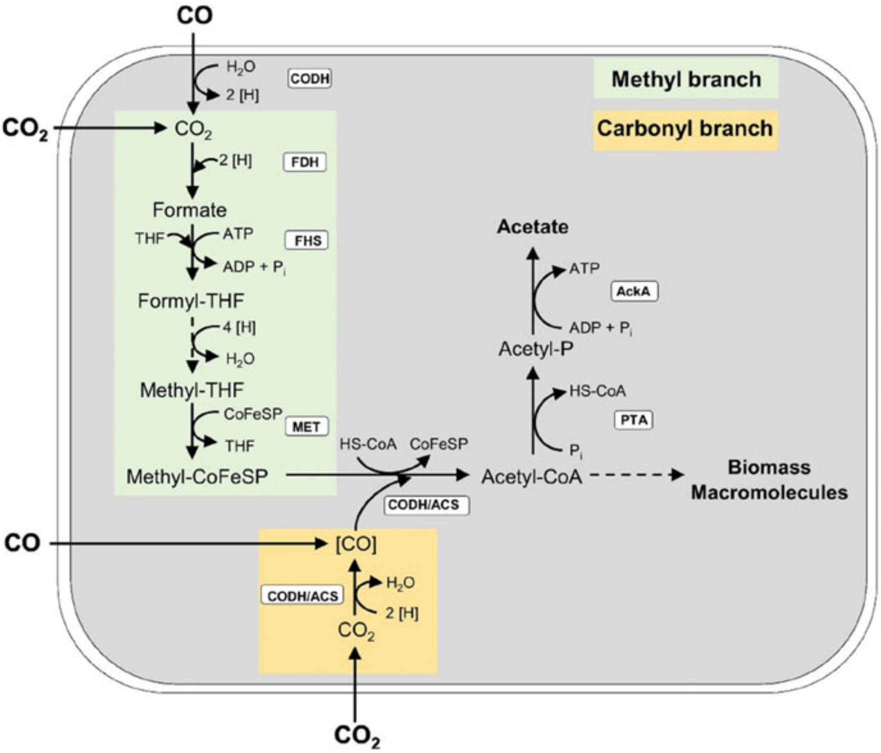

Fig. 13.1 Wood-Ljungdahl pathway or reductive acetyl-CoA pathway utilized for syngas fermentation. Abbreviations: ACS, acetyl-CoA synthetase; AckA acetate kinase; [CO], enzyme-bound carbon monoxide; CODH, carbon monoxide dehydrogenase; CoFeSP, corrinoid sulfur protein; FDH, formate dehydrogenase; FHS, formyl-THF synthetase; [H], reducing equivalents; HS-CoA, coenzyme A; MET, methyltransferase; P_i, inorganic phosphate; PTA, phosphotransacetylase; THF, tetrahydrofolic acid [reused from Kiefer et al. 2021; Copyright (2021) with permission from Elsevier]

(Borrel et al. 2016). It consists of two branches, eastern branch and western branch (Fig. 13.1). The eastern branch has a number of reductive steps where CO_2 is reduced to produce the methyl group of acetyl-CoA. Whereas in the western branch, CO obtained from CO_2 or directly from the source forms the carbonyl group for the acetyl-CoA synthesis (Diender et al. 2015). There are two ways to generate reducing equivalents by this pathway. Most commonly, a hydrogenase enzyme supplies the reducing equivalents from H_2 as per the following reaction (Eq. 13.1) (Diender et al. 2015):

$$H_2 \rightleftharpoons 2H^+ + 2e^- \tag{13.1}$$

If the hydrogenase enzyme is inhibited or the amount of H_2 gas present in the medium is insufficient, the CODH enzyme generates reducing equivalents by oxidation of CO to CO_2 as per the following reaction (Eq. 13.2) (Diender et al. 2015):

$$CO + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^- \tag{13.2}$$

These microorganisms are mostly mesophilic, although thermophilic conversion of syngas using anaerobic consortia has also been reported (Shen et al. 2018). The pH of the medium plays a vital role in their product formation from syngas. In most cases, a low pH range tends to favour solventogensis over acetogenesis (Abubackar et al. 2018).

13.2.2 Hydrogen Production

Similar to the catalytic water gas-shift reaction, carboxydotrophic hydrogenogenic microorganisms use CO as the sole source of carbon and energy to form equimolar amounts of CO_2 and H_2. Over the past decade, a number of such microorganisms have been described (Table 13.2), which are mainly classified into three different groups: mesophilic Gram-negative bacteria, thermophilic Gram-positive bacteria and thermophilic archaea.

Gram-negative mesophilic bacteria are facultative anaerobes, but produce H_2 from CO under strict anaerobic conditions. These are mostly non-sulfur purple photosynthetic bacteria, including *Rhodopseudomonas gelatinosa* (Mörsdorf et al. 1992), *Rhodocyclus gelatinosa* (Klasson et al. 1993), *Rubrivivax gelatinosus* (Henstra et al. 2007), *Rhodopseudomonas palustris* (Oelgeschläger and Rother 2008) and *Rhodospirillum rubrum* (Najafpour et al. 2003). Among these bacteria, the phototrophic *R. rubrum* is well studied, its genetic map and enzyme system have been described and it has been employed in bioreactors. The optimum temperature and pH of this microorganism are in the range of 34–40 °C and 6.5–7.5, respectively (Klasson et al. 1993). In general, high levels of CO are inhibitory to this bacterial species and its light requirement causes additional costs. Other than these phototrophic organisms, certain non-phototrophic Gram negative anaerobes are capable of converting CO to H_2. These are *Citrobacter* strain Y19, isolated from an activated sludge plant (Jung et al. 2002), an anaerobic microbial consortium with predominantly *Petrobacter* sp. (Pakshirajan and Mal 2013) and anaerobic granular sludge consortia from a full-scale upflow anaerobic sludge blanket reactor with predominantly *Acinetobacter* sp. (Sinharoy et al. 2015).

A large number of carboxydotrophic organisms are extremophiles, isolated from extreme environments such as hot springs and submarine hot vents. This group of bacteria contains mainly anaerobic prokaryotes of the *Bacillus/Clostridium* subclass, such as *Carboxydothermus hydrogenoformans* (Henstra and Stams 2011), *Carboxydobrachium pacificum* (Sokolova et al. 2001), *Thermincola carboxydophila* (Zavarzina et al. 2007), *Carboxydocella sporoproducens* (Slepova et al. 2006) and

Table 13.2 Hydrogen production from syngas in different bioreactor systems

Microorganism	Reactor	Temp °C	pH	Agitation (rpm)	Feed gas composition	Any other carbon substrate	H_2 production rate /yield	Reference
Rhodospirillum rubrum	CSTR	30	6.5	NR	$P_{CO} = 0.55$ atm	Acetate	16 mmol H_2/h	Najafpour et al. (2003)
Rhodospirillum rubrum	CSTR	30	6.9	350–800	55% CO, 15% H_2, 20% Ar, 10% CO_2	Malic acid/ sodium acetate	9.6 mmol H_2/h	Ismail et al. (2008)
Rhodospirillum rubrum	CSTR	30	6.9	150–500	55% CO, 15% H_2, 20% Ar, 10% CO_2	Malic acid/ sodium acetate	80% mol/mol of CO	Younesi et al. (2008)
Rhodospirillum rubrum	CSTR	30	7.0	400–750	17.2% CO, 16.3% CO_2, 8.8% H_2, 56.0% N_2	Acetate	0.75 mol H_2/ day	Do et al. (2007)
Thermoanaerobacter kivui	BSB	60	7.5	NR	100% CO	NR	45 mmol/L	Weghoff and Müller (2016)
Rubrivivax gelatinosus	BSB	30	7.0	250	20% CO	Sodium malate	0.9 mmol/ min/ g cell	Vanzin et al. (2002)
Rhodopseudomonas palustris P4	BSB	30	7.0	NR	60% CO, 10% CO_2, 20% H_2, 10% Ar	Sodium acetate	7 mmol/L	Pakpour et al. (2014)
Rhodopseudomonas palustris P4	CSTR	30	7.0	500–700	20% CO, 80% Ar	NR	41 mmol/g cell/h	Oh et al. (2005)
Citrobacter sp. Y19	Two stage Batch stirred tank reactor	30	7	300–700	20% CO, 80% Ar	Sucrose	20 mmol/g cell/h	Jung et al. (2002)
Carboxydothermus hydrogenoformans	GLR	70	6.8–7.2	NR	100% CO	Bacto-peptone	95% mol/mol of CO	Haddad et al. (2014)
Carboxydothermus hydrogenoformans	HFMBR	60–70	6.8–7.0	Nil	100% CO	NR	92% mol/mol of CO	Zhao et al. (2013)

Carboxydothermus hydrogenoformans	BSB	65	7.0	100	100% CO	NR	NR	Henstra and Stams (2011)
Carboxydothermus pertinax	BSB	50–70	6.0–6.5	NR	100% CO	Ferric citrate	NR	Yoneda et al. (2012)
Moorella stamsii	BSB	65	7.5	NR	100% CO	NR	NR	Alves et al. (2013)
Clostridium thermoaceticum	BSB	NR	NR	NR	100% CO	NR	7 mmol/L	Martin et al. (1983)
Anaerobic sludge biomass	BSB	30	7.0	120	100% CO	Acetic acid (during startup)	60.8 mol	Pakshirajan and Mal (2013)
Anaerobic granular sludge biomass	UASB	55	7.5	NA	45–90 mmol/day	NR	45.3 % (*v/v*) biogas produced	Liu et al. (2016)
Anaerobic sludge biomass	GLR	30	7.0	NA	100% CO	NR	30.7 mmol/L	Sinharoy and Pakshirajan (2020)
Anaerobic sludge biomass	MBBR	30	7.0	NA	100% CO	NR	19.5 mmol/L	Sinharoy and Pakshirajan (2021)

NR, not reported; NA, not applicable; BSB, batch serum bottle; HFMBR, hollow fiber membrane bioreactor; GLR, gas lift reactor; UASB, upflow anaerobic sludge blanket reactor; MBBR, moving bed biofilm reactor

Thermosinus carboxydivorans (Sokolova et al. 2004). The optimum temperature and pH for these bacteria is in the range of 50–90 °C and 6.8–8.0, respectively (Table 13.2).

Though a large number of archaea have been isolated from extreme temperature environments, only a few of these are capable of chemolithotrophic growth on CO and H_2 production, which include *Thermococcus* AM4 and *Thermofilum carboxyditrophus* (Sokolova et al. 2009). The use of thermophilic microorganisms is more advantageous than mesophilic ones for syngas fermentation, as the temperature of syngas exiting from a gasifier is around 700–800 °C and the cost of reducing the temperature of raw syngas to a moderate range can be avoided (Griffin and Schultz 2012). However, the high energy requirement of maintaining a large scale reactor at an elevated temperature is still not economically feasible.

13.2.3 Methane Production

Production of methane from syngas can be advantageous, particularly in case of highly lignified biomass or biomass containing pathogenic microorganisms (Li et al. 2020). Further, biomass gasification followed by syngas biomethanation can also avoid generation of unwanted end products such as digestate produced in case of anaerobic digestion of lignocellulosic substrates. Although biochar is produced as byproduct during biomass gasification, quantity wise it is much less ($<1\%$ of the biomass) than digestate produced during anaerobic digestion (Swart 2013).

Only a few methanogenic archaea are capable of utilizing CO as the sole carbon and energy source. CO is not a very efficient substrate for methane production, as only three pure strains produce methane while growing on CO, namely *Methanobacterium thermoautotrophicus, Methanosarcina acetivorans* and *Methanosarcina barkeri* (Oelgeschläger and Rother 2009).

The direct CO conversion to methane can be achieved by the following reactions (Eqs. 13.3 and 13.4):

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{13.3}$$

$$4CO + 2H_2O \rightleftharpoons 3CO_2 + CH_4 \tag{13.4}$$

An excess amount of H_2 in the syngas is required for methane production to take place using Eq. (13.3). In case of Eq. (13.4), CO is first converted to other products (H_2 or acetate) from which methane is produced by hydrogenotrophic or aceticlastic methanogenesis (Guiot et al. 2011; Li et al. 2020). The H_2 to CO ratio plays a very important role in this case and by increasing the H_2 concentration methane production can be improved. For example, the methane content in the biogas increased from 66.37 to 73.35% by changing the H_2/CO ratio from 3:1 to 5:1 (Li et al. 2020).

In some microorganisms, such as *Methanococcus jannaschii* the gene coding carbon monoxide dehydrogenase (CODH) is located on the same operon of hydrogenase, signifying its potential for hydrogenogenic carboxydotrophic metabolism (Bult et al. 1996). In spite of having one or more CODH enzyme systems in most of the methanogenic organisms, many of them have never been tested for CO utilization (Ferry 2010). Hence, their growth potential on CO or product formation capabilities are mostly unknown.

Many researchers have studied anaerobic mixed consortia for their capability of CO utilization and methane production (Table 13.3). For example, Sinharoy et al. (2015) found that anaerobic granular sludge from three different upflow sludge blanket reactors treating municipal sewage were capable of biological CO conversion with methane as the main product along with low concentrations of H_2 and acetic acid. To illustrate the methane production pathway using CO at mesophilic conditions (35 °C), two selective inhibitors namely 2-bromoethanesulfonate (BES) and vancomycin were used (Navarro et al. 2014). Carboxydotrophic methanogenesis was found to be a two-step process in this case, where CO is first converted to acetate, from which methane is subsequently produced.

Sipma et al. (2003) studied CO conversion using seven different sludges sampled from anaerobic wastewater treatment plants. All the sludges were capable of converting CO to methane and acetate at 30 °C, and this methane production occurred via acetate, not H_2. At a higher temperature (50 °C), CO was rapidly converted into hydrogen or methane, produced with H_2 as the intermediate. The increase in temperature has a positive impact on the methane production from syngas. Guiot et al. (2011) reported a more than fivefold increase in methane productivity from CO by increasing the incubation temperature from 35 to 60 °C. This could be attributed to the change in microbial community to enrich carboxydotrophic hydrogenogenic bacteria at elevated temperature resulting in higher CO bioconversion rates (Grimalt-Alemany et al. 2018).

Methane production from syngas has been realised even at extreme thermophilic (70 °C) conditions with 83–97% CO conversion to CH_4 (Bu et al. 2018). The carboxydotrophic methanogenic archaea *Methanothermobacter thermoautotrophicus* was the predominant strain at this elevated temperature. CO_2 was used preferentially during hydrogenotrophic methanogenesis and once it was exhausted, methanogens started to consume CO.

13.3 Conventional Bioreactors for Syngas Fermentation

13.3.1 Reactor Consideration

Proper design and operation of a bioreactor are important considerations for successful scale up of syngas bioconversion to useful products (Yasin et al. 2015). The key parameters necessary while selecting a suitable bioreactor are mainly related to gas-liquid mass transfer, which is governed by agitation speed, impeller design, power consumption, temperature, pressure conditions and bioreaction kinetics (Munasinghe and Khanal 2010a; Yasin et al. 2015). Both batch and continuous

Table 13.3 Methane production from syngas in different bioreactor systems

Inoculum	Reactor	Temp °C	pH	Agitation (rpm)	Feed gas composition	Any other carbon substrate	CH_4 production rate /yield	Reference
Anaerobic granular sludge	GLR	35.2	7.1	NA	CO loading = 15–122-mmol/g VSS/day	NR	0.49–4.77 mmol/g VSS/day	Guiot et al. (2011)
Enriched mixed microbial consortia	TBR	37, 60	7.0	NA	45% H_2, 25% CO_2, 20% CO, 10% N_2	NR	30–70% CH_4 in biogas	Asimakopoulos et al. (2021a)
Enriched thermophilic mixed microbial consortium	TBR	60	7.0	NA	45% H_2, 25% CO_2, 20% CO, 10% N_2	NR	17.6 ± 0.6 mmol/L/h	Asimakopoulos et al. (2021b)
Anaerobic sludge	CSTR	37, 55	8.5	400–500	10% CO_2, 40% CO, 50% H_2	NR	66–73% CH_4 in biogas	Li et al. (2020)
Anaerobic granular sludge	UASB	37	7.28–7.65	NA	100%, 2.5 L CO/day	Glucose	1709–2628 mL/L/day	Jing et al. (2017)
Anaerobic sludge	RMBR	55	7.0	NA	55% CO, 20% H_2, 10% CO_2	NR	186 mL/L/day	Westman et al. (2016)
Anaerobic sludge	TBR	37, 60	7.0	NA	45% H_2, 25% CO_2, 20% CO, 10% N_2	NR	8.49 mmol/L/h	Asimakopoulos et al. (2020)
Anaerobic sludge	TBR	25, 50	7.0	NA	80% H_2, 20% CO_2	NR	13.1 m^3/m^3/day, 97.5% CH_4 in biogas	Strübing et al. (2018)
Anaerobic sludge	TBR	55	7.0	NA	80% H_2, 20% CO_2	NR	15.4 m^3 CH_4/m^3/day	Strübing et al. (2017)
Enrichment anaerobic cultures	Sealed flasks	37, 60	7.2	100	P_{H2} = 1 atm, P_{CO} = 0.2–0.8 atm	NR	18.8 mmol/g VSS/day	Grimalt-Alemany et al. (2020)
Anaerobic granular sludge	BSB	35	7.5	200	20–100% CO	NR	1 mmol/g VSS/day	Sancho Navarro et al. (2016)

Thermophilic mixed culture	FMBR	55	8.0	NA	20% H_2, 55% CO, 10% CO_2	NR	34.41 mmol/L/day	Chandolias et al. (2019)
Sewage sludge	CSTR-HFM	37	7.6	NA	2% H_2, 8% CO	NR	1322 mL/day biogas production, 98.8% CH_4	Wang et al. (2013)
Anaerobic mixed cultures	BSB	70	7.5	NA	80% H_2, 5% CO, 15% CO_2	NR	78.6–89.5 mL/day	Bu et al. (2018)
Co-culture of *Carboxydothermus hydrogenoformans* and *Methanothermobacter thermoautotrophicus*	CSTR	65	7.2	NR	66.66% H_2, 33.33% CO	Acetate	4.91 mmol/L/h	Diender et al. (2018)

NR, not reported, NA, not applicable; BSB, batch serum bottle; CSTR, continuous stirred tank reactor; RMBR, reverse membrane bioreactor; FMBR, floating membrane bioreactor; GLR, gas lift reactor; UASB, upflow anaerobic sludge blanket reactor; TBR, trickle bed reactor; HFM, hollow fiber membranes operation modes using a few bioreactor configurations have been applied for syngas fermentation to useful products. Continuous stirred-tank reactor (CSTR) is the most commonly used bioreactor system for syngas fermentation, but other types of reactors such as bubble column reactor (BCR), trickling bed reactor (TBR), packed bed bioreactor (PBR), gas lift reactor (GLR) and membrane bioreactor (MBR) (primarily hollow fibre membrane bioreactor) have also been examined under different modes of operation and experimental conditions (Asimakopoulos et al. 2018). Table 13.4 compares the commonly used reactors for gas fermentation along with their volumetric gas to liquid mass transfer coefficient (*K*La) values. The different types of bioreactor configurations studied for syngas fermentation to useful products are depicted in Fig. 13.2 and discussed further in the following sub-sections. Table 13.5 overviews the relative advantages and drawbacks of the different types of bioreactors for syngas fermentation.

13.3.2 Continuous Stirred Tank Reactor

The continuous stirred tank reactor (CSTR; Fig. 13.2a) is the most commonly used bioreactor type employed for syngas fermentation research as it offers good mixing. Mixing of gaseous substrates in the liquid media inside the reactor is achieved by impellers and baffles which enhance mass transfer between the substrate and microorganisms inside the reactor (Munasinghe and Khanal 2010b). The hydrodynamic shear generated by a high level of agitation or mixing creates small sized bubbles from bigger ones, which increases the interfacial area for mass transfer and subsequent enhancement in the bioavailability of gaseous substrates (Bredwell et al. 1999). Besides, the slow rising velocity of the finer gas bubbles lead to a prolonged gas retention time in the liquid medium, resulting in high mass transfer rates. In this type of reactor, gaseous substrate is supplied continuously and liquid medium containing the nutrients is fed into the bioreactor to support microbial growth and metabolism (Bredwell et al. 1999; Sinharoy et al. 2020a). Products formed in the reactor by microbial conversion are drawn out from the system at the same flow rate as the feed to maintain steady state profiles under continuous mode of operation.

The effect of different operational parameters, such as agitation speed, medium flow rates and composition as well as syngas flow rate on ethanol and acetate production by *Clostridium ljungdahlii* was studied using a CSTR (Aghbashlo et al. 2016). The sustainability and renewability of the process was also evaluated by a thermodynamic model. From the calculated model parameters, the maximum exergetic productivity index was 6.82 and 6.90 using, respectively, the conventional exergy and eco-exergy concepts at an optimum condition of 450 rpm agitation speed, 0.55 mL/min liquid medium flow rate and 8 mL/min syngas (55% CO, 20% H_2, 10% CO_2 and 15% Ar) volumetric flow rate. A six fold increase in ethanol concentration by *Clostridium ragsdalei* was achieved in a pilot scale (100 L) stirred tank reactor compared with that in a serum bottle (Kundiyana et al. 2011). The

Table 13.4 Commonly used bioreactor systems for biological CO conversion and their volumetric mass transfer coefficients

Reactor type	Agitation speed (rpm)	Volumetric mass transfer coefficient K_La (h^{-1})	Gaseous feed	Products	Reference
Continuous stirred tank reactor (CSTR)	200	14.2	CO	NR	Bredwell et al. (1999)
CSTR	300	35	Syngas	NR	Bredwell et al. (1999)
CSTR	450	101	Syngas	NR	Bredwell et al. (1999)
CSTR	500	86.4	CO	H_2 = 9.6 mmol/h	Ismail et al. (2008)
CSTR	450	153	CO	NR	Ungerman and Heindel (2007)
CSTR	600	154.8	CO	NR	Riggs and Heindel (2006)
CSTR	700	192.8	Syngas	NR	Kapic et al. (2006)
CSTR	300	14.9	CO	NR	Klasson et al. (1993)
CSTR	400	21.5	CO	NR	Klasson et al. (1993)
CSTR	700	35.5	CO	NR	Klasson et al. (1993)
Trickle bed reactor (TBR)	NA	137	Syngas	NR	Cowger et al. (1992)
TBR	NA	121	Syngas	NR	Bredwell et al. (1999)
Bubble column reactor (BCR)	NA	72	CO	Acetate = 15.6–90 mM, butyrate = 0.7–1.3 mM	Chang et al. (2001)
Hollow fiber membrane reactor (HFMR)	NA	400	CO	NR	Munasinghe and Khanal (2012)
HFMR	NA	1096.2	CO	Acetate = 8.2 g/L, ethanol = 23.93 g/L, butanol = 0.45 g/L	Shen et al. (2014a)
HFMR	NA	385	CO	NR	Lee et al. (2012)
Packed bed reactor	NA	21	Syngas	NR	Bredwell et al. (1999)

(continued)

Table 13.4 (continued)

Reactor type	Agitation speed (rpm)	Volumetric mass transfer coefficient K_La (h^{-1})	Gaseous feed	Products	Reference
Gas lift reactor (GLR)	NA	129.6	CO	NR	Munasinghe and Khanal (2014)
GLR	NA	1.5–2.0	CO	H_2 production = 74.6–96.7% of CO (mol basis)	Haddad et al. (2014)
GLR	NA	91.08	CO	NR	Munasinghe and Khanal (2010b)
GLR	NA	153, 122	CO, H_2	Acetate = 7.2 mM, ethanol = 32.3 mM, 1-butanol = 5.1 mM, 1-hexanol = 1.0 mM	Riegler et al. (2019)
GLR	NA	80.28	CO	Acetate = 328–711 mg/L, ethanol = 44–498 mg/L, butyrate = 83–389 mg/L, butanol = 10–251 mg/L	Park et al. (2013)
Stirred tank with microbubble sparger	200	90.6	CO	NR	Bredwell et al. (1999)
Stirred tank with microbubble sparger	300	104	CO	NR	Bredwell et al. (1999)

NA, not applicable, NR, not reported

ethanol concentration reached a maximum value of 25.26 g/L along with the co-products 2-propanol, 1-butanol and acetic acid.

A two-stage CSTR for ethanol production from syngas was studied using *Clostridium carboxidivorans*, in which the pH of the first reactor was maintained at pH 6 for acidogenesis and the second one was maintained at pH 5 for solventogenesis (Abubackar et al. 2018). This two-stage approach achieved a high biomass concentration in the first stage and increased the ethanol production in the second stage.

Bioconversion of CO rich syngas to hydrogen using a CSTR with the anaerobic photosynthetic bacterium *Rhodospirillum rubrum*, capable of performing the biological water-gas shift reaction, was studied (Younesi et al. 2008). The best performance in terms of hydrogen production rate and conversion efficiency of 16 (± 1.1) mmol/g cell/h and 87 (± 2.4) %, respectively, was achieved at an agitation speed and gas flow rate of, respectively, 500 rpm and 14 mL/min. In order to achieve a high gas liquid mass transfer a CSTR equipped with a dual-impeller agitation and

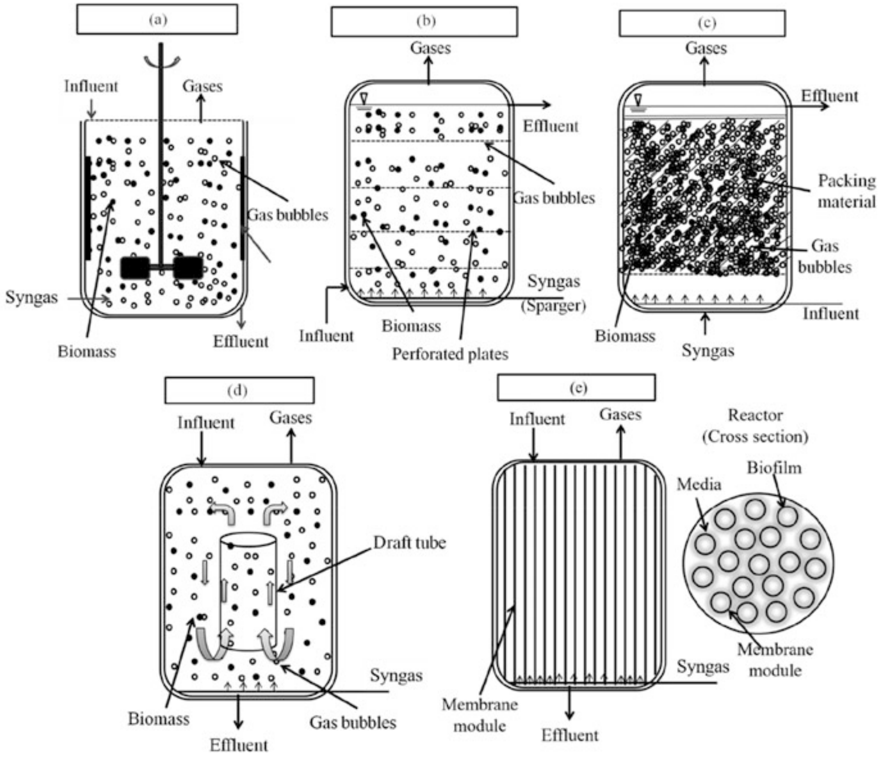

Fig. 13.2 Schematic of various commonly used bioreactor systems for syngas fermentation. (**a**) Stirred tank reactor, (**b**) bubble column reactor, (**c**) packed bed reactor, (**d**) gas lift reactor and (**e**) membrane bioreactor

microsparger system was utilized (Najafpour et al. 2003). A very high H_2 production rate of 16 mmol/g cell/h and 80% conversion efficiency on CO by *R. rubrum* at a syngas flow rate of 14 mL/min was achieved. The maximum cell density during steady state operation reached 1.3–1.4 g/L with a specific growth rate of 0.0225/h.

13.3.3 Bubble Column Reactor

A bubble column reactor (Fig. 13.2b) offers a high gas-liquid mass transfer due to the high surface area of bubbles and increased turbulence as the bubbles rise through the liquid column. Small-sized finer bubbles produced in this type of reactor have high surface-to-volume ratios and low rise velocities through the liquid, resulting in improved contact times in the reactor. The short gas residence time and high pressure drop in the bubble reactor are some drawbacks limiting its scale-up and commercialization. Other drawbacks of this bioreactor type include back-mixing and

Table 13.5 Relative advantages and disadvantages of different bioreactors used for syngas fermentation

Reactor type	Advantages	Disadvantages
Continuous stirred tank reactor	• Simple to operate • Mixing improves gas-liquid mass transfer • Gaseous substrates are more accessible to microbes due to breaking of large bubbles into finer ones by increasing rotational speed of impellers	• High agitation causes shear stress on microbes • Large power requirement • High operating cost
Bubble column reactor	• High gas-liquid mass transfer rates • Low operating and maintaining cost • Low shear stress	• Back mixing and coalescence
Trickle bed/ packed bed reactor	• Gas and liquid flow could be either in co-current or counter-current direction • No need of mechanical agitation • Power requirement is less	• Clogging of bed
Membrane bioreactor	• Gases easily diffuses through wall of the membranes • Membrane wall provides excellent support for microbial growth and improves biomass retention • High product yield, high reaction rate, high tolerance to toxic elements	• Not yet commercially used for CO conversion or syngas fermentation • High installation cost • Clogging problems
Gas lift reactor	• Mechanical simplicity • Low energy requirement • No focal points for energy dissipation • Low shear stress • Suitable for process with variable gas feeding requirements	• Not suitable for viscous broths • Minimum process volume • Dead zones inside the reactor • Insufficient mixing at high biomass densities
Moving bed biofilm reactor	• Good biomass retention • High surface area for biofilm formation • Auto-control of biomass due to shear and tear during mixing • Less area requirement	• Prolonged startup time • Loss of biomass support over time • Troubleshooting is difficult due to complicated design

coalescence in the bubble column (Datar et al. 2004). But the main attraction of this type of reactor is the ease of obtaining the desired amount of biomass in the reactor.

Syngas fermentation by *Clostridium carboxidivorans* was studied in a continuously operated bubble column bioreactor (4.5 L volume): ethanol, butanol, and acetic acid yields were 0.15, 0.075 and 0.025 g/mol CO, respectively, under steady state condition (Rajagopalan et al. 2002). The authors further suggest different approaches such as cell recycle to increase the cell concentration without altering the ethanol yield, H_2 addition in the gas stream to improve the CO conversion to ethanol and optimization of nutrient supplements to the medium to further improve the bioreactor performance.

Amos (2004) evaluated the performance of a bubble column reactor for CO bioconversion to H_2 with or without gas recycle. The reactor with added gas recycle loop performed better with an overall conversion efficiency of over 50% for a 10:1

recycle-to-feed ratio. The performance of the bioreactor was attributed to a prolonged residence time, high cell mass, buffering capacity of the liquid and low inlet CO concentration to the reactor.

13.3.4 Packed Bed Bioreactor

The trickle-bed bioreactor or trickling filter (Fig. 13.2c) contains a tubular reactor with solid support for biomass to grow and attach to. The cells can either be immobilized on the solid packing or suspended in the liquid medium (Bredwell et al. 1999). Generally, such bioreactor system is operated under counter current flow of liquid to gas, where gaseous substrate rises upwards and the water flows downwards through the packed bed (Stoll et al. 2020). Special care needs to be taken to maintain a low water flow rate to prevent flooding in the column. The liquid flow is mainly provided to keep the cells moist along with nutrient supplementation for cell growth (Sinharoy et al. 2020c). Various packing materials, including wood, activated carbon, lava rock, plastic and porous ceramic supports have been tested for biofilm formation (Amos 2004). The primary advantage of this bioreactor configuration is the improved gas transfer area with a minimum pressure drop. Also, it is easy to enhance the mass transfer by controlling the liquid flow rates (Sinharoy et al. 2020c).

The effect of the reactor packing material on syngas fermentation by the photosynthetic bacterium *Rubrivivax gelatinosus* was examined using two geometrically similar reactors, but with different volumes (1 and 5 L) and non-porous glass beads of two different diameters (3 and 6 mm) as the support material (Wolfrum and Watt 2001). The CO conversion efficiency with the glass beads of 3 mm diameter at different superficial liquid velocities was better than with the 6 mm diameter glass beads, which was attributed to a high mass transfer with the smaller diameter particles owing to their high surface area to volume ratio. However, the reactor volume did not significantly affect the CO conversion, indicating consistency in performance of this bioreactor configuration which is helpful in predicting its performance.

A trickle bed bioreactor with 6 mm size soda lime glass beads as packing material was studied for ethanol fermentation from syngas (Devarapalli et al. 2016). CO inhibition could be overcome by a high amount of biomass available in the form of biofilm formed over the beads, resulting in 1.9 times enhanced H_2 uptake and conversion. The final ethanol and acetic acid concentrations inside the reactor reached a maximum value of 5.7 and 12.3 g/L, respectively. It was also found that the co-current mode of gas and liquid flow in the reactor reduced the gas bypass and reactor flooding problems that were encountered in counter-current operation.

Apart from passive immobilization methods to grow biomass on support materials, active immobilization techniques to entrap the anaerobic biomass inside polyvinyl alcohol (PVA) or sodium alginate beads have also been studied (Kumar et al. 2018). PVA addition to the sodium alginate beads improves their strength and recycle potential for long term use. High CO utilization (90%) efficiencies were achieved using a CO fed PBR operated at an HRT of 48 h. The superior performance of the PBR containing immobilized beads is attributed to the excellent gas-liquid mass transfer due to counter current flow of the liquid and the feed gas. Moreover, the use of biomass immobilization in PVA-alginate beads can prevent CO toxicity to the anaerobic biomass by avoiding direct exposure of the biomass to high CO concentrations (Kumar et al. 2018).

Methane production from syngas using a trickle bed reactor was studied to understand the effect of temperature on the process efficiency (Asimakopoulos et al. 2020). Thermophilic conditions (60 °C) were best suited for methane production with a maximum methane productivity of 8.49 mmol/L/h. The microbial community change at mesophilic conditions resulted in high accumulation of acetate in the reactor and lowering of the final methane productivity. The absence of acetoclastic methanogens in both the mesophilic and thermophilic reactor indicates that the methane production occurred through the hydrogenotrophic route. A scale up study using a 7.5 L volume reactor was also carried out during which a very high methane productivity of 17.6 mmol/L/h was achieved at a 0.33 h empty bed residence time (Asimakopoulos et al. 2021b). The reactor showed a maximum of 100% H_2 and 92.4% CO utilization without any process inhibition during the continuous bioreactor operation.

13.3.5 Gas Lift Reactor

A gas lift reactor (GLR; Fig. 13.2d) is similar to the bubble column reactor, but it differs by the fact that it contains a draft tube, through which syngas flows (Sinharoy et al. 2020b). The draft tube is either an inner tube (called gas lift bioreactor with an internal loop) or an external tube (called gas lift bioreactor with an external loop) which improves circulation and gas liquid mass transfer and equalizes shear forces in the reactor (Negi et al. 2020; Sinharoy et al. 2020c). The major advantages of a gas lift bioreactor are its simple design with no moving parts or agitators, low energy requirement as well as homogeneous distribution of nutrients and shear force (Riegler et al. 2019). The gas stream facilitates the exchange of material between the gas phase and the liquid phase, thus enhancing effective mass transfer. For example, a very high mass transfer coefficient of 91.08/h for CO was reported in a gas lift reactor combined with a bubble diffuser compared to other reactor configurations (Munasinghe and Khanal 2010b).

A CO and H_2 fed GLR with a high gas-liquid mass transfer coefficient ($kLa = 80.28/h$) was used to enrich acetogenic microorganisms from different animal faeces to isolate strains capable of syngas fermentation (Park et al. 2013). Ten out of 42 strains isolated from this enriched animal faeces were able to utilize CO/H_2 and produce alcohols and volatile fatty acids. The enriched consortium isolated from chicken faecal samples showed the highest product formation from syngas, i.e. 711 mg/L acetate, 498 mg/L ethanol, 389 mg/L butyrate and 251 mg/L butanol (Park et al. 2013).

CO conversion to H_2 by *Carboxydothermus hydrogenoformans* in a gas lift reactor (35 L volume) was examined to study the effect of different operating conditions, i.e. gas recirculation rate, CO feeding rate and addition of bacto-peptone to the medium (Haddad et al. 2014). The ratio of gas recirculation over CO feeding rate was the most important parameter affecting the reactor performance, which kinetically limited both the CO conversion and H_2 production rates.

A high amount of biohydrogen (20.5 mM) was produced from 36 mM CO using an anaerobic microbial consortium in a continuously operated GLR (Sinharoy and Pakshirajan 2020). The hydrogen production was further enhanced to 30.7 mM with addition of biologically synthesized iron nanoparticles to the bioreactor. The CO utilization by the anaerobic consortium was well above 80% for the low CO concentrations of 7.6 and 15 mM, but gradually depleted with further increase in the CO concentration.

Immobilized cells of *Butyribacterium methylotrophicum* have been studied in a GLR system for syngas fermentation by immobilizing it on different biosupports, namely celite, molecular sieves, alumina, activated carbon, wood, and ion exchange resins (Chatterjee et al. 1996). Among the different materials, molecular sieves were the best suited for cell growth, whereas celite was better for cell attachment than the other materials. Moreover, the product formation from syngas measured in terms of total electron content was higher in case of molecular sieves based system.

In addition to GLR operated under mesophilic conditions, its performance has also been evaluated under thermophilic conditions. For example, hydrogenogenic CO conversion for biological sulfate reduction was studied using a gas lift reactor and the effect of different HRT was investigated under thermophilic (55 °C) conditions (Sipma et al. 2007). The authors reported that at a high retention time (>5.5 h) the CO conversion resulted in hydrogenotrophic methane production, whereas H_2 production was higher at a short HRT (4 h). Overall, a CO conversion of 85% was achieved (Sipma et al. 2007).

13.3.6 Membrane Bioreactor

A membrane bioreactor (MBR) consists of a membrane module that is partially or completely submerged in liquid media (Fig. 13.2e). The syngas is diffused through the walls of the membranes without forming bubbles. Biomass grows on the outer wall of the membranes as a biofilm, which converts the syngas to useful products. Several studies on hollow fibre membrane (HFM) reactors have suggested that the MBR can potentially replace the universally used bioreactors with high gas liquid mass transfer rate for syngas bioconversion (Gunes 2021). A number of choices for membrane materials are available, among which hydrophobic membrane materials, e.g. polypropylene (PP), polyethylene (PE) and polyvinylidene fluoride (PVDF), are the most commonly used (Cho et al. 2018). Advantages of MBR over conventional bioreactor types are effective gas liquid mass transfer and low energy requirement. Moreover, a MBR provides a high yield, high reaction rate, and increased tolerance to toxic compounds (e.g. tar, acetylene, NOx and O_2) (Campanario and Ortiz 2017). Besides, this reactor type can operate at high CO partial pressure (P_{CO}). Main disadvantages are clogging and biofouling of the membrane due to excessive biomass growth (Munasinghe and Khanal 2010a; Yasin et al. 2015).

Ethanol fermentation from syngas by *Clostridium carboxidivorans* P7 was studied in a hollow fibre membrane biofilm reactor (Shen et al. 2014a). The *K*La value (1096.2/h) was higher than most of the commonly used bioreactors. A very high ethanol concentration of 23.93 g/L was achieved with an ethanol to acetic acid ratio of 4.79.

CO bioconversion to H_2 by *Carboxydothermus hydrogenoformans* was investigated in a hollow fiber membrane bioreactor under thermophilic (70 °C) conditions (Zhao et al. 2013). The reactor demonstrated consistent performance under different operational conditions such as liquid flow rate, temperature, CO pressure and CO loading rate. The CO utilization was 0.44 mol CO/g VSS/day for a partial CO pressure of 2 atm along with a maximum H_2 yield of 92% (mol basis).

A thermophilic reverse membrane bioreactor with a flat plain hydrophilic polyvinylidene fluoride (PVDF) membrane was used for biomethane production from CO (Westman et al. 2016). The maximum methane production rate reached 186.0 mL/L/day with a very high syngas consumption, i.e. 7.0, 15.2 and 4.0 mL/L/day for H_2, CO and CO_2, respectively. In a separate study, a thermophilic floating membrane bioreactor was examined for methane production from syngas (Chandolias et al. 2019). The maximum methane productivity amounted to 34.41 mmol/L/day along with H_2 and CO utilization rates of 22 and 50 mmol/L/day. The results obtained using the membrane bioreactor system for H_2 and CO utilization were, respectively, 38% and 28% higher than the values obtained using a free cell suspended bioreactor.

13.4 Novel Bioreactors for Syngas Fermentation

In order to improve the process efficiency of syngas fermentation, a few novel bioreactor configurations have been studied. These are biofilm based bioreactor systems with innovative designs to increase the gas-liquid mass transfer (Fig. 13.3).

13.4.1 Horizontal Rotating Packed Bed Reactor

The horizontal rotating packed bed (HRPB) reactor is one such novel bioreactor used for syngas fermentation (Shen et al. 2017). This bioreactor (Fig. 13.3b) is a combination of two distinct types of bioreactors, viz. the rotating biological contactor and the packed bed reactor. In this system, similar to the rotating disks in a conventional

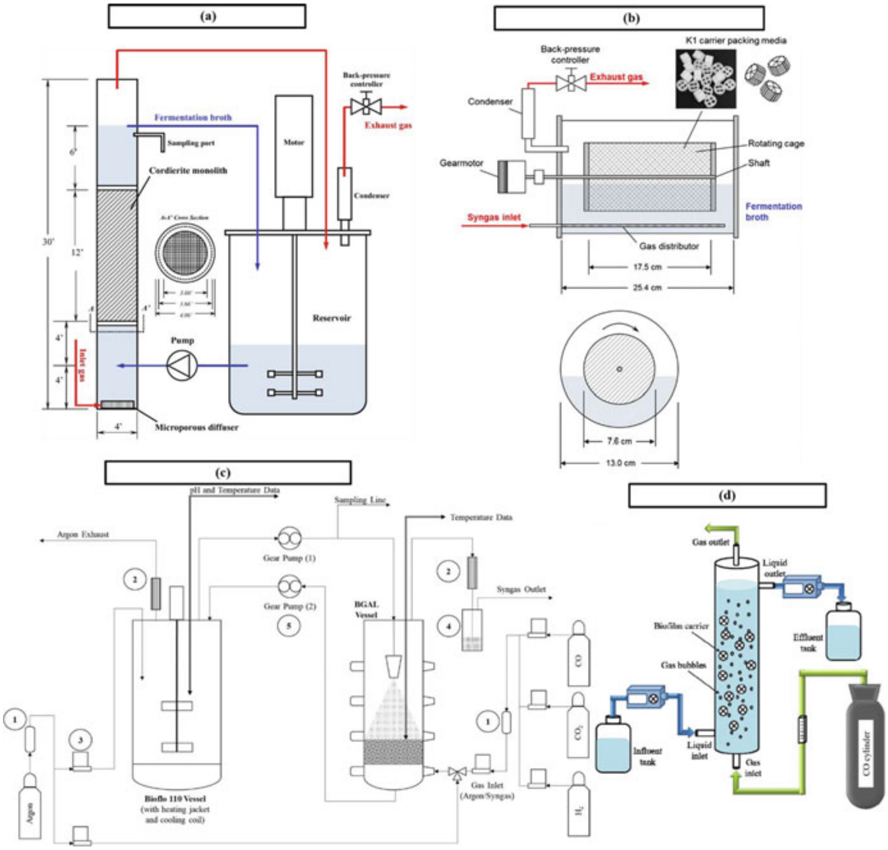

Fig. 13.3 Schematic of some selected novel bioreactor systems for syngas fermentation. (**a**) Monolithic biofilm reactor [reused from Shen et al. (2014b), Copyright (2014) with permission from Elsevier], (**b**) horizontal rotating packed bed reactor [reused from Shen et al. (2017), Copyright (2017) with permission from Elsevier], (**c**) bulk-gas-to-atomized-liquid reactor [reused from Sathish et al. (2019), Copyright (2019) with permission from Elsevier] and (**d**) moving bed biofilm reactor [reused from Sinharoy and Pakshirajan (2021), Copyright (2021) with permission from Elsevier]

rotating biological contractor, a packed bed column with biosupport materials is fixed on the rotating horizontal shaft. The internal packed bed column configuration is similar to a cage where biofilm carrying support materials are retained inside, whereas the liquid phase can move freely in and out of the column during rotation (Shen et al. 2017). In this reactor, a portion of the packing material is submerged, whereas the remaining portion is exposed to the headspace. Due to continuous rotation the biofilm is in alternate contact with the liquid phase and the headspace gas. The mass transfer coefficient and available surface area for biofilm growth is very high in this system (Shen et al. 2017). Due to proper packing in the internal rotating column and the rotation of the packed column, bed clogging is completely avoided in this bioreactor configuration. This novel bioreactor type was studied for ethanol production from syngas by *Clostridium carboxidivorans* P7 strain and a high ethanol titre and productivity of, respectively, 7.0 g/L and 6.7 g/L/day was achieved (Shen et al. 2017).

13.4.2 Monolithic Biofilm Reactor

Ethanol production from syngas by *C. carboxidivorans* P7 was carried out using a monolithic biofilm reactor (MBFR) (Shen et al. 2014b). Monoliths are structures made up of parallel straight channels with thin walls separating them (Fig. 13.3a). Using the MRFR at optimum process conditions, i.e. 300 mL/min of syngas flow rate, 500 mL/min of liquid flow rate and 0.48/day of dilution rate, ethanol concentration and productivity values were 4.89 g/L and 2.35 g/L/day. The values of syngas utilization and product formation were much higher than those obtained using a conventional bubble column reactor. This is due to high kLa values of the MBFR in comparison to the bubble column reactor (BCR), due to the slug flow pattern in the monolithic channels present in the MBFR.

The major advantage of the MBFR is that the pressure drop in this reactor is much smaller than in other biofilm-based reactor configurations, such as the trickling-bed or packed bed reactors, since the flow in the channel does not have bends and obstructions. However, a critical factor that influences the performance of this reactor type is the biofouling or sloughing of the biofilm attached on the monolithic channel wall due to fluid flow through the channel. Although the monoliths have been previously used extensively as catalyst support for multi-phase reactions such as hydrogenation and oxidation in chemical industry, their application in biological systems is limited, in particular as biofilm support. In comparison to other biofilm reactors, the MBFR provides added benefits such as high surface area for biofilm formation and good mechanical stability to the formed biofilm (Ebrahimi et al. 2006).

13.4.3 Bulk-Gas-to-Atomized-Liquid Contactor Reactor

Another novel bioreactor used for enhancing gas-liquid mass transfer during syngas fermentation is the bulk-gas-to-atomized-liquid (BGAL) contactor reactor (Sathish et al. 2019). The BGAL reactor consists of a packed bed with biosupport materials to allow biofilm growth, and syngas saturated liquid micro-droplets are dispersed into the packing inside the reactor. The syngas-rich liquid droplets then percolate through the bio-bed and CO is converted to ethanol by the biofilm present on the support material. The study reported a high ethanol productivity of 746 mg/L/h with an ethanol to acetic acid ratio of 7.6 from syngas using *Clostridium carboxidivorans* P7 strain (Sathish et al. 2019).

In this bioreactor system, liquid is supplied as discrete minute size droplets which causes a significant increase in the liquid and bulk gas interface (Fig. 13.3c). The superior mass transfer was demonstrated with oxygen as a model gas, which resulted in a very high oxygen transfer rate (OTR) of 569 mg/L/min and a KLa value of 2.28/s. These values are 100 times higher than the values obtained using any other bioreactor configuration.

Kaldness® biosupport material was used for biofilm formation due to its large surface area. Use of immobilized biomass in this reactor configuration is more advantageous than suspended biomass as dispersion of the syngas containing liquid droplets into the bulk liquid in suspended biomass system (such as CSTR) causes dilution of the dissolved gases, which in turn reduces the mass transfer and conversion efficiency. The overall energy consumption for transferring the gas to the liquid phase was also much lower (four-fold) in this BGAL bioreactor in comparison to a CSTR.

13.4.4 Moving Bed Biofilm Reactor

The moving bed biofilm reactor (MBBR; Fig. 13.3d) is another biofilm based reactor configuration with specially designed biofilm carriers, known as Kaldness® biosupport material, which offer a large surface area for biofilm formation (Sinharoy et al. 2020c; Sinharoy and Lens 2020). Although it has not been studied for liquid biofuel production from syngas, CO bioconversion for H_2 production has recently been reported (Sinharoy and Pakshirajan 2021). A very high H_2 production value of 19.5 mmol/L along with ~2 mmol/L of acetate were obtained for 36 mM inlet CO concentration in the MBBR. The CO utilization was better (>70%) at low inlet CO concentrations (in the range 9.05–15 mM). Methane production could be completely avoided in the reactor by 2-Bromoethanosulfonate supplementation to the reactor during its continuous operation.

The main advantages of the MBBR include high biomass retention, high treatment efficiency, resistance to shock loading conditions and small footprint (Sinharoy et al. 2019; Sinharoy et al. 2020c). In addition, bed clogging, which is mostly observed with other attached growth bioreactor configurations, is uncommon in a MBBR due to continuous mixing. Furthermore, due to the gaseous feed, mixing inside the reactor can be easily achieved without the need for supplying a separate (additional) gas stream for mixing, thus keeping the process costs low.

13.5 Bioreactor Strategies to Overcome Gas Liquid Mass Transfer Problems

In a bioreactor system involving gaseous substrates, e.g. syngas, a high product yield directly depends upon its bioavailability to the microorganisms, which in turn can be limited by the high mass transfer rate of the substrate (Liu et al. 2014). A high cell concentration necessary for the high yield also depends on mass transfer rate of the gaseous substrates: a low mass transfer rate leads to reduced cell concentrations in the fermentation media (Yasin et al. 2015). The most important factor limiting the bioconversion of gaseous substrates is gas-to-liquid mass transfer, similar to oxygen in aerobic fermentations (Worden et al. 1997). However, limitation due to gas liquid mass transfer is more problematic for synthesis gas fermentations compared to that in aerobic fermentations, as the solubility of CO (0.0225 g/kg water) or H_2 (0.0015 g/kg water) is less than O_2 (0.033 g/kg water) solubility (on a mass basis, at 30 °C) (Abubackar et al. 2011; Munasinghe and Khanal 2012). The different strategies suggested to improve syngas solubility and gas-liquid mass transfer are discussed below.

13.5.1 Agitation Speed and Impeller Configuration

An easy way to improve the gas liquid mass transfer is by enhancing the agitation speed (rpm) in a bioreactor. Bredwell et al. (1999) reported a high $K\mathrm{L}a$ value of 101/h for CO at 450 rpm agitation speed. In another study, an increase in the agitation speed up to 700 rpm is reported to enhance the CO liquid mass transfer (Klasson et al. 1993). For achieving a high mechanical agitation speed, a high power input is required, and, therefore, a high ratio of power required per reactor volume makes this strategy economically weak for large scale industrial reactors, merely because of the excessive power costs (Yasin et al. 2015).

A different strategy to improve the mass transfer is by employing different impeller design (Ungerman and Heindel 2007). The effect of six different impeller configurations, namely Rushton-type, Philadelphia Mixing concave (hollow blade) turbine, Philadelphia Mixing pitched blade turbine (PBT), Philadelphia Mixing LS hydrofoil, Lightnin A315 fluidfoil and Lightnin A310, on the gas liquid mass transfer rate was analyzed. The Rushton-type performed better compared to the other five impeller types. Also, the dual Rushton type showed a 27% higher gas liquid mass transfer compared to the conventional single Rushton type impeller. However, its performance in terms of the ratio of volumetric mass transfer coefficient to power input was poor. Hence, it should be emphasized that improved gas liquid mass transfer in a stirred system demands a high power consumption and cost associated with it. Also, the increase in the agitation speed to enhance the gas liquid mass transfer may be damaging to shear sensitive microorganisms, thereby hampering microbial growth in the bioreactor (Munasinghe and Khanal 2012).

13.5.2 Additives

The use of additives such as electrolytes, surfactants, alcohols and nanoparticles (with or without surface modification) have been reported to enhance the gas liquid mass transfer (Wainaina et al. 2018). The effect of various electrolytes such as sulfate, nitrate, and chloride on the gas-liquid mass transfer was studied, and the results show an enhancement of 3.4–4.7 times using the sulfate electrolytes (Cu, Co, Mn, Ni and Fe) compared to a system without any added electrolytes (Zhu et al. 2009). Among the different metal ions, viz. copper, cobalt, nickel, iron, manganese and magnesium, copper containing electrolyte is the best for enhancing the volumetric gas liquid mass transfer (Zhu et al. 2009). This is attributed to an increase in the gas-liquid interfacial area and a reduction in the gas bubble coalescence in the liquid phase. These findings on enhancement in the gas liquid mass transfer in water due to the addition of electrolyte or metallic salts are also valid for aerobic systems. For example, Zuidervaart et al. (2000) reported a 250% enhancement in the oxygen mass transfer rate when metal sulfate based electrolytes [e.g., $CuSO_4$, $FeSO_4$, $ZnSO_4$, and $Al_2(SO_4)_3$] were added to the liquid media. Use of surfactants such as Tween (polyoxyethylene sorbitans) and Brij (polyoxyethylene alcohols) for enhancing the gas-liquid mass transfer is also reported (Bredwell et al. 1997).

The increase in gas-liquid mass transfer due to the addition of nano- or microparticles was reported by Zhu et al. (2008). Nanoparticles made of mesoporous silica materials and coated with different hydroxyl, mercaptopropyl or organic groups enhanced the gas-liquid mass transfer. The mercaptopropyl group grafted nanoparticles yielded the maximum gas-liquid mass transfer (upto 1.9 times increase). The presence of functional groups on nanoparticles and their hydrophobicity significantly enhanced the gas-liquid mass transfer (Zhu et al. 2008). Biologically synthesized iron nanoparticles enhanced the CO aqueous solubility by 56% (Sinharoy and Pakshirajan 2020). The enhancement in CO solubility was attributed to the presence of hydrophobic functional groups, such as amides, polyphenols and proteins obtained from green tea extract, which was used as the reducing agent for the iron nanoparticle synthesis.

The different mechanisms of gas liquid mass transfer enhancement due to small particle addition include physical adsorption, homogeneous reactions in a slurry, dissolved particles and suspended particles in heterogeneous reactive systems (Beenackers and Van Swaaij 1993). The small particles transport an additional amount of gas to the bulk liquid through gas adsorption at the gas liquid diffusion layer followed by desorption in the bulk liquid (Zhu et al. 2008), which is referred to as the shuttle effect as depicted in Fig. 13.4 (Cheng et al. 2019). This method of enhancement is greatly influenced by the size and surface characteristics of the particles.

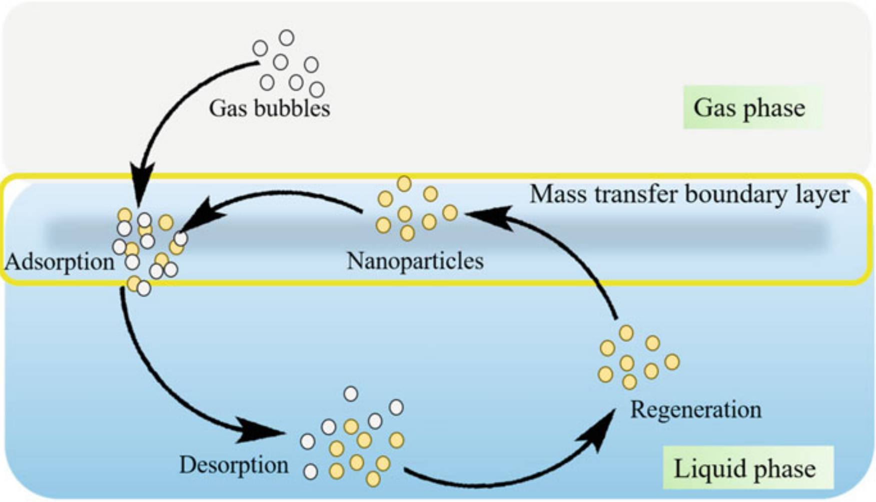

Fig. 13.4 Schematic of nanoparticle mediated enhancement of the gas-liquid mass transfer

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Part VI
Life Cycle Analysis

Chapter 14

Up and Downstream Technologies of Anaerobic Digestion from Life Cycle Assessment Perspective

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Abstract The development of anaerobic digestion (AD) plants has been considered as a solution to overcome the depletion of fossil resources and the increasing environmental pollution caused by the over-use of fossil fuels. However, there are some challenges which may undermine the sustainability of the AD including its associated up- and downstream strategies. In order to sustain the development of AD plants it is necessary to calculate the environmental hotspots through their whole life cycle and represent the possible solutions to mitigate the potential pollution. Among different methods, life cycle assessment (LCA) is widely employed to quantify and evaluate the environmental impacts of AD and its related up- and downstream technologies. This chapter comprehensively summarizes the environmental impacts of AD plants from an LCA point of view and proposes advanced strategies to alleviate the negative impacts and bring biogas plants into sustainable circular bio-economy.

Keywords Anaerobic digestion · Life cycle assessment · Biorefinery · Sustainability

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14.1 Introduction

In the last decades, the development of anaerobic digestion (AD) plants have contributed to achieving both environmental pollution mitigation and energy independency by utilizing waste streams, such as livestock manure and organic fraction of municipal solid waste (OFMSW) to produce biogas and biofertilizer (Duan et al. 2020). Biogas and nutrient-rich digestate produced by the AD plants bring about significant environmental savings, specifically, in terms of mitigation of greenhouse gas (GHG) emissions (Fusi et al. 2016). However, properly designed AD plants consist of upstream and downstream technologies for the appropriate treatment of the feedstock and suitable biogas and digestate conditioning. Some upstream and downstream processes rely on the consumption of considerable amounts of chemicals as well as energy; thereby they could significantly undermine the environmental sustainability of the AD plants (Khoshnevisan et al. 2016, 2018b; Tsapekos et al. 2021). Furthermore, taking the environmental savings into consideration, biogas utilization and digestate management are leading criteria to assess the sustainability of AD facilities (Ardolino et al. 2020; Kohlheb et al. 2020). Therefore, to sustain the processing of any type of feedstock in AD plants, the environmental footprints of every constitution of the AD processes should be concerned.

In this regard, life cycle assessment (LCA), covering energy flow, mass flow, GHG emissions, and other environmental impacts, is a well-established method which can be employed as a standard tool to evaluate the sustainability of any given system through its whole life cycle (Finkbeiner 2014). LCA enables the quantification of the environmental impacts of the systems under consideration and find the environmental hotspots and possible opportunities for future improvements (Dastjerdi et al. 2021). In this context, considerable studies have already been published under the framework of LCA to assess the environmental impacts of the AD plants and their related subsystems. This chapter aims to comprehensively review the state-of-the-art progress in the sustainability of AD plants by scrutinizing the environmental impacts caused by both up and downstream processes (i.e., pretreatment technologies, biogas desulfurization and upgrading, as well as biogas and digestate utilization) to show the recent advancements and the roadmaps for future work.

14.2 LCA to Determine the Sustainability of AD Systems

LCA has long been used as a valuable tool to assess the environmental footprints of AD systems. Since AD has been considered as a waste management strategy along with a decentralized energy technology, LCA has been widely employed during the past decades to scrutinize the sustainability of AD plants and their associated sub-systems as part of the waste management system and waste to energy scenario (De Jong et al. 2017). The AD technology has been in use for over 100 years and is known as an effective approach to reduce the environmental impacts of fossil-based energy sources (McCarty 1982). Moreover, it has been considered as a more sustainable solution compared to other waste management strategies such as landfill or incineration (Rao et al. 2010). Hence, numerous studies have been conducted to compare either the environmental impacts of biomethane production via AD with fossil based energy carriers, or different waste management strategies for a given waste stream. These LCA studies have highlighted various aspects of the AD technology, such as the use of AD for food waste management and bio-energy production (Chiu and Lo 2016; Piao et al. 2016; Righi et al. 2016), utilization of municipal solid and liquid wastes for bioenergy production with a focus on algal biofuel production (Chiu and Lo 2016), biogas production in Europe (Hijazi et al. 2016) and sustainable management of agricultural residues (Bacenetti et al. 2016). Table 14.1 summarizes some of the previous studies conducted in this context.

14.3 LCA of Upstream Technologies

14.3.1 Pretreatment Requirement

Organic waste, agricultural waste, manure, and energy crops are the most frequently used biomass in AD plants (Aziz et al. 2019). The environmental performance of AD systems largely depends on the feedstock used within the plants and the amount of biogas exploited (Montgomery and Bochmann 2014). However, some specific types of biomass such as lignocellulosic materials are critically slow to be degraded during the AD process to produce reasonable amount of biogas (Lee et al. 2020). Accordingly, prior to being fed into anaerobic digesters, specific pretreatment technologies are needed depending on the feedstock used and the AD technology (Carrere et al. 2016).

AD consists of four main steps, i.e., hydrolysis (formation of sugar, long chain fatty acid, amino acid), acidogenesis (acid formation i.e., alcohols and carbonic acid), acetogenesis (acetic acid formation, i.e., CH_3OH, NH_3, H_2S, and CO_2), and methanogenesis (biogas) (Koupaie et al. 2019). Pretreatments target enhancing the hydrolysis step to facilitate the breakdown of the complex molecules, shortening the biodegradation time, and enhancing biomethane formation (Tabatabaei et al. 2020). Pretreatment technologies are divided into physical, chemical, biological, and combined process (Gnaoui et al. 2020). Further information and subcategories of main classes of pretreatment methods are illustrated in Fig. 14.1.

14.3.2 Biological Pretreatment Methods

From the LCA point of view, any pretreatment technology performed upstream of AD, apart from the effectiveness for increasing the biomethane yield, should be

Table 14.1 Overview of studies related to LCA of AD systems

Surveyed location	Goal and Scope	System Boundary				Impact assessment method	Feedstock type	Reference
		Feedstock production and collection	AD	Biogas Upgrading	Product use			
Italy	Co-digestion of sewage sludge and fruit and vegetable wastes	No	Yes	No	Yes	ILCD Metrics	Co-digested fruit and vegetable waste with waste mixed sludge from municipal wastewater treatment plants	Di Maria et al. (2016)
USA	Compare areal productivities of AD and wind farms	No	Yes	No	Yes	No	Dairy waste water	Ciliberti et al. (2016)
France	LCA of microalgae AD	Yes	Yes	Yes	Yes	ReCiPe 2008	Microalgae	Shimako et al. (2016)
Spain	AD of sewage sludge	No	Yes	No	Yes	ReCiPe v.1.08 (midpoint)	Sewage sludge	Blanco et al. (2016)
Sweden	AD of food waste and sewage sludge	No	Yes	No	Yes	CML 2001 (GHG results only)	Municipal solid waste	Eriksson et al. (2016)
Germany	Electricity production from agriculture feedstock	Yes	Yes	Yes	Yes	ReCiPe v.1.06 (midpoint) and CED v.1.08	Co-digestion of maize (or sunflower, horse manure and biogenic waste), grass, rye silage, and chicken manure	Junne and Junne (2016)
Germany	Compare organic WM systems	Yes	No	No	No	A method with similar indicators as specified in ReCiPe midpoint metrics	Organic waste	Jensen et al. (2016)
Austria	Biogas from pretreated maize silage	Yes	No	Yes	No	ReCiPe v.1.08 (mid-point) and ILCD 2011	Maize silage	Kral et al. (2016)

USA	Comparative analysis of	No	Yes	No	No	IMPACT 2002+ and TRACI 2.0	Wastewater	Pericault et al. (2017)
Turkey	AD of agricultural farm waste	No	Yes	No	Yes	EDIP 2003	Agricultural wastes	Nayal et al. (2016)
Australia	Co-digestion of sewage sludge and municipal food waste	No	Yes	Yes	Yes	CML-IA	Sewage sludge and sorted food waste	Edwards et al. (2017)
Germany	Electricity production from microalgal feedstock	Yes	Yes	Yes	Yes	ReCiPe v.1.06 (midpoint)	Co-digestion of marine Microalgae or maize, grass, rye silage, and chicken manure	Ertem et al. (2016)
France	AD of sewage sludge and methanation	No	Yes	Yes	Yes	GHG Emissions; ReCiPe v.1.08 (endpoint)	Sewage sludge	Collet et al. (2017)
Denmark	Different strategies for energy and nutrient recovery from source sorted organic fraction of AD	No	Yes	Yes	No	IMPACT 2002+	Household waste	Khoshnevisan et al. (2018b)
Denmark	Environmental impacts of biogas production from grass	Yes	Yes	Yes	Yes	IMPACT 2002+	Grass	Tsapekos et al. (2021)
Denmark	Biowaste biorefinery concepts	No	Yes	Yes	Yes	IMPACT 2002+	Municipal solid waste	Khoshnevisan et al. (2020b)
China	LCA of AD of pig manure	No	Yes	No	Yes	IMPACT 2002+	Pig manure	Duan et al. (2020)

Adapted from Rajendran and Murthy (2019)

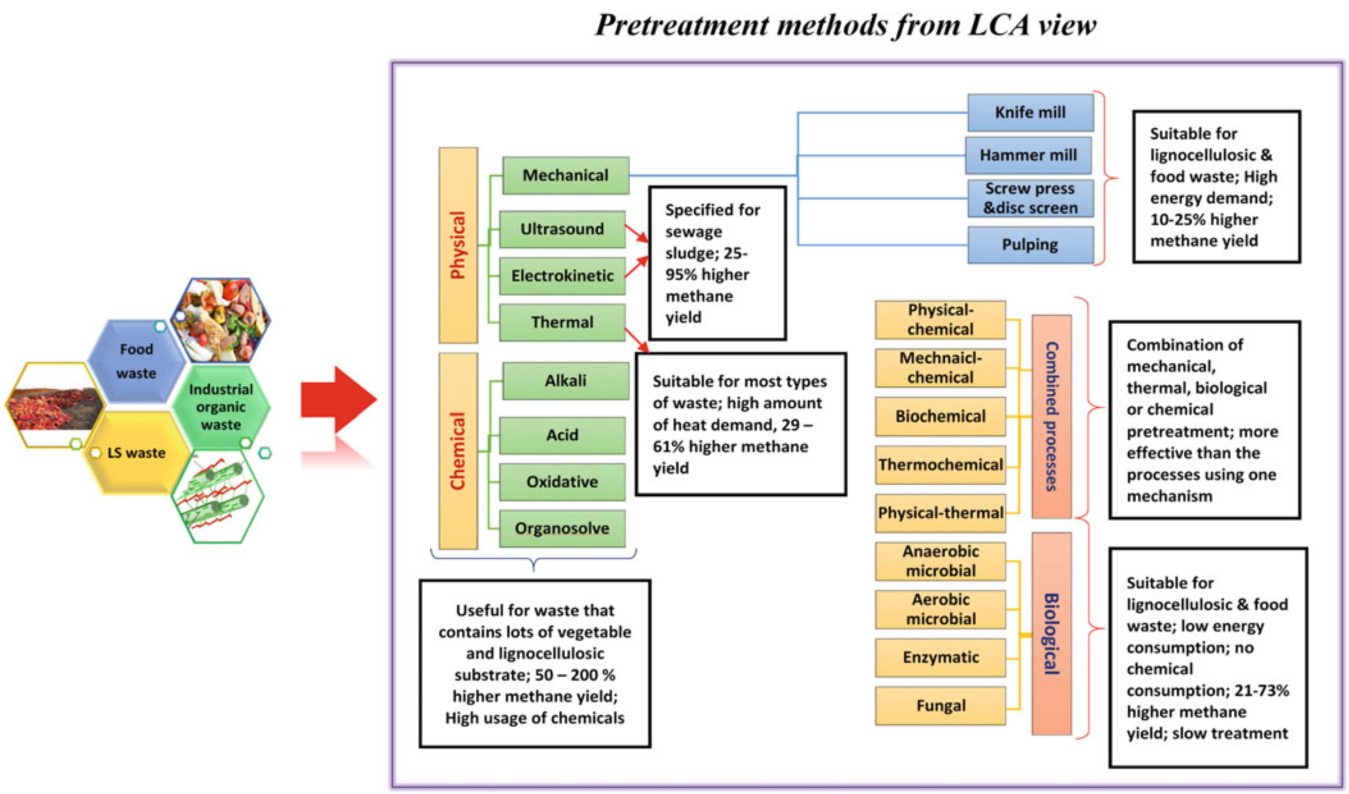

Fig. 14.1 Pretreatment technologies utilized in AD plants. LS, lignocellulosic. Characteristics taken from Chiu and Lo (2016), Shrestha et al. (2020), Torres and Lloréns (2008), Wang et al. (2015) and Zhang et al. (2011)

eco-friendly in terms of water, energy, and chemical consumption with less environmental burdens (Ravindran et al. 2018). Table 14.2 summarizes the previous studies with focus on pretreatments prior to AD. Among the existing technologies for the pretreatment of bio-feedstock, biological routes have low energy demand and could take part in the AD plants at low temperature in the absence of chemical additives (Chiu and Lo 2016; Tabatabaei et al. 2020). The enzymatic pretreatment has shown high efficiency to significantly improve the biogas production potential while being independent of water consumption and has minor environmental impacts (Asgher et al. 2014). Besides, fungi, specifically white-rot fungi, enable removal of the environmental pollutants from solid and liquid waste before being used for AD (Jayachandra et al. 2011; Montgomery and Bochmann 2014).

Biological pretreatment technologies, such as micro-aeration and anaerobic methods, are carried out too slowly compared with physical and chemical processes (Bochmann and Montgomery 2013). Therefore, some of the organic matter is degraded to CO_2 instead of being converted into methane in the subsequent AD process (Chiu and Lo 2016). In order to alleviate this bottleneck to some extent, it is recommended to combine microaeration with an anaerobic pretreatment reactor and thereby enhancing the methane yield (Montgomery and Bochmann 2014). Apart from the mentioned advantages and disadvantages, biological methods are commonly used in combination with other physical-chemical technologies to tackle the aforementioned limitations (Khoshnevisan et al. 2018b; Tabatabaei et al. 2020). Accordingly, the requirements for auxiliary pretreatment technologies have undermined the wide industrial application of biological methods in AD systems (Tabatabaei et al. 2020).

14.3.3 Physical Pretreatment Methods

As illustrated in Fig. 14.1, physical methods have a number of subcategories which are different in terms of operation and energy demand as well as types of biofeedstock for which they are best suited (Mudhoo 2012). The most prevailing types of physical pretreatment technologies are mechanical methods in which large and unwanted objects are properly separated and the size of the bulk substrate is reduced (Chiu and Lo 2016). Mechanical pretreatment technologies, which are mostly applied for conditioning of food waste, and lignocellulosic biomass normally have a high power demand and consume large amounts of energy (Hernández-Beltrán et al. 2019; Khoshnevisan et al. 2018b; Montgomery and Bochmann 2014). Meanwhile, they can lead to higher energy recovery which compensates the background environmental burdens from the electricity consumption (Chiu and Lo 2016). Moreover, by incorporating more renewable power into the electricity grids, the GHG intensity of electricity could be alleviated to a great extent (Prasad et al. 2016).

Among the mechanical facilities and from LCA viewpoint, pulping technology is the most preferred method for the pretreatment of food waste due to appropriate

Table 14.2 Studies conducted over the LCA of pretreatment technologies of AD plants

Feedstock	Pretreatment method			LCA			Reference
	Physical	Chemical biological	Combined	Functional unit	Goal	Investigated impact	
Sludge	Thermal			1 t dry mass of sludge	Evaluating the environmental impact of the configurations of AD fed sludge	GWP; POCP; EP; AP; ADP	Mills et al. (2014)
OFMSW	Mechanical			1 t OFMSW	Environmental impact assessment of physical pretreatment	GHG	Carlsson et al. (2015)
SSOHW	Mechanical			1 t SSOHW	LCA of upstream/downstream technologies	GWP; Human health; Ecosystem quality; Resources	Khoshnevisan et al. (2018b)
Sludge	Thermal	Alkali & acid		1000 kg dry	LCA evaluation pretreatment methods in methane generation	GWP	Wang et al. (2020)
MSW	Thermal & mechanical			Biomass 1 t MSW	LCA of alternative management options for MSW in Brazil	GWP; EP; AP; TP; ODP; OFP; PMF	Lima et al. (2018)
Oil palm empty fruit bunches			Chemical-thermal	1 ml methane	Analyzing the environmental impact of generating methane as a useful material with and without the pretreatment technology	GWP	Lee et al. (2020)
MSW			Mechanical-biological	46,929 t MSW	Environmental performance of mechanical biological pre-treatment MSW fed biogas plant	GWP; POF; PMF;TA; ME,FSD;HT	Beylot et al. (2015)
Sludge	Thermal & Ultrasound			1 t mixed sludge (dry basis)	Environmental performance of mechanical biological pre-treatment MSW fed biogas plant	Climate change, abiotic depletion, acidification and eutrophication	Cartes et al. (2018)

Microalgae	Thermal			1 kWh biogas	Comparing the hydrothermal and solar driven hydrothermal	GHG	Xiao et al. (2020)

GWP, global warming potential; TP, toxicity potential; EP, eutrophication potential; AP, acidification potential; GHG, greenhouse gas emissions; ODP, ozone depletion potential; PMF, particulate matter formation; OFP, ozone formation potential; POCP, photo ozone creation potential; ADP, abiotic depletion; POF, photochemical oxidant formation; TA, terrestrial acidification; ME, marine eutrophication; SFD, fossil resource depletion; HT, human toxicity; SSOHW, source sorted organic fraction of household waste; OFMSW, organic fraction of municipal solid waste sorting of food waste into a substrate and reject fraction as well as producing a homogeneous feedstock for the AD process to have a higher methane recovery (Khoshnevisan et al. 2018b). Furthermore, thermal pretreatment methods which falls into physical pretreatment technology accelerates the hydrolysis of biofeedstock by disintegrating cell membranes and facilitating the dissolution of recalcitrant organic compounds, specially sewage sludge, microalgae, and food waste (Chen et al. 2012; Gnaoui et al. 2020; Karuppiah and Azariah 2019). This method is normally performed at very high temperature and thus requires a significant amount of heat (Rajput et al. 2018). Although thermal pretreatment technology increases the methane yield of specific feedstock which otherwise have a low biodegradability during the AD process, it may not increase the net environmental savings of AD systems due to the high energy demand (Mills et al. 2014). It is worth mentioning that, if the heat demand of thermal pretreatment methods could be supplied from renewable sources such as solar systems, the environmental performance would be more reasonable than using fossil-based heat sources. To illustrate, the total GHG emissions from the production of biogas with hydrothermal pretreatment and solar-driven hydrothermal pretreatment methods were estimated at –129.94, and –166.13 g CO_2 eq/kWh biogas, respectively (Xiao et al. 2020).

Last but not least, ultrasound and electrokinetic disintegration are available physical pretreatment technologies that are not applied for lignocellulosic substrate and are only specified for sewage sludge (Dhar et al. 2012; Montgomery and Bochmann 2014). Previous studies show that ultrasound and electrokinetic disintegration could be useful technologies to improve the AD fed sludge by disordering microbial cell walls in the liquid (Bochmann and Montgomery 2013; Cano et al. 2015; Cartes et al. 2018). However, generally, these pretreatment methods consume electricity and reduce the net environmental profits since a part of exploited electricity from biogas should be utilized internally (Cano et al. 2015).

14.3.4 Chemical Pretreatment Methods

Chemical pretreatment approaches are popular for treating substrate with a high share of lignocellulosic composition in which various types of chemicals such as HNO_3, H_2SO_4, HCl, H_3PO_4, KOH, NaOH, and CaO are applied to break the complex structures and reduce the digester hydraulic retention time (Vannarath and Thalla 2019; Zhen et al. 2017). The application of chemical pretreatment routes could increase the methane yield up to 200% (Torres and Lloréns 2008; Wang et al. 2015; Zhang et al. 2011). For example, oxidative pretreatment by utilizing hydrogen peroxide doubled the biogas production from rice straw (Song et al. 2012). However, the use of chemicals for this purpose, specifically in the case of alkali and acid methods, increases the concerns over the sustainability of chemical pretreatment (Smullen et al. 2017, 2019). Accordingly, the chemical methods have not been widely used in large scale biogas plants despite their vast utilization for the production of ethanol (Carrere et al. 2016). Nevertheless, there are increasing attempts at developing this pretreatment method whilst decreasing the environmental impacts by recycling chemicals and residues (Smullen et al. 2019).

14.3.5 Combined Pretreatment Methods

In order to take the advantage of previously mentioned technologies and reduce their bottlenecks to some extent, combined processes have been developed which cannot be classified into the former categories (i.e., mechanical, thermal or chemical pretreatment). Such pretreatment methods are more efficient since they are a combination of two or more types of main pretreatment technologies (Montgomery and Bochmann 2014). These methods are in forms of physicochemical, physical-thermal, thermo-chemical, mechanical-chemical, and bio-chemical technologies. Such integrated technologies require less energy, lower capital costs, and easy operation compared to each individual technology (Shrestha et al. 2020). As a matter of fact, by combining chemical methods with mechanical, thermal, and biological technologies, the amounts of energy and chemical consumption by individual technologies are reduced while the biomethane yield is increased. For example, thermal-alkaline and microwave-alkaline pre-treatment have been shown to decrease the consumption of alkali compounds whilst increasing the biogas production (Pilli et al. 2020). As another example, some integrated thermal-based technologies such as steam explosion and extrusion consume lower energy compared to individual thermal and hydrothermal methods. Nonetheless, they are carried out at elevated temperature with high positive effect on the methane yield on straw in AD system (Martínez-Gutiérrez 2018).

14.4 Downstream Processes

In addition to the AD and its upstream processes, downstream technologies also play a critical role in the sustainability of AD plants. Downstream processes include biogas conditioning (i.e., purification and upgrading), biogas utilization, and digestate management. In the following sub-sections, the effects of downstream processes and technologies on the sustainability of AD plants are discussed in detail.

14.4.1 Biogas Conditioning

14.4.1.1 H_2S Removal

The generated biogas in the AD process consists of 40–70% (v/v) CH_4, 30–60% (v/v) CO_2, 0–1% (v/v) H_2, 0–3% (v/v) H_2S, and 0–5% (v/v) other gases (Tabatabaei

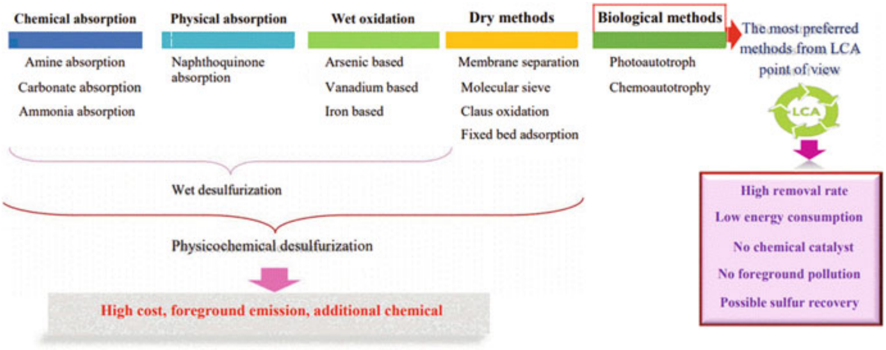

Fig. 14.2 Physiochemical and biological desulfurization technologies from LCA perspective

and Ghanavati 2018). For further application of the biogas and the subsequent production of heat and electricity in conventional conversion systems including large turbines, gas micro-turbines, combined heat and power (CHP), and internal combustion engines, the H_2S content of biogas should be removed to avoid corrosions (Santos-Clotas et al. 2019). The removal of H_2S, which is formed by microbial reduction of sulfur compounds, is the most important downstream process for biogas conditioning since the H_2S content of biogas can cause corrosion or toxicity (Hauser 2017). There are various physicochemical and biological technologies available for H_2S removal. Figure 14.2 illustrates all types of available technologies employed for H_2S removal. Previous studies have widely characterized various types of desulfurization technologies (Xiao et al. 2017; Zăbavă et al. 2019; Zulkefli et al. 2016).

Taking into account the desulfurization of biogas from LCA point of view, in all the evaluated technologies so far, daily operation of desulfurization is the highest contributor to the overall environmental impacts rather than the construction and disposal of desulfurization units alongside their auxiliary equipment (Cano et al. 2018). Among various technologies commercialized, bio-desulfurization which is normally performed in bioreactors are the most environmentally friendly and economically favourable approach, especially compared with their physicochemical competitors (Syed et al. 2006; Xinqiao et al. 2003; Zăbavă et al. 2019). This can be attributed to the fact that bio-desulfurization technology normally doesn’t need a high amount of energy and supplementary chemical compounds (Tabatabaei and Ghanavati 2018; Zăbavă et al. 2019). Besides, the recovery of sulfur is also possible so that the recovered sulfur in different forms (depending on the availability of oxygen in the process) can substitute its chemical-based counterpart (Ramos et al. 2013). This brings more environmental savings and therefore can compensate the environmental impacts caused by the consumption of energy resources.

Having considered the physicochemical biogas upgrading technologies, the use of chemicals significantly contributes to the environmental impacts of the upgrading technology. In other words, the background emissions caused by the production of chemicals and materials are the most important contributors to the environmental burdens of physicochemical biogas desulfurization technologies (Zulkefli et al.

2016). For instance, in chemical scrubbing and immobilized activated carbon desulfurization, the H_2O_2 production stage as well as active carbon production and preparation imposed the highest impacts on the biogas upgrading facility (Cano et al. 2018).

In order to inject biogas into the natural gas grid or utilize it as transportation fuel, apart from the H_2S, the CO_2 content of biogas should also be removed to a great extent. The existing technologies for upgrading the biogas into the natural gas grade biomethane, are chiefly divided into physicochemical methods and methanation technologies (Sun et al. 2015). In the former, the CO_2 content of biogas is separated while in the latter the CO_2 components of biogas react with H_2 in a Sabatier reaction either biologically or chemically and thereby forms additional CH_4 (Angelidaki et al. 2018). Among the diverse types of physicochemical upgrading technologies, pressure swing adsorption, water scrubbing, amine scrubbing, membrane separation, and cryogenic separation are the most widely applied technologies which have been commercialized and long been employed in biogas plants (Kapoor et al. 2019)

The previous LCA studies with focus on biogas upgrading technologies have shown that biogas upgrading units are among the top two contributors to the environmental impacts of AD systems (Hauser 2017; Wang et al. 2016). Correspondingly, many studies have been conducted to compare and introduce the most environmental friendly biogas upgrading technologies (Ardolino and Arena 2019; Florio et al. 2019; Lombardi and Francini 2020; Starr et al. 2012). Table 14.3 summarizes some of those studies dedicated to the LCA of biogas upgrading technologies. The results of LCA studies over the biogas upgrading technologies demonstrated "win-win" situations compared to the fossil routes for the production of transportation fuel and natural gas. However, comparing different forms of upgrading technologies have shown that each technology has specific merits and drawbacks over the others. This attributes to the difference between the input-output analysis of each technology, including energy, material and emissions.

14.4.1.2 CO_2 Removal

Methane slippage is the main contributor to the global warming damage category among different biogas upgrading technologies (Ardolino et al. 2020). Chemical absorption has the least methane leakage as illustrated in Table 14.4; however, this facility requires high amounts of heat and further addition of chemicals such as amines and alkali solutions (Angelidaki et al. 2018). Correspondingly, chemical absorption would have high background emissions associated with the heat and chemicals production. Generally, the results of LCA studies of physicochemical technologies depend on hypothesis made by authors over methane slippage, energy and chemical consumption. This makes it difficult to directly compare the results of the previous studies (Ardolino et al. 2020; Hauser 2017; Lombardi and Francini 2020). Furthermore, another parameter which affects the LCA of physicochemical upgrading technologies, is the possible recovery of CO_2 to substitute its conventional industrial counterpart. Although the CO_2 released into the environment from

Table 14.3 Overview of LCA studies on different biogas upgrading technologies

Physicochemical technologies						Methanation		Products and by products					
OPS	WS	CA	PSA	MS	CS	Biological	Chemical	CO_2	O_2	Transportation fuel	Natural gas	Power	Reference
			✓										Cozma et al. (2013)
		✓									✓		Adelt et al. (2011)
	✓										✓		Rehl and Müller (2013)
✓	✓	✓									✓	✓	Morero et al. (2015)
		✓									✓		Leonzio (2016)
	✓	✓	✓	✓	✓			✓			✓		Hauser (2017)
		✓		✓			✓				✓		Collet et al. (2017)
				✓						✓			Ardolino et al. (2018)
	✓	✓	✓							✓			Khoshnevisan et al. (2018b)
	✓	✓	✓	✓							✓		Lombardi and Francini (2020)
			✓										Kohlheb et al. (2020)
	✓	✓	✓	✓	✓						✓		Florio et al. (2019)
		✓	✓	✓			✓			✓			Zhang et al. (2020)
	✓						✓		✓		✓		Lorenzi et al. (2019)
						✓			✓	✓			Khoshnevisan et al. (2020b)
	✓									✓			Ardolino and Arena (2019)
	✓									✓			Tsapekos et al. (2021)
	✓	✓	✓	✓						✓			Ardolino et al. (2020)
		✓	✓								✓		Moioli et al. (2020)

OPS, organic physical scrubbing; WS, water scrubbing; CA, chemical absorption; PSA, pressure swing absorption; MS, membrane separation; CS, cryogenic separation, biological methanation, chemical methanation

Table 14.4 Specific characteristics of dominant and emerging biogas upgrading technologies

	Physicochemical Biogas upgrading						Methanation	
Features	Water scrubbing	Organic physical absorption	Chemical absorption	PSA	Membrane separation	Cryogenic separation	Biological	Chemical
Electricity requirement (kWh/Nm^3 raw biogas)	0.24–0.5	0.1–0.3	0.05–0.15	0.31–0.43[a]	0.15–0.3	0.2–0.79	nf[e]	nf[e]
Heat requirement (kWh/Nm^3 raw biogas)	na	< 0.2	0.55	na	na	na	nf[f]	nf[f]
CH_4 loss (%)	< 3	1.5–4	< 0.1	1.6–4	0.5–13.5	0.5–3	nf[g]	nf[g]
Purity (%)	95–9	93–98	96–99	95–99	96–98	97–99	97–99	97–99
Pre purification requirement	Not required [b]	Not required [b]	Required	Required	Required	Required [b]	Required	Required
Simultaneous H_2S removal	Yes	Yes	No	Possible	Possible	Yes	No	No
CO_2 recovery	No	Yes	Yes [c]	No	Yes [c]	Yes [d]	na	na
Consumable material	Antifouling, drying agent	Organic solvents, polyethylene glycol	Amines, alkali solutions, antifouling, drying agent	Activated carbon zeolite	Silicone rubbers, cellulose acetate hollow fibers	Glycol refrigerant	Inoculum supplied From digestate	Chemical catalyst

nf, not found

Data from: Adnan et al. (2019); Angelidaki et al. (2018); Ardolino et al. (2020); Hauser (2017); Hoyer et al. (2016); Kapoor et al. (2019)

[a] Value includes required electricity for upgrading, drying and compressing

[b] H_2S removal is required for high concentrations of sulfur (500 mg H_2S/m^3 biogas)

[c] Recovering CO_2 needs energy consumption

[d] 98% purified

(continued)

[e] Indirect electricity consumption of 5.94 kWh_e for the production of 0.11 kg hydrogen which is required for upgrading 1 kg biogas, and direct electricity consumption for the main process

[f] Process temperature for chemical and biological methanation, are, respectively, ~ 270 °C and 60 °C

[g] Depends on the type of the reactor

upgrading processes is accounted as biogenic, its reuse for industrial purposes brings more environmental benefits. As illustrated in Table 14.4, recovering highly purified CO_2 from cryogenic separation technology without further energy demand for its conditioning, could compensate the utilization of high amounts of electricity and glycerol refrigerant (Hauser 2017).

Biogas methanation technologies referred to as “power to gas” have been introduced as a promising approach to integrate biogas plants in the renewable electricity sector, which could overcome the challenges of surplus electricity production from renewable sources (Duan et al. 2020). This novel technology could form a closed-loop cycle under the concept of circular bioeconomy in which: (1) hydrogen is converted into biomethane with higher energy content, i.e., the energy content of biomethane (36 MJ/m^3) is almost three times as much as that of hydrogen (10.88 MJ/m^3) (Luo et al. 2012) and (2) the CO_2 fraction of biogas is also transformed into an energy product instead of releasing to the atmosphere without any implication. However, the greenhouse gas (GHG) emission intensity of the electricity used for the upstream water electrolysis technology supplying the hydrogen demand of the methanation process plays a key role in the sustainability of this novel biogas upgrading method (Zhang et al. 2020). Therefore, if the renewable share of electricity utilized in electrolyzer units is less than 80%, the methanation process at the downstream leads to higher impacts in all environmental damage categories, compared to physicochemical biogas upgrading processes (Lorenzi et al. 2019).

Apart from the GHG intensity of the electricity, the type of feedstock used for the production of biomethane at the initial stage is a predominant criterion since biomass with higher methane potential decreases the hydrogen demand for biogas upgrading and thereby increases the environmental benefits of the methanation process. More specifically, in case of chemical methanation a part of the environmental burden is attributed to the chemical catalyst, alumina supported Nickel-based catalyst ($Ni\text{-}\alpha\text{-}Al_2O_3$), utilized in the methanation reactor (Lorenzi et al. 2019). It is worth noting that, if oxygen, which is produced as a co-product in electrolyzer units is given credit, the net environmental impacts from the AD systems will decrease. This is due to the fact that the oxygen demand is growing in municipal solid waste (MSW) and wastewater treatment plants, as well as electric furnace and glass melting industries and thereby utilizing high amounts of oxygen instead of its prevailing conventional counterpart from cryogenic air separation that would provide economic, environmental and energetic merits (Kato 2007; Khoshnevisan et al. 2020b).

14.4.2 Biogas and Digestate Utilization

14.4.2.1 Biogas Utilization

The final use of biogas and digestate and the products they substitute are key parameters which can affect the overall LCA results. Some of the previous studies demonstrated that if biogas is used as transportation fuel to substitute fossil-based fuel, better environmental impacts will be achieved compared to their combustion in gas engines to produce heat and electricity (Ardolino et al. 2018; Khoshnevisan et al. 2020b). There are some studies which concluded that the utilization of biomethane as transportation fuel is a more environmentally friendly than its application as natural gas (Kampman et al. 2017; Pérez-Camacho et al. 2019). However, it can vary from one country to another based on regionalized parameters such as source of heat and electricity and the marginal transportation fuel which may be substituted in this context. For instance, in a country like Denmark with dominant wind electricity, the use of biogas for electricity and heat production will be constrained in the future due to the high penetration of other types of renewable energy such as solar and wind. Wind and solar energy are considered as the most environmentally friendly electricity sources because of having no direct emissions at wind or solar farms (Jacobson et al. 2015). Accordingly, the generated biogas in the forthcoming years would be more likely to be used as transportation fuel or be injected into the natural gas grid or valorized into value added products (Khoshnevisan et al. 2020a; Zha et al. 2021). However, some studies discussed that the production of value added products from biogas and digestate under the biorefinery concept still cannot compete with the production of transportation fuels (Khoshnevisan et al. 2020b).

14.4.2.2 Digestate Utilization

Apart from biogas, the digestate remaining at the end of AD process contains reasonable amounts of macro- and micro-nutrients and is thereby considered as a substitution for chemical fertilizers (Styles et al. 2018). In fact, utilizing the remaining slurry after AD as soil amendment not only avoids the generated emissions from the production of chemical fertilizer but also from its application. However, the limitations such as long storage time, emissions from storage systems, oversupply of digestate on the farmlands, and the application out of cropping season or at improper time undermine the sustainability of using digestate as a substitute for chemical fertilizers (Khoshnevisan et al. 2021). In the previous LCA studies, ammonia and methane emissions from digestate storage and application as well as emissions caused by the transportation of such bulky materials imposed the highest environmental burdens associated with digestate management (Tsapekos et al. 2021). Although transportation of digestate is still challenging, some studies demonstrated that application of digestate on surrounding farmlands would still have better environmental performance than their use for microalgae or powder biofertilizer production (Duan et al. 2020)

Depending on the feedstock used for biogas production, the digestate may contain heavy metals or soil contaminants such as Cu, Zn, and Mn, hence increase the risk of soil contamination (Valeur 2011). Therefore, digestate may need some pretreatment to remove contaminants and hazardous components from the digestate before field application. Moreover, in regions with intensive biogas plants, if long distance transportation is needed, composting and pelletizing are widely employed as post-treatment of the digestate (Rehl and Müller 2011). The type of technology used for digestate treatment is related to the composition of the remaining slurry from the AD reactor (Styles et al. 2018). Normally digestate management is carried out through mechanical, physicochemical or biological processes (Monfet et al. 2018). The characteristics of each type of technology employed for the post-treatment of digestate have been thoroughly described in the review paper by Monfet et al. (2018). From an LCA point of view, the high energy demand of post-treatment technologies has been found as the environmental hotspot. Mechanical treatment, i.e., belt drying and thermal concentration have the highest energy demand which affects the environmental performance of AD systems (Rehl and Müller 2011). Furthermore, the consumption of specific amounts of chemicals such as sulfuric acid, sodium hydroxide and powered polymers in physicochemical and biological treatments would further increase the environmental damages caused by the post-treatment of the digestate (Vázquez-Rowe et al. 2015).

14.4.3 AD in the Biorefinery Concept

The recent advancement in biotechnological sciences and rising environmental awareness have encouraged the expansion of biogas plants with more attention to the circular bio-economy. Attempts are made to produce more value-added products and building block chemicals than biogas and digestate. Hence, some researchers have studied different valorization pathways of bio-feedstocks and the effluents from anaerobic digestion under the biorefinery concept (Elyasi et al. 2021). Figure 14.3 shows a simplified process design of an AD based biorefinery. Agricultural waste, forestry residues, food waste, and industrial organic waste have shown great potential for being treated under the biorefinery approach to produce a wide range of bioenergy and biomaterials (Nizami et al. 2017). The production of succinic acid, ethanol, single cell protein, phenolic compounds, dietary fibres, animal feed, enzymes, polymers, and lactic acid, among others, have been widely tested and their sustainability has been addressed (Dermeche et al. 2013; Ertem et al. 2016; Khoshnevisan et al. 2020b; Lam et al. 2018; Strazza et al. 2015).

The transition from conventional biogas plants toward biorefineries would bring about controversial sustainability challenges such as energy efficiency, economic printability, direct/indirect emissions which should be addressed in a standard framework. Therefore, a number of well-established sustainability assessment tools have to be implemented towards a successful multi-functional biorefinery (Hetemäki et al. 2017). In this context, LCA as a standard sustainability assessment tool could be employed to characterize the environmental impacts of feedstock biorefining. Such evaluations lead to attaining more mature knowledge about opportunities to improve the circular production of bioproducts. This also enables decision-makers to find out how such value chains have pros & cons over the traditional biogas production. Table 14.5 illustrates some the LCA studies conducted on the biorefining of different types of biomass.

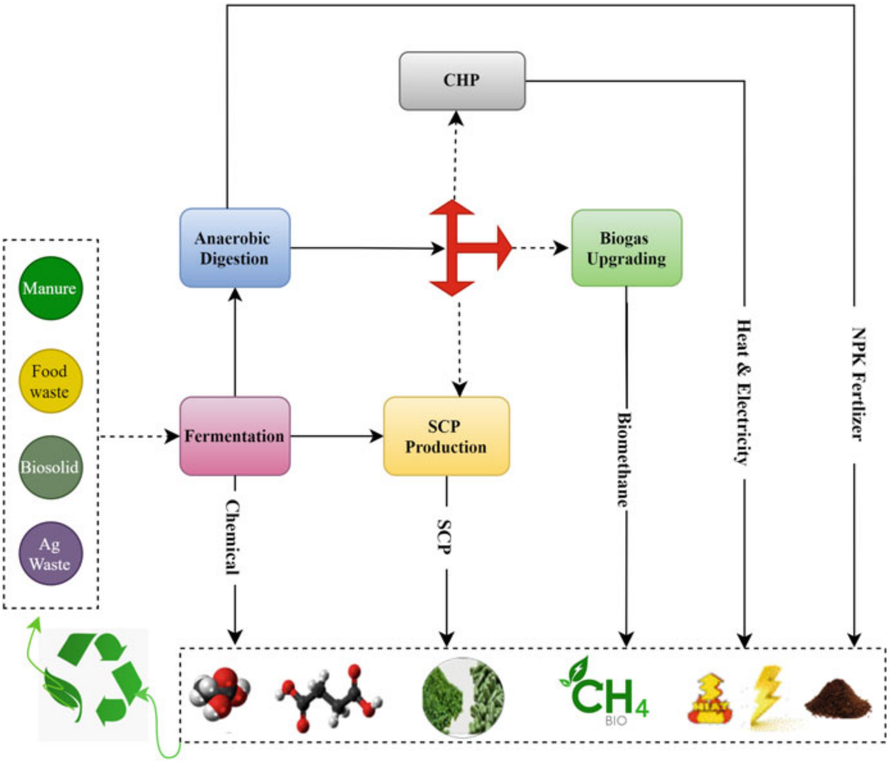

Fig. 14.3 A simplified process design of an AD based biorefinery. SCP, single cell protein; CHP, combined heat and power generation; Ag waste, agricultural waste

It is worth noting that the biorefining approach can have a positive influence on one aspect, but a negative point in another aspect. Holistically, investigating the LCA and environmental impacts of biorefineries have shown that the cascading use of biomaterials through integral bioprocesses would lead to economic growth, positive environmental impacts, expansion of fossil-free bioprocesses, and positive social effects in terms of improving the regional economy following the product diversification (Bello et al. 2018; García-Bustamante et al. 2018; Husgafvel et al. 2017). Specifically, the production of various bioproducts through biorefinery pathways lead to climate mitigation compared with their chemical processes (Khoshnevisan et al. 2020b; Sadhukhan and Martinez-Hernandez 2017; Seghetta et al. 2016). Furthermore, under the concept of a biorefinery, the worthless materials are returned back into the supply chain more efficiently. To illustrate, by applying the digestate and biogas downstream for the production of single cell protein (SCP), the usage of environmental-costly protein sources such as soybean meal would be limited (Khoshnevisan et al. 2018b).

The exploitation of a wide range of bioproducts under the biorefinery concept requires higher quantities of energy and additive chemicals/materials (Bello et al.

Table 14.5 LCA studies focusing on the valorization of various types of biofeedstock to diverse bioproducts

Type of biomass	Products	Remark on LCA	Reference
Seaweed	Ethanol, proteins and liquid fertilizer	Environmental restoration & climate mitigation The major environmental hotspot is energy consumption	Seghetta et al. (2016)
Residual beech woodchip	Bioethanol, acetic acid, lignin, and furfural; Glucose, hemicellulose	Identified hotspot: Pre-treatment of biomass; energy demands of the process and enzyme production	Bello et al. (2018)
Municipal solid waste	Levulinic acid, electricity, fertilizer	Global saving of 0.4 kg CO_2-eq per kg levulinic acid	Sadhukhan and Martinez-Hernandez (2017)
Organic fraction of municipal solid waste	Succinic acid, lactic acid, single cell protein, biomethane, heat, electricity, biofertilizer	Biorefining pathway and biogas usage are the determinable effect on LCA results	Khoshnevisan et al. (2020b)
Vine shoots	Lactic acid, and furfural	Production of bio-based lactic acid or furfural has strong environmental benefits	Pachón et al. (2020)
Castor	Electricity, biodiesel, ethanol, heat, biomethane, glycerol	Improvement effect on global warming and resources; Negative environmental impacts on the Human Health and Ecosystem Quality	Khoshnevisan et al. (2018a)
Citrus peel	Phenolic compounds, oil, methane, syngas, ethanol	Replacement of microwave and ultrasound-assisted technologies by conventional intensifying technology improve the environmental effects	Joglekar et al. (2019)
Sugars and lignin	Succinic acid, adipic acid, Biodiesel	The life-cycle GHG results are highly sensitive to co-product handling methods	Cai et al. (2018)
Wheat straw & alfalfa	Bioethanol, lactic acid, electricity, feed protein, biofertilizer, fodder silage	Net environmental saving compared to petrochemical competitors of bioproducts Energy consumption, specifically for the production of enzymes in biorefinery was a major hotspot	Parajuli et al. (2017)
Olive wastes	Biofuel, phosphate salts, natural antioxidant, and an oxygenated fuel additive (triacetin)	Mitigation of environmental impacts of foods Transition from olive agri-food to agro-biorefinery is environmentally favorable	Khounani et al. (2021)

2018). For instance, the production of lactic acid under a biorefinery approach requires high energy and chemical consumption (Liu et al. 2021). Thus, the choice of biorefinery technologies in terms of energy and pollutant intensity have major environmental effects (Bello et al. 2018; Seghetta et al. 2016). Such limitations are the reason that the production of biofuel still outperforms the production of biochemicals (Khoshnevisan et al. 2018a, 2020b). This is due to the low conversion efficiency as well as the energy intensity of biorefining technologies (Bello et al. 2018; Khoshnevisan et al. 2020b; Seghetta et al. 2016). Overall, downstream biogas usage, bioproduct substitutions, and the conversion rate are the most effective parameters affecting the LCA of biorefineries (Khoshnevisan et al. 2020b). If agricultural biomass is used in biorefineries, some other criteria such as crop cultivation and land use change should not be neglected in the boundary of LCA studies (Katakojwala and Mohan 2020; Liu et al. 2021)

Despite all the attempts made so far to investigate the LCA of biorefineries, it still suffers from low transparency and clarity. Hence, future research should critically evaluate the environmental impacts of the AD process under the biorefinery concept to attain more sophisticated knowledge and thereby selecting the most suitable interlocked bioprocesses for biogas production. Also, further attempts should be made for process optimization to satisfy the environmental indicators. This would lead to the production of more value-added products alongside bioenergy and thus overcoming the environmental hazards of the petrochemical based production of building block chemicals and materials.

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Chapter 15
Life Cycle Assessment of Anaerobic Digestion Systems: An Approach Towards Sustainable Waste Management

Marlia M. Hanafiah, Iqbal Ansari, and Kalppana Chelvam

Abstract The wastes generated from different human activities such as agricultural or crop wastes, livestock, food wastes are biodegradable wastes, which can be utilized for various purposes including biogas generation and production of other value added products. The main aim of this chapter is to provide information on the types of waste that can be used to produce biogas through anaerobic digestion (AD) system. Anaerobic digestion is a process of conversion of biodegradable waste into biogas by the action of microbial communities. The gases obtained during AD mainly consist of methane, carbon-dioxide and some amount of water vapour. Better understanding of the different processes, including the pretreatment and post-treatment involved in the AD, is necessary to develop the green technology to achieve sustainable development. In this regard, LCA is a great tool to study the feasibility of the AD process for environmental sustainability. In this chapter, an introduction to life cycle assessment (LCA) and description of previous studies on the LCA of anaerobic digestion systems towards environmentally sustainable management practices are presented. The chapter also discusses LCA for improvement of the performance of the anaerobic digestion process of various biodegradable wastes for generation of biogas. The findings suggest that more future research is needed for process improvement and to promote the wide application of the AD process for generation of green energy.

Keywords Environmental LCA · Organic waste · Renewable energy · Waste-to-energy · Circular economy · Sustainable management

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15.1 Introduction

Biodegradable waste like agricultural and crop residue, food waste, livestock wastes, sewage sludge, organic municipal waste are rich sources for energy production, including biogas or biofuels (Appels et al. 2011; Banch et al. 2020b). Conversion of organic wastes to energy and by-products has become increasingly important for achieving the circular economy (Banch et al. 2020a). Utilization of such wastes for bioenergy production provides many advantages such as low-cost of substrate, minimizing environmental impacts by reducing waste generation, providing extra revenue to the producers, reducing fossil fuel dependency and making energy sufficient (Hanafiah et al. 2018; Nizam et al. 2020). Anaerobic digestion systems, embracing the concept of waste-to-energy is one of the environmentally friendly technologies for generating biofuel and biogas (Aziz et al. 2019; Vambol et al. 2019).

However, in many areas, solid wastes are being dumped directly to the environment without proper treatment and management (Ashraf et al. 2019). Issue related to improper waste management affects human health and the environment (Al-Raad et al. 2020; Ashraf and Hanafiah 2019; Hanafiah et al. 2020). A common disposal method such as landfill consumes large amounts of land resources, energy, and causes significant atmospheric greenhouse gas emissions (Banch et al. 2019). Apart from that, landfills also produce a substantial amount of landfill leachate containing high concentrations of organic and inorganic pollutants that poses hazards to the environment. Therefore, in recent years, research in alternative renewable energy generated from organic wastes is gaining more interest.

The waste-to-energy concept has been introduced to solve environmental degradation related to waste disposal (Ashraf and Hanafiah 2017). Various technologies and methods have been used to convert waste into bioenergy. However, this further requires investigation on the impacts of these technologies on the environment, human health and economical aspects. In this context, holistic and comprehensive assessment of the impacts of anaerobic digestion (AD) systems used to convert waste to energy is important. This will help to identify strategic and feasible improvements in waste management and renewable energy generation towards environmental sustainability (Aziz et al. 2020). This chapter provides useful information to researchers, students, and policy makers on life cycle assessment (LCA) of AD systems.

15.2 Anaerobic Digestion Systems

15.2.1 Anaerobic Digestion Process

Anaerobic digestion is a process by which biodegradable materials such as animal waste, food, lignocellulosic waste and agricultural waste are broken down by microorganism through the process of decomposition in the absence of oxygen to produce biogas. Anaerobic digestion (AD) is a complex biodegradation process of organic matter, by the synergistic action of a range of microorganisms (Kougias and Angelidaki 2018). The main end products obtained during AD are biogas (CH_4 and CO_2) and digestate (Carlsson et al. 2015). The schematic of the anaerobic digestion process is shown in Fig. 15.1. The biogas produced during AD consists of CH_4 (53–70%) and CO_2 (30–50%) and some small amount of water vapor (5–10% or higher in thermophilic phases), oxygen (0–5%), hydrogen sulfide (0–20,000 ppm), siloxanes (<0.08–0.5 mg/g-dry), ammonia (< 100 ppm), hydrocarbons, carbon monoxide, along with nitrogen (2–6%) (Mao et al. 2015). Biogas is considered to be a green and renewable source of energy. Several techniques including pre-treatment of substrate, co-digestion, additives and optimization of parameters have been applied for improving biogas production (Gupta et al. 2012a).

Apart from that, biogas can also be produced by thermochemical conversion of biomass that can be achieved through a process known as gasification. The bio-gasification of vegetable waste could be a potential source of biogas generation by using some indigenous microbes from natural sources (Gupta et al. 2010). In general, biogas is generated from many other sources such as landfills, municipal waste, green waste, energy crops, sewage, and industrial wastewater. Biogas is treated to remove carbon dioxide to be used as renewable natural gas, which is also known as biomethane. On the other hand, digestate, which is the co-product of anaerobic digestion, is rich in ammonia and phosphate which are essential for the growth of photosynthetic organisms like microalgae. These products can be further refined through certain processes to meet specific requirements to aid the growth of plants.

The efficiency of biogas production is mostly dependent on the biodegradation process and the optimum conditions increase the process efficiency and rate (Li et al. 2017). According to Saraswat et al. (2019), factors such as temperature, carbon to nitrogen (C/N) ratio, compression ratio, total solid concentration and the pH value greatly influence the biogas production. The pH influences the activity of the microorganisms during the process. Each class of microbes has a definite range of pH where they perform optimal. For instance, a pH more than 6.5 is more suitable for methanogenic bacteria/archaea; however, acidogenic bacteria work better at a pH value of 5–6.5. Sitorus et al. (2013) have investigated the biogas production with variations in temperature and pH throughout the process from mixed fruit and vegetable wastes during AD. The study found great influence of these factors on the biogas production rate as well as on the biogas composition.

The substrate composition is also important in the AD process, where the degradability rate of the feedstock varies with its composition (Winichayakul et al. 2020; Hundal et al. 2019). For example, a higher carbohydrate content in the substrate will result in a higher yield of biogas due to the high degradability rate and rapid transformation of carbohydrates (Yang et al. 2015). Li et al. (2017) have studied different types of food wastes and showed the effect of carbohydrates, proteins and lipids on the AD process and the methane production. In the study,

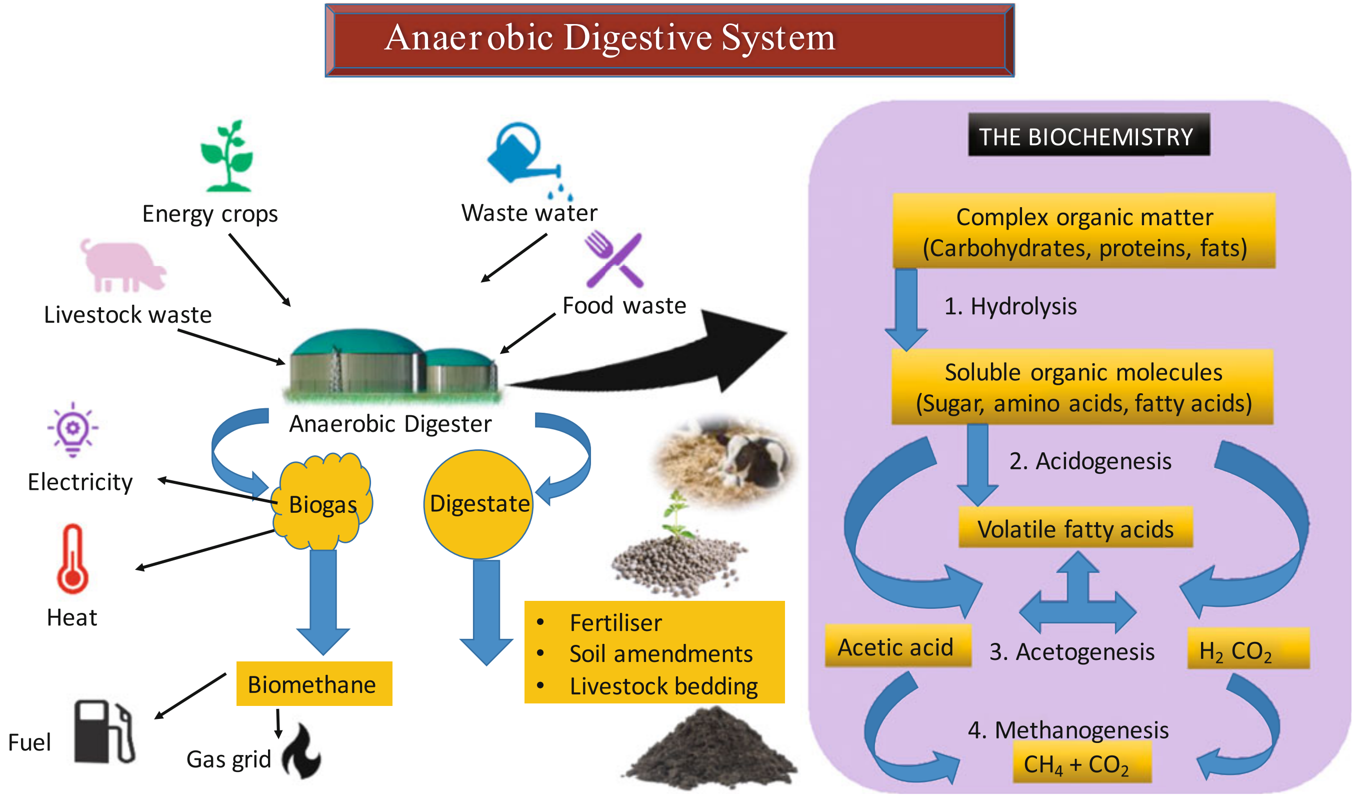

Fig. 15.1 Overview of the anaerobic digestion process along with the applications of its products in different sectors

different food wastes contained different organic compositions which lead to a change in methane production.

15.2.2 Products from Anaerobic Digestion Process

The biogas produced is mostly methane (CH_4) and carbon dioxide (CO_2) with a minimal amount of water vapour and other gases. The carbon dioxide and other gases can be removed leaving only methane which is the primary component of interest. This biogas purification process will increase the energy value of the biogas as a source of renewable energy to produce heat and electricity for power engines, heat generation in digesters, boilers and heating furnaces, run alternative-fuel vehicles and domestic and industrial usage as alternative to natural gases.

Digestate is the other product which is a wet mixture of the material that is left after the anaerobic digestion. It is separated into solid and liquid which are rich in nutrients and can be used as fertilisers for crops. Digestate can be applied directly on the land and added into the soil to improve soil quality which will promote plant growth. Moreover, some engineering techniques can be applied post-digestion to recover the phosphorus and nitrogen present in the digestate and produce concentrated nutrient products such as struvite (magnesium-ammonium-phosphate) and ammonium sulfate fertilisers. Other than that, digestate can also be made as bedding for livestock and be used for soil amendments. Figure 15.2 illustrates the elements of the biogas recovery system.

15.3 Biogas from Organic Wastes

15.3.1 Food Waste

Waste generation in recent times is quite high in amount and particularly for food waste it is up to 32% from all food produced throughout the world (Morales-Polo et al. 2018). This leads to a remarkable social and economic loss as well as environmental issues (Browne and Murphy 2013; FAO 2011; Papargyropoulou et al. 2014). According to the Ministry of Housing and Local Government (MHLG) Malaysia, disposal of food waste directly to the landfill sites is one of the main sources of greenhouse gases (GHG) emissions in Malaysia (Hoo et al. 2017). Another research carried out by Paritosh et al. (2017) also states that the carbon footprint of food waste is estimated to contribute to the GHG emissions by accumulating approximately 3.3 billion tonnes of CO_2 in the atmosphere annually.

Food waste makes up a large percentage of a landfill, where only a very minimal amount of food waste is being recycled into soil improver or fertiliser. The remaining food waste in landfills releases methane to the atmosphere as it breaks down. However, the energy potential produced from food waste is very significant. During

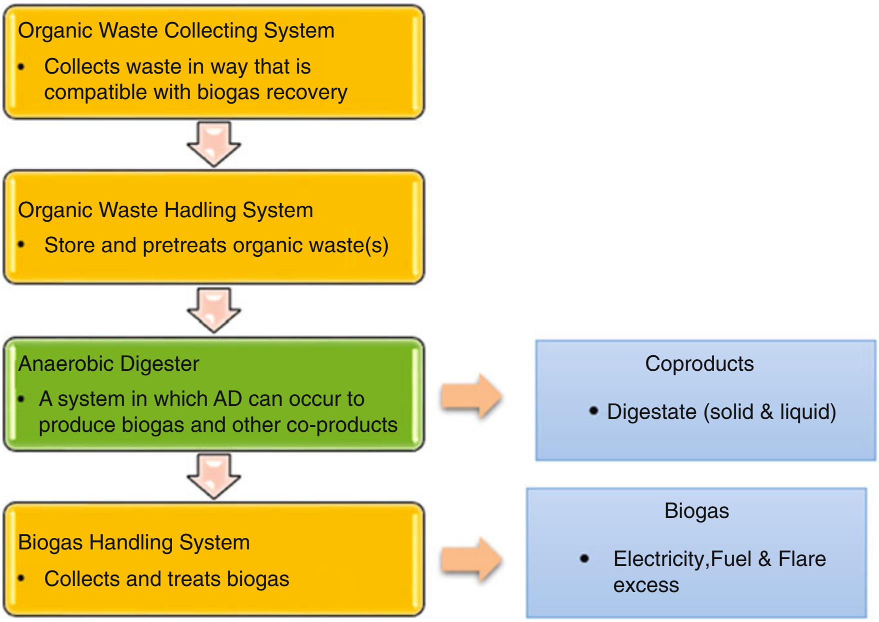

Fig. 15.2 Steps in biogas production from organic wastes

recent years, due to the generation of tremendous amounts of food waste, it can be a promising substrate for the AD process (Lin et al. 2013; Paritosh et al. 2017). Food waste (FW) poses the characteristics of high moisture and organic contents due to which it is easily degradable (Li et al. 2019a; Ren et al. 2018). During the AD process, organic matter present in FW is converted into CH_4, CO_2 and other gases. However, FW is characterized by a low C/N ratio (Akindele and Sartaj 2017). Hence, many times the AD process of FW results in the accumulation of volatile fatty acids (VFAs) in the reactor, due to the imbalanced nutritional level in the substrates (Chukwudi et al. 2019; Yazdanpanah et al. 2018).

There are many studies on biogas generation using food waste (Table 15.1). El-Mashad and Zhang (2010) investigated the production of biogas from food waste in batch digesters under mesophilic conditions (35 °C). The methane produced from the food waste was 353 L/kg VS after 30 days of digestion. Al-Wahaibi et al. (2020) carried out a techno-economic investigation of biogas production from different types of food waste. The methane production during the fermentation period showed a good correlation between the theoretical and experimental values with a coefficient of determination $R^2 = 0.99$. The cumulative gas production from mixed food waste samples was 1550 mL/1 g of dry matter at day 21. Jeong-Ik et al. (2018) have studied the biogas production from food waste with wood chips via anaerobic co-digestion. Use of wood chips as co-substrate increased the rate of methane and hydrogen production in AD. 20 mL/g of methane and 13.9 mL/g of hydrogen were generated at the food waste to wood chip ratio of 0.5, during 15 days at 35 °C.

Table 15.1 Biogas production from different types of waste using different AD systems

Waste/location	Study	Method	Type of biogas	Quantity/ productivity	Reference
Fruit and vegetable waste (FVW), Johannesburg market, South Africa	Lab	Anaerobic digestion (biochemical methane potential), bioprocess AMPTS II	Methane	50–60% in volume	Maile et al. (2016)
Kitchen waste (KW) and fruit/ vegetable waste (FVW), China	Both lab & pilot-scale	The batch digestion in lab-scale in 2-L conical flasks, Single-phase co-digestion A10-L completely stirred tank reactor (CSTR)	Methane	Productivity (0.725L CH_4/g VS)	Wang et al. (2014)
Fruit and vegetable waste (FVW), Tunisia	Lab	Single-stage anaerobic sequencing batch reactors (ASBRs) and continuously stirred tank reactor (CSTR)	Methane	Methane yield of 340 L/kg volatile solids (VS) Biogas (8% H_2, 28.5% CO_2 and 63.5% CH_4)	Farhat et al. (2018)
Municipal solid waste (MSW) and fruit and vegetable waste (FVW), Brazil	Lab	Anaerobic co-digestion (batch)	Biogas and methane	Biogas 493.8 N mL/g VS, methane- 396.6 N mL/g VS,	Pavi et al. (2017)
Fruit and vegetable waste (FVW) Johannesburg Market, South Africa	Lab	Anaerobic digestion semi-continuous digester	Biogas and methane	Biogas: 0.87 Nm^3/kg VS with 57.58% methane	Masebinu et al. (2018)
Market waste (vegetables & fruits), Pune, India	Lab	Anaerobic digestion 200L Biogas plant	Biogas	35 L/kg MW/day	Ranade et al. (1987)
Fruit and vegetable waste (FVW), municipal sewage sludge (MSS), Malaga, Spain	Lab	Anaerobic co-digestion	Methane	MSS: 0.303 m^3/(kg VS) FVW: 0.403 m^3/(kg VS), average methane content of digester biogas was about 62–64%	Arhoun et al. (2019)
Fish waste (FW) Fruit and vegetable waste (FVW), Tunis, Tunisia	Lab	Anaerobic co-digestion anaerobic sequencing batch reactors (ASBR)	Biogas	Average biogas production rate varied between 1.53 and 2.53 L/ day	Bouallagui et al. (2009)

(continued)

Table 15.1 (continued)

Waste/location	Study	Method	Type of biogas	Quantity/ productivity	Reference
Fruit and vegetable waste (FVW) and food waste (FW), Tsinghua, China	Lab	Lab-scale continuous stirred-tank reactor at 35 °C	Biogas and methane	Biogas at rate of 2.17 $m^3/(m^3$ day) and methane at 0.42 m^3 CH_4/kg VS. Methane production was 0.49 m^3 CH_4/kg VS at the optimum mixture ratio 1:1 for co-digestion	Lin et al. (2011)
Fruit and vegetable wastes (FVW), Bangalore, India	Lab	Solid-state stratified bed (SSB) process	Biogas	Gas production about 0.5 L/L/day at a 2 g/L/day feed rate	Chanakya et al. (2007)
Fruit and vegetable waste (FVW), Mexico City, Mexico	Lab	Continuous culture setup (glucose as substrate) and anaerobic reactor volume of 3 L	Hydrogen (H_2)	H_2 production rate (1.7 mmol/day), the highest cumulative H_2 volume (310 mL)	Garcia-Peña et al. (2013)
KW (Kitchen waste), fruit–vegetable waste (FVW) Hangzhou, China	Lab	Acidogenic-phase reactor (APR) and methanogenic-phase reactor (MPR)	Methane	Highest methane daily capacity 325 mL (50 % KW)	Yang et al. (2013)
Fruit and vegetable waste (FVW), Mexico	Lab (batch)	Batch anaerobic digestion, stainless steel tubular reactor	Biogas and Methane	Biogas production: 0.42 m^3/kg VS), methane: 0.25 (m^3/kg TS)	Garcia-Peña et al. (2011)
Agroindustrial wastes (AW), banana waste, Chiapas, México	Lab	Anaerobic digestion	Methane	After 63 days, 63.89 mL CH_4 per gram of chemical oxygen demand of the waste	González-Sánchez et al. (2015)
Anaerobic sludge, Beijing, China	Lab	Two-phase anaerobic digestion, up flow anaerobic sludge bed reactor	Methane	Methane: 261.4 mL/g COD removed. High methane-348.5 mL/g VS removed	Wu et al. (2016)
Municipal biomass waste (MBW), China	Pilot-scale	Anaerobic co-digestion in Continuous stirred-tank reactor (CSTR)	Biogas	Biogas production @ rate of 4.25 $m^3/(m^3$ day) at organic loading rate of 6.0 kg VS/(m^3 day) and hydraulic retention time of 20 days	Liu et al. (2012)

(continued)

Table 15.1 (continued)

Waste/location	Study	Method	Type of biogas	Quantity/ productivity	Reference
Fruit and Vegetable Wholesale Market of Sardinia, Italy	Pilot scale	Full-scale anaerobic digestion system, Pilot scale tubular reactor, Single waste substrate	Biogas and Methane	Average specific biogas production was about 0.78 Nm^3/kg VS, with a specific methane yield of about 0.43 Nm^3/ kg VS	Scano et al. (2014)
Garden waste (GW) CIMFR, Dhanbad, India	Lab	Anaerobic digestion Glass apparatus that contained one reaction vessel and one reservoir for the collection of gas by water displacement method	Methane	First enrichment produces methane: 19.74 cc on 49th day Second enrichment produces methane: 107.90 cc on 49th day	Gupta et al. (2012b)
Fruit and vegetable wastes (FVW), India	Lab	Anaerobic digestion (60-liter digester)	Biogas	Biogas yield of 0.6 m^3/kg VS major yield (74.5%) of gas within 12 h of feeding at a 16-day HRT whereas at a 24-day HRT only 59.03% of the total gas	Viswanath et al. (1992)
Fruit and vegetable waste (FVW) British Columbia, Canada	Lab	Co-digested with first stage (FSS) and second stage anaerobic digester sludge (SSS) separately, in batch reactors	Methane	FSS + FVW produced 514 ± 57 L CH_4 kg/VS and SSS + FVW produced 392 ± 16 L CH_4	Park et al. (2012)
Waste activated sludge (WAS)/ vegetable waste Hyder plc. DL, UK	Lab	Two-stage anaerobic co-digestion of waste activated sludge and fruit/ vegetable waste using of inclined tubular digesters	Biogas	Biogas yield of 0.37 m^3 kg/VS added. The biogas methane content was 68% and bicarbonate alkalinity in the methanogenic stage was over 4000 mg $CaCO_3$/ L	Dinsdale et al. (2000)

Gaby et al. (2017) studied the effect of the retention time and temperature on microbial community composition and methane production in staged anaerobic digesters fed with food waste. During this experiment, two anaerobic digestion parameters were studied, namely the effect of 55 and 65 °C as acidogenic reactor temperature, and the effect of lowering the hydraulic retention time (HRT) from 17 to 10 days in the methanogenic reactor. Higher acetate and butyrate concentrations were found in the 65 °C acidogenic reactor. The CH_4 production was increased from ~3600 mL/day to ~7800 mL/day when the HRT was decreased to 10 days. The effect of yeast on the performance of biogas production from food waste has been studied (Gao et al. 2020). The result showed that biogas production increased by 520 and 550 mL with addition of 2.0% (of volatile solids; VS) of activated yeast on, respectively, the 12th and 37th day of anaerobic digestion and the gas production was relatively stable (Gao et al. 2020).

Pallan et al. (2018) reported that anaerobic digestion of organic wastes like banana stalk (BS), banana peel (BP), vegetable waste (VW), spent tea waste (TW) and food waste (FW) in different combinations can be utilized to produce methane in lab scale fabricated digesters of one litre capacity. The combination of vegetable waste (VW) and spent tea waste (TW) has produced a maximum biogas yield of 3.75 L.

Viswanath et al. (1992) carried out a study on anaerobic digestion of fruit and vegetable wastes for biogas production in a 60 L digester. A maximum biogas yield of 0.6 m^3/kg VS was obtained at a 20 day HRT and 40 kg TS/m^3/day organic loading rate. The biogas production was observed in the digesters operated at 16 and 24 day HRT. The maximum biogas yield of 74.5% was observed within 12 h of feeding at a 16 day HRT, whereas at a 24 day HRT only 59.03% of biogas yield on substrate could be generated. Kitchen waste (KW) and fruit/vegetable waste (FVW) could be a potential candidate for methane production (Wang et al. 2014). The results of lab-scale experiment showed a higher methane productivity of 0.725 L CH_4/g VS. Similarly, during the anaerobic digestion process of FVW in a batch reactor, 514 (± 57) L CH_4/kg VS was produced (Park et al. 2012). Dinsdale et al. (2000) studied two-stage anaerobic co-digestion of waste activated sludge and FVW using inclined tubular digesters. The design system could achieve a high biogas yield of 0.37 m^3/kg VS. The methane content in the biogas was 68% and bicarbonate alkalinity in the methanogenic stage was over 4000 mg $CaCO_3$/L.

15.3.2 Livestock Waste

Manure produced from dairy cows are primarily stored in holding tanks before being applied to fields in rural areas. This leads to methane emissions in the environment as the manure decomposes and also may contribute to excess nutrients release in waterbodies. Biogas production from livestock manure through AD can minimise such problems, and can also prevent other associated issues of odours and manure pathogens.

Most of the rural areas of Asia is still facing problems of large quantities of manure from dairy, pigs and poultry and the suitable treatment and management of these waste is required (Vu et al. 2015). By utilizing these large wastes for energy generation in the form of biogas will help to prevent direct discharge of animal wastes into aquatic bodies, a common practice in various parts of the Asian region that lack proper waste management systems (Anenberg et al. 2013; Vu et al. 2015). Khalil et al. (2019) have reviewed the potential of sustainable biogas production from animal waste in Indonesia. It was found that about 9597.4 Mm^3/year of biogas can be produced from animal waste in Indonesia and this will generate an electric power up to 1.7×10^6 KWh/year.

Achinas and Euverink (2019) have reviewed the biogas production from the anaerobic co-digestion of farmhouse waste and have studied their performance and kinetics. El-Mashad and Zhang (2010) have investigated the effect of manure-screening on the biogas yield from dairy manure in batch digesters under mesophilic (35 °C) conditions. The production of methane from the fine and coarse fraction of screened manure were 302 and 228 L/kg VS, respectively, and for unscreened manure it was 241 L/kg VS. Mähnert and Linke (2009) have studied biogas production from whole-crop rye silage, maize silage and fodder beet silage along with cattle slurry at mesophilic temperatures. The maximum biogas production and the rate of biogas generation were in the range of 0.61–0.93 m^3/kg volatile solids and 0.032–0.316 per day, respectively. Abubakar and Nasir (2012) have investigated the effectiveness of cow dung for biogas production using a 10 L volume bioreactor in batch and semi-continuous mode at mesophilic (53 °C) temperature conditions. The average cumulative biogas yield and methane content were 0.15 L/kg VS and 47%, respectively. Their study showed that cow dung is an effective feedstock for biogas production with stable performance.

The AD process of animal manure with other biomass increases the yield of biogas and it provides advantages for the proper management of manure and such organic wastes simultaneously (Nielsen et al. 2002). Biogas production from manure and digestible organic wastes coming from food industry can be an example (Braun and Wellinger 2003). Uzodinma and Ofoefule (2009) have studied biogas production from cow dung, poultry dung, swine dung and rabbit dung blended with field grass in a 50 L capacity digester. On blending with rabbit dung, cow dung, swine dung and poultry yielded an average of 7.73 ± 2.86, 7.53 ± 3.84, 5.66 ± 3.77 and 5.07 ± 3.45 L of biogas per total mass of slurry, respectively. The biogas yield improved during codigestion due to improvement in nutritional quality.

Ojolo et al. (2007) investigated biogas production from poultry wastes, cow dung and kitchen waste in a 9 L volume reactor. The highest production of biogas was observed on the 14th day with 85×10^{-3} dm^3 of biogas. The biogas obtained from poultry droppings, cow dung and kitchen waste were 0.0318 dm^3/day, 0.0230 dm^3/day and 0.0143 dm^3/day, respectively. In another study, Zhang et al. (2013) found high biogas production from goat manure by adding with three crops residues at 35 °C. The highest cumulative biogas production was 16,023 mL for different co-substrates after 55 days of digestion.

15.3.3 Crop Residues

Crop residues include materials such as stalks, straw, and plant trimmings, which needs further processing to dispose of after the cultivation. In general, the crop residue can be left behind in the fields by which the organic and moisture content of the soil can be improved. However, where multiple crop cultivations are carried out successively, this method can cause hindrance to subsequent crops. Furthermore, higher crop yields leads to higher amounts of residue that need to be taken care of, creating more problem for the cultivators. Thus, converting such crop residues into biogas promotes better environmental sustainability. Crop residues are usually co-digested with other organic materials as it contains a high lignin content that makes it difficult to break down. However, growing energy crops for the sole purpose of bioenergy resources comes with a number of downsides such as requirement of high costs and large land use, water, and nutrient requirements. In this context, the biogas obtained from wastes such as crop residues is more advantageous.

Several agricultural residues in the form of agricultural biomass can be categorised as the food based portion (oil and simple carbohydrates) of crops (such as beets, corn and sugarcane) and the non-food waste (complex carbohydrates) portion (such as rice husk, leaves, orchard trimmings, stalks, corn stover, wheat straw and pearl millet stalk), perennial grasses and biogenic waste. Rice, maize, and wheat are the world top three growing crops and their residues are potentially being used as a good substrate for biofuel production (Sims 2004; Chandra et al. 2012).

Kumar et al. (2018) have reviewed the potential of some cereal crop residues in India for enhanced biogas production via chemical pre-treatment. They have mainly focused on chemical pre-treatment of cereal crop residues to generate biogas by removing lignin. Li et al. (2019b) have evaluated the anaerobic digestion of vegetable crop residues and their biochemical methane potential. Svensson et al. (2005) have studied the financial feasibility and prospects of biogas production from crop residues on a farm-scale level. The study revealed that the high-solids single-stage fed-batch operation provides the best option for high biogas yield. The methane yield, operational costs and degree of gas utilization had the strongest impact on the financial success of the process. Kalra and Panwar (1986) have investigated husk and straw of rice crops for the AD process in 190 L capacity digesters. 1 kg of rice straw has yielded about 220 L of biogas during the batch digestion process. A ratio of rice straw and cattle dung (1:1 dry weight basis) produced 9.1% more gas as compared to rice straw alone.

In a study using a mixture of agricultural wastes with semi-solid chicken manure, a maximum methane production of 502 and 506 mL/g VS obtained at 55 °C and 35 °C, respectively. However, an additional 42% increase in methane production (695 mL/g VS) was also observed with pretreated (ammonia stripped) chicken manure compared to other control (untreated) systems (Fatma et al. 2014). The anaerobic co-digestion of swine manure mixed with crop residues produced 3.5 L/day of biogas (Cuetos et al. 2011). The semi-continuous experiment was conducted in mesophilic reactors having 3 L working capacity for 30 days. Elena et al. (2012) showed the production of biogas from a mixture of cattle slurry and cheese whey as the substrate with a maximum biogas production up to 79%.

15.4 Life Cycle Assessment Framework

Life cycle assessment (LCA) is an important decision making tool for determining alternative methods to reduce the environmental impacts of any process and its products (Aziz and Hanafiah 2020). Sustainability is the main priority when it comes to LCA as this methodology suggests the most eco-friendly solution throughout the process and always has room for improvement to reduce the environmental impacts (Ismail and Hanafiah 2019a). LCA can help organizations and industries to evaluate and understand the holistic environmental performance of their products or activities depending on their sustainability goals towards product improvement, product innovation or strategic marketing and business plan (Aziz et al. 2019). It allows organizations and industries to involve in a decision-making process for implementing and achieving sustainable development and green solutions and adopt life cycle thinking into their business. Incorporating LCA into their practice provides the best design and technology options for their products and also ensure that it does not cause any adverse environmental impact (Ismail and Hanafiah 2020).

15.4.1 Steps in Conducting an LCA

Based on ISO 14040 series (ISO 2006a, b), there are four phases in the framework of the LCA as shown in Fig. 15.3.

The first phase is to identify the goals and scope of a process. During this phase, the type of product or service, functional units and system boundaries are identified. Functional units (FU) are the quantity of products to be studied while the boundaries of the system provide an overview to explain the processes covered in the evaluation. A functional unit is one the most important aspects in modelling or constructing a system of a product in LCA. FU is the measurement of a product that describes its function and it is used in all the calculations throughout the assessment. Products must have the same functional unit to make comparisons. A product's feature can vary from performance, aesthetics, technical quality and additional services up to costs (Arzoumanidis et al. 2020). For instance, a material such as food waste can be described as 1 tonne of food waste, whereas energy can be described as 1 kWh of electricity. System boundaries determine the inputs that should be included or excluded in the LCA assessment.

The second phase is the analysis of the life cycle inventory (LCI). It is a part of a LCA where all the data of a system are collected. It is a complex portion of an assessment as it tracks and analyses the entire flow of the input and output data of a

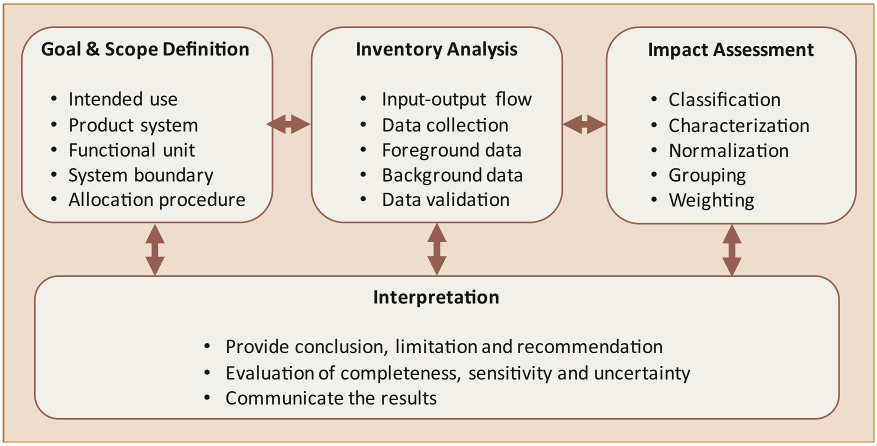

Fig. 15.3 Main phases of life cycle assessment (LCA)

product's system. LCI can include material use, energy use, coproduct generation, waste generation, raw material extraction, refining and processing, product manufacturing, product use, and recycling or disposal of a product in a system (DeRosa and Allen 2017)

The third phase in the LCA framework is the life cycle impact assessment (LCIA). The environmental impact potential is identified using the results of the life cycle inventory analysis that will be sorted into major impact categories which are divided into three different groups: ecosystem impacts; human impacts; and resource depletion. These categories will subsequently be assessed for decision making. The fourth phase is the interpretation. In this phase, the results obtained from the previous phases are interpreted in an informative form. In addition, evaluations and recommendations to reduce the environmental impact of the production of a product or service are also reported. The four phases in this life cycle evaluation framework demonstrate a systematic process of providing relative and quantitative information to measure the environmental load at each stage of the product's life cycle.

As illustrated in Fig. 15.4, LCA uses cradle-to-cradle or cradle-to-grave techniques which analyse raw material extraction through materials processing, manufacture, distribution, product usage and disposal or end of life.

15.4.2 *History and Evolution of LCA*

LCA is a systematic method to determine and calculate environmental impacts associated with all stages of the life cycle of a product or service (Aziz and Hanafiah

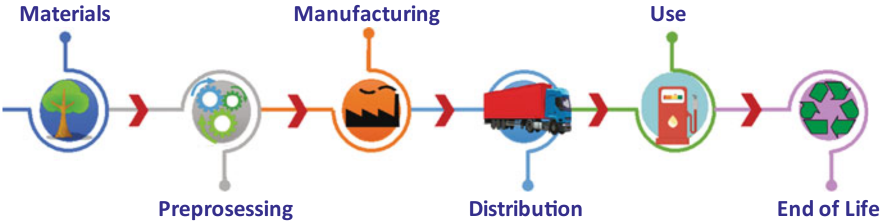

Fig. 15.4 An LCA cradle-to-grave approach

2021; Harun et al. 2020; Ismail and Hanafiah 2019b). Below are the historical background of the introduction and application of LCA for products and systems.

(a) **1960–1990: decades of genesis**

The initial studies that are now recognised as partial LCAs, date from the late 1960s to early 1970s. The scope of study during this era was limited to energy analyses but gradually broadened to encompass resource requirements, emission loadings and generated waste. LCA mainly focused on covering the alternatives in this period. The first impact assessment method was introduced in the early 1980s, separating the airborne and waterborne emissions by semi-political standards for those emissions and aggregating them into 'critical volumes' of air and 'critical volumes' of water, respectively. From 1970s to 1980s, there was a lack of international scientific discussion and information exchange on LCA platforms. Thus, LCAs were performed using different methods and without any common standard structure. This prevented LCA to be accepted more generally as an analytic tool as there were great differences in the results obtained even when the same materials were used (Guinee 2011).

(b) **1990–2000: decade of standardisation**

The tremendous elevation in scientific and coordination activities world-wide reflected in the increasing number of LCA guides and handbooks produced. The International Organisation for Standardisation (ISO) has been involved in LCA since 1994. Other than that, the first scientific journal papers began to appear in the Journal of Cleaner Production; Resources, Conservation and Recycling; International Journal of LCA; Environmental Science and Technology; Industrial Ecology and other journals. Moreover, LCA became part of policy documents and legislation during these years. Several well-recognised impact assessment methods such as CML 1992 environmental theme approach that are still being used till today were developed in this period.

(c) **2000–till now: decades of expansion**

The attention towards LCA began to grow in the first decade of the twenty-first century. In 2002, the United Nations Environment Programme (UNEP) and the society for Environmental Toxicology and Chemistry (SETAC) launched an International Life Cycle Partnership known as the Life Cycle Initiative, where their main aim was formulated as putting life cycle thinking into practice and improving the supporting tools through better data and indicators. The European

Platform on Life Cycle Assessment was established in 2005, mandated to promote the availability, exchange and use of quality assured life cycle data, methods and studies for reliable decision support in (EU) public policy and business. In the USA, the US Environmental Protection Agency started promoting the use of LCA and simultaneously environmental policy gets increasingly life cycle based all over the world. The decade 2000–2010 can be characterised as the decade of elaboration. Over the years, several types of LCA have been evolved such as environmental life cycle assessment (E-LCA) which is now known as LCA, social LCA (S-LCA), and life cycle sustainability assessment (LCSA). New approaches of LCA have also emerged such as consequential LCA, attributional LCA, dynamic LCA and Input-output (IO) LCA, that specify the need for the study to be carried out.

15.5 Life Cycle Assessment of Anaerobic Digestion Systems

Figure 15.5 illustrates the phases involved in the LCA of AD system. Some previous studies on life cycle assessment of anaerobic digestion system are given in Table 15.2.

Mezzullo et al. (2013) evaluated the environmental impacts of biogas production and utilization through the framework of LCA. The production of biogas and fertilizer (from digestate) from a cattle farm waste is compared with other alternative forms of energy including fossil fuel. The biogas based system was much more advantages in terms of greenhouse gas emission and fossil-fuel usage. In terms of

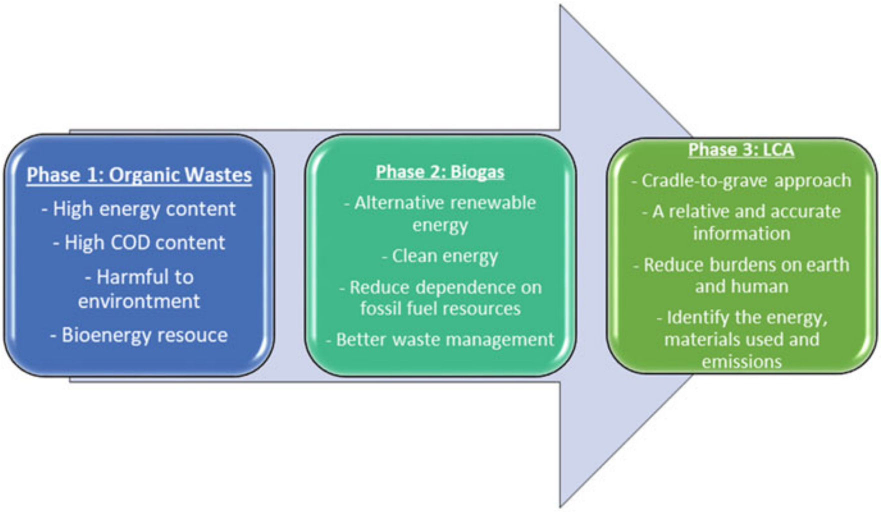

Fig. 15.5 Phases involved in LCA of AD system

Table 15.2 Selected studies on life cycle assessment of anaerobic digestion process

Location	Organic waste source	Functional unit	Software	Impact method	Reference
Australia	Food waste	1 kg of food waste	SinaPro v.8	ReCiPe	Opatokun et al. (2017)
Italy	Agricultural products and waste	1 MWh of electricity	Gabi LCA v6.11	CML 2001	Fusi et al. (2016)
United Kingdom	Cattle waste	1 m^3 of biogas	SimaPro	EI 99	Mezullo et al. (2013)
United States	Cow manure	1 kg of excreted manure	GaBi 5	IPCC, 2006	Andres and Rebecca (2019)
Vietnam	Pig manure	100 kg of solid pig manure 1000 kg of liquid pig manure		ReCiPe, 2008	Vu et al. (2015)
Norway	Fuel	1 kg of CO_2	SimaPro v8.5.2	CMLIAb v3.05 IPCC (2013)	Lyng and Brekke (2019)
Malaysia	Palm oil mill effluent (POME)	1 tonne of POME	SimaPro v8.5	ReCiPe, 2016	Aziz and Hanafiah (2020)
Italy	Organic waste	1 tonne of organic waste		CML	Di Maria and Micale (2015)

both environmental and energy impact, the system contributed negligible amounts towards the whole life cycle impacts.

Fusi et al. (2016) evaluated the environmental impacts (through LCA) associated with generation of electricity from biogas produced by AD of agricultural wastes in five actual plants. The results suggest that the main contributors to the impacts are the use of maize silage, the operation of the anaerobic digester, including open storage of digestate. The small scale system using animal slurry is the best option among the different plants considered in this study. The only impacts an animal slurry based biogas plants has are marine and terrestrial ecotoxicity. However, in comparison to other renewable sources and natural gases for electricity generation, biogas based electricity performed poorly with higher environmental impacts. According to the author, the environmental impacts could be mitigated by undertaking better practices such as avoiding digestate storage, preventing biogas emissions and reducing digestate application to land.

Vu et al. (2015) reported that loss of biogas from digesters as well as the intentional release of biogas and emissions of CH_4 from manure storage compromise the beneficial effects of biogas use. However, from the sensitivity analysis, it is also clear that biogas digesters can become a means of reducing global warming impacts relatively easy if CH_4 emissions into the environment can be kept low. In another study, Lyng and Brekke (2019) stated that when applying life cycle assessment to evaluate the environmental impacts from biogas as a fuel for transport, the results are largely dependent on the underlying assumptions. Biogas appears to be one of the fuels on the market with the lowest environmental impacts. Aspects that have considerable impact on the results for biogas used as a fuel are system boundaries, transport distances and methane leakages.

In Malaysia, Aziz et al. (2020) concluded that waste-derived biogas is a promising technology that can be used to meet the national goals for a sustainable renewable energy and highlighted the sustainability of biogas production for a proper waste management and energy recovery in the Malaysian context. There are some previous studies that compared AD in terms of its sustainability with other processes for their waste management capability using LCA. For example, environmental impacts and benefits of three treatment scenarios for food waste management, namely anaerobic digestion, pyrolysis and integrated anaerobic digestion followed by pyrolysis have been investigated (Opatokun et al. 2017). The results revealed that the integrated system and anaerobic digestion have similar high overall benefits and low impacts in comparison to the pyrolysis process. In contrast, Di Maria and Micale (2015) reported that incineration of organic waste leads to maximum environmental benefits compared to anaerobic digestion and composting. Furthermore, anaerobic digestion and composting were characterized by negative impacts due to high gaseous emissions.

15.6 Sustainable Waste Management

Most countries deal with the wastes according to their respective waste hierarchy. Although, the steps of the waste hierarchy of a country may slightly vary from one another, its ultimate motive is to work towards sustainable waste management. In general, the first step of a waste hierarchy is to reduce waste generation at the point of source. Reducing waste needs to be considered from the beginning of designing any sort of product in order to minimise the toxicity and the amount of waste generated throughout the product’s life. This step emphasises the importance to carry out a LCA before manufacturing a product. Apart from that, reducing waste can be practiced in every household as this is the simplest way to curb problems related to waste management. However, this step might have a drawback when it comes to changing from citizens’ up to stakeholders’ behaviour and attitude towards sustainable waste management as this step can only be completely effectively if everyone joins forces to do their responsibility in reducing waste.

The second step of the waste hierarchy is to reuse a product more than once. Accumulation of the amount of waste in the landfill can be decreased by practicing this step. This step also requires a strong commitment from the majority of the people to succeed. Recycling is the third step in the hierarchy of waste. Similar to the two other steps mentioned before, recycling also starts from home by segregating waste according to its type. Recycling is a very resourceful step as it extracts the raw material from a product to be reused or to generate new products and reduce landfilling as well. Anaerobic digestion and composting are included in this step as it recovers useful organic compounds from biodegradable waste.

Although composting is a traditional method that recovers and dissolves organic material back to the land, it is considered one the most effective methods as it is simple to carry out and the cost is minimal. However, this method may attract pests in an area. The next level of this hierarchy is the treatment or energy recovery step, whereby energy is recovered from waste through various types of treatment or recovery techniques. Anaerobic digestion can also be included in this category as it generates biogas that can be used as a source of energy to produce electricity and fuel as discussed in this chapter. Biological anaerobic digestion gains more importance among the various conversion processes of biomass due to its economical and efficient way of recovering carbon in the form of renewable biogas fuel (Achinas et al. 2020). Other recovery techniques include mass burn, pyrolysis and refuse-derived fuel (RDF). Lastly, the bottom of the hierarchy is categorised as landfilling because it causes many environmental issues such as pollution and global warming due to high emissions of GHGs, leachate, and toxicants.

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