Chapter 6
Biogas from Lignocellulosic Materials

Maryam M. Kabir, Gergely Forgács and Ilona Sárvári Horváth

Abstract Methane production via anaerobic digestion is a steadily growing industry in Europe and all over the world. Biomethane reduces the demand for fossil fuels, since it can be used for the production of power and heat or converted to vehicle fuel. Anaerobic digestion is a renewable energy technology; however, it can also be considered as a low-cost environmental-friendly waste management process, since it reduces the emission of greenhouse gases (GHGs), while it stabilizes the wastes. Currently, mainly the organic fraction of household waste, food waste, sewage sludge, manure, and energy crops is used for biogas production; nevertheless, there are a wide range of other organic substrates which can be utilized for biogas production. Among the organic matters, lignocellulosic materials have a great potential. Great abundance worldwide and carbohydrate-rich contents make them an attractive feedstock for biofuel production. Currently, anaerobic digestion of energy crops is widespread; however, biogas production from lignocellulosic residuals and wastes is still under investigation. This chapter focuses on anaerobic digestion of lignocellulosic materials. It explains the anaerobic digestion process and the current technologies used for crops digestion. It also summarizes the biogas potential of different lignocellulosic materials and the latest research on pretreatments to improve the methane yield. Finally, this chapter compares anaerobic digestion of lignocellulosic materials with energy production from these kinds of materials through thermochemical processes.

6.1 Introduction

At present, around 80 % of the world's energy demand is provided from fossil fuels (oil, gas, and coal) (IEA BIoenergy 2013), which are limited energy sources and eventually become exhausted. Furthermore, the increasing prices of the fuels speed

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up the need for replacing fossil fuels with renewable, green alternatives. In addition to the high price of the conventional fuels and increase the energy demand, it is known that the emission of greenhouse gases (GHGs) causes severe damages in the environment, resulting in global warming and climate change. Among the GHGs, methane has a 72 times higher potential of global warming than carbon dioxide over a 20 years period (Forgács 2012; Aardenne and Fernandez 2010). Almost half of the emitted methane was generated by the agricultural sectors, mainly related to rice cultivation and enteric fermentation. Moreover, waste management sectors (e.g., wastewater treatment and landfill) generate one-third of the methane emission, while the rest of the methane is produced from combustion sectors and oil and natural gas systems (Aardenne and Fernandez 2010). The European Environmental Agency reported that a decrease of methane emission would have a significant impact on the climate change (Forgács 2012; Aardenne and Fernandez 2010). It has been shown that biogas production in a controlled environment can considerably reduce the emission of GHGs, since methane as a potent greenhouse gas can be captured (Abbasi and Abbasi 2010). In addition to that the worldwide energy demands can be largely met by production of biogas; therefore, the efforts are being made to develop and distribute technologies enabling the use of biogas as a promising substitute to fossil fuels in the production of power, heat, and gaseous vehicle fuel. (Börjesson and Mattiasson 2008; Tippayawong and Thanompongchart 2010).

Biogas is formed during microbial degradation of organic matters in oxygen-free environments, a process known as anaerobic digestion (AD). A wide variety of organic materials, i.e., food waste, municipal waste, and animal manure, have been used as feedstocks in AD. Lignocellulosic biomass, including agricultural, forestry residues, energy crops, has recently gained more attention as suitable feedstocks for biogas production due to the increased demands for bioenergy and their abundant accessibility (Montoneri et al. 2009). Lignocelluloses have been accounted for approximately 50 % of the biomass in the world. Yearly production of lignocelluloses is about 200 billion tons per year (Claassen et al. 1999; Zhang 2008). These organic residues have a high energy potential which are currently under-utilized. However, anaerobic digestion of these residues may considerably reduce the volume of waste and provide biogas as an energy source. Besides, the undigested materials can be used for production of biofertilizer and soil conditioners (Lettinga 2005).

The process flow diagram of conversion of lignocellulosic biomass to biomethane is presented in Fig. 6.1.

The methane yield during AD is affected by biodegradability and the composition of lignocellulosic biomass. However, the biodegradability of lignocellulosic biomass during AD is hindered by the recalcitrant structure attributed to the highly crystalline cellulose and lignin around carbohydrates (cellulose and hemicelluloses) (Frigon and Guiot 2010). Therefore, in most cases, the utilization of lignocellulosic biomass can only be economically feasible after pretreatment. Pretreatment processes are considered as key enabling technologies, which allow the use of these cheap and available feedstocks for design of mass- and economically efficient, second generation biofuel processes.

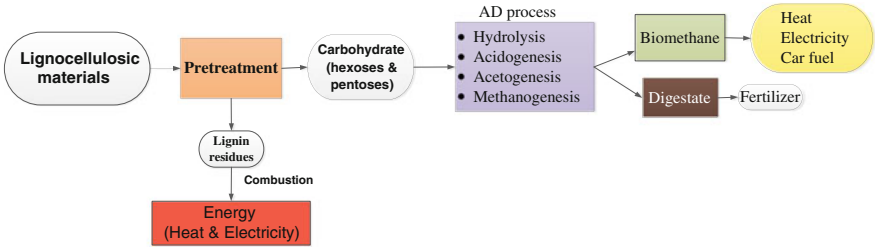

Fig. 6.1 Simplified process flow diagram of conversion of lignocellulosic materials to biomethane

6.2 Anaerobic Digestion

Biogas is a renewable energy source, which is produced by microbiological breakdown of organic matters in the absence of oxygen. One of the major benefits of anaerobic digestion is its versatility to receive wide range of organic substrates (Dolan et al. 2011). The produced gas is mainly composed of methane and carbon dioxide and some smaller amount of other gases such as hydrogen sulfide, hydrogen, nitrogen, ammonia NH_3, oxygen, and water (Ziemiński and Frąc 2012; Naik et al. 2010). The by-product of anaerobic digestion is a nutrient-rich "digestate residue" which can be utilized as a fertilizer on agricultural land (Schnürer and Jarvis 2009). This digestate residue has been proved to achieve a similar improved effect on crop production, as using the commercial fertilizers (Odlare 2005). Additional environmental benefits are the reduction of fossil energy which otherwise would be used in the production of traditional chemical fertilizers. Therefore, biogas production from organic residuals is becoming a very attractive and rapidly developing industry as it is a low-cost waste management technology and does not entail harsh conditions and a complex process design (Börjesson and Mattiasson 2008; Forgács 2012). Under optimal conditions, the energy output/input ratio can reach 28 MJ/MJ, revealing a high efficient use of the biomass (Deublein and Steinhauser 2008b).

Anaerobic digesters can be built locally, and they can be fed with a variety of substrates locally available. The largest number of digesters can be found today in developing countries, and they are small-scale household digesters. It is assumed that there are more than 30 million household digesters operating in China and 3.8 million in India, as well as 200,000 in Nepal and 60,000 in Bangladesh (Jiang et al. 2011; Rajendran et al. 2012). The biogas technology in the African countries is not developed yet; however, a few small-scale digesters are already in operation there (Amigun et al. 2008). Farm-scale digesters found in Europe and America are larger in size, compared to the household digesters in the developing countries. Approximately, 10,000 biogas plants are currently operated in Europe, producing biogas from animal manure, energy crops, sludge, and different types of wastes.

According to the prediction of the German Biogas Association, the number of the biogas plants would increase by a factor of five within the next 10 years in

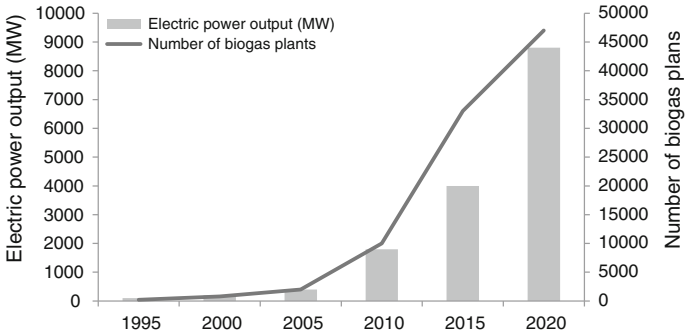

Fig. 6.2 The estimated development of biogas industry in Europe 1995–2020 (Forgács 2012)

Europe (Fig. 6.2). In China, the number of biogas plants is estimated to reach around 200 million by the year of 2020 (Deublein and Steinhauser 2008c).

6.3 Biochemistry of Anaerobic Digestion

Anaerobic digestion is regarded as a multistep biological and chemical process which is favorable not only in waste minimization but also for energy formation. As a result of anaerobic digestion process, the organic compounds are anaerobically degraded and converted to biogas by the action of different groups of microorganisms.

The main steps of the anaerobic digestion process are hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Fig. 6.3) (Ziemiński and Frąc 2012). Each individual phase is carried out by different groups of microorganisms including bacteria and archaea, which partially has syntrophic relation to each other with different needs on the environment (Deublein and Steinhauser 2008a).

6.3.1 Hydrolysis

Hydrolysis is the first step in the anaerobic digestion process. Hydrolytic bacteria (facultative anaerobes) hydrolyze the substrates using extracellular enzymes, either attached to or excreted from their cell surfaces. During this step, the polymers are broken down into soluble monomers and oligomers. The enzymes involved in this process are cellulases, hemicellulases, lipases, amylases, and proteases (Taherzadeh and Karimi 2008). Since, a variety of enzymes are in action throughout this degradation process, almost all kinds of compostable substrates can be hydrolyzed. However, waxes and lignin which are among the main components in lignocelluloses are not degraded (Fernandes et al. 2009).

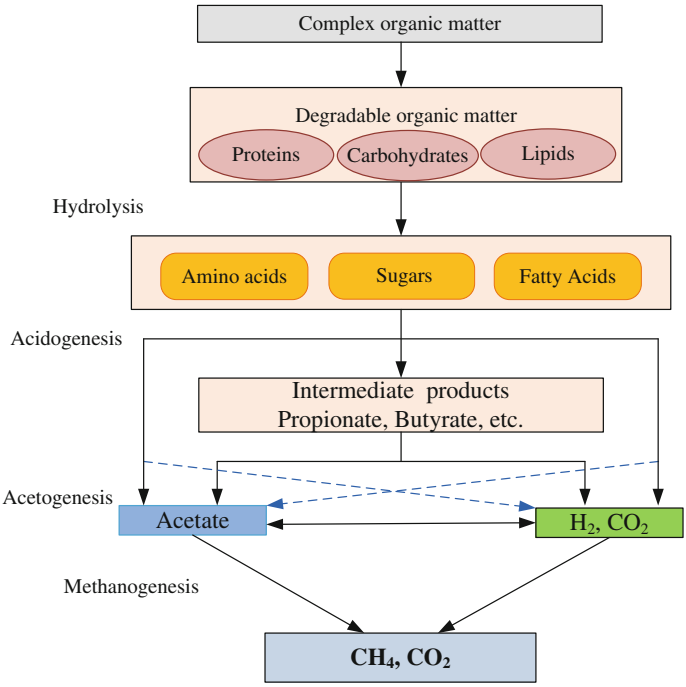

Fig. 6.3 Process flow diagram of anaerobic digestion system (Batstone et al. 2002)

The duration of the hydrolysis step is highly dependent on the characteristics of substrate. Hydrolysis can be achieved relatively fast if the suitable enzymes are produced by microorganisms and enough physical contact between the enzymes and the substrate is provided (Taherzadeh and Karimi 2008). However, substrates with recalcitrant structure, such as cellulose, require weeks to become degraded, and usually, the degradation is not completed (Deublein and Steinhauser 2008a). Hence, in biogas production from complex and rigid substrates, such as lignocelluloses, which are barely accessible to the enzymes, the hydrolysis steps are considered as the rate-limiting step (Taherzadeh and Karimi 2008) (Table 6.1).

Table 6.1 The important groups of enzymes and their functions (Schnürer and Jarvis 2009)

Enzymes	Substrate	Degradation products
Cellulases	Cellulose	Cellobiose and glucose
Hemicellulases	Hemicelluloses	Sugars such as glucose, xylose, mannose, and arabinose
Pectinases	Pectin	Sugars such as galactose and arabinose
Proteinases	Protein	Amino acids
Lipases	Fat	Fatty acids, glycerol

6.3.2 Acidogenesis

In the acid-forming phase, the products from the hydrolysis step will be further degraded by the action of both obligate and facultative anaerobes which will convert them into volatile fatty acids (VFAs) such as valeric acid, butyric acid, propionic acid, acetic acid, and formic acid, as well as hydrogen and alcohols. The partial pressure of the hydrogen regulates the expected products in this step. In general, the most favorable pathway of primary fermentative bacteria is the production of acetate via pyruvate with production of hydrogen. In a well-balanced process, with low partial pressure of hydrogen, the main products are acetate, carbon dioxide, and hydrogen. However, if the environmental conditions are not optimal, at high partial pressure of hydrogen, more intermediates such as volatile fatty acids and alcohols are formed. These products are more reduced than the products that would be produced under optimal conditions (Schnürer and Jarvis 2009; Schink 1997). Thus, these products have to be further modified before they can be converted into biogas.

Non-favorable environmental conditions are formed usually due to an overload of substrates, or the presence of toxic compounds.

6.3.3 Acetogenic Phase

Degradation products from the acidogenesis phase are undergone two different pathways.

Some of the degradation products of the acidogenesis (acetate, carbon dioxide, and hydrogen) can be directly used by methanogens to produce methane. However, VFAs containing more than two carbon atoms and alcohols containing more than one-carbon atom (Schink 1997; Bryant 1979) have to be further oxidized to acetate and H_2 in the acetogenic step by obligatory hydrogen-producing bacteria. At standard conditions, the reactions accomplished by acetogenic microorganisms are not exergonic. For the hydrogen-producing microorganisms, low partial pressure of hydrogen (lower than 10^{-5} bar) is needed for the reactions to be energetically feasible. The syntrophic association between the hydrogen-producing bacteria and the archaea in the methanogenic phase can preserve the partial pressure of hydrogen within the range suitable for the growth of the acetogenic microorganisms (Schink 1997).

6.3.4 Methanogenesis

In the methanogenesis step, obligate anaerobic archaea convert acetate or H_2 and CO_2 to CH_4 and CO_2. The methanogenic archaea can grow directly on H_2/CO_2, acetate and one-carbon compounds, such as formate and methanol (Schink 1997; Bruni 2010).

Acetoclastic microorganisms use acetate, while hydrogenotrophic microorganisms use hydrogen and carbon dioxide as substrates to produce methane. Even though acetoclastic pathway provides much lower energy for microbial growth compared to the hydrogenotrophic one (Klass 1984), approximately 70 % of methane production is performed via the acetoclastic pathway. Since the hydrogenotrophic microorganisms use hydrogen as substrate, the partial pressure of hydrogen has to be above a minimum level (higher than 10^{-6} bar) for the reaction to be exergonic.

Methanogenic archaea are more sensitive group of microorganisms compared to bacteria that are easily affected by environmental stresses in the reactor, such as changes in temperature and pH, or the presence of toxic compounds, such as heavy metals and different toxic organic substances (Chen et al. 2008; Liu and Whitman 2008). Besides, they grow slower and hence have longer generation times (2–25 days) compared to other groups of microorganisms in the reactor, which makes this step the time-limiting step for easily hydrolyzed materials (Schnürer and Jarvis 2009).

In general, as it is described above, these four groups of microorganisms involved in the anaerobic digestion process, function in sequence; in a way that the products from one group are used as feed for another group in the subsequent step (Gerardi 2003). Nevertheless, there is a closer connection between hydrolytic and acidogenic bacteria as well as between acetate- forming bacteria and methane-forming archaea. These connections divide the entire process into two main stages, with different environmental needs in each of these stages. Provided that the degradation rate is almost equal in both of these stages, the process is in balance (Weiland 2010).

6.4 Process Parameters

Accomplishment of the anaerobic digestion system relies on environmental factors, including pH, temperature, mixing rate, organic loading rate (OLR), retention time, and micro- and macronutrient availability. Therefore, to preserve a high efficiency within the process, these parameters should be effectively controlled and kept within the optimum range for the microorganisms involved in the anaerobic digestion process (Ward et al. 2008). The feedstock structure and characteristics also have a significant impact on the performance of the digestion process.

6.4.1 Organic Loading Rate and Hydraulic or Solid Retention Time

OLR is an important parameter to maintain a stable process and to measure the biological performance of anaerobic digestion systems. OLR is referred to the added solid feedstock based on volatile solids (VS) per reactor volume and time

(kg VS $m^{-3}day^{-1}$). For liquid feedstock, it is measured based on chemical oxygen demands (COD); in this case, the OLR is expressed as kg COD $m^{-3}day^{-1}$ (Vandevivere et al. 2003).

In general, the start-up period of the process needs a lower OLR, while a balanced and well-functioning process can handle a higher OLR. The biological performance of AD system is very sensitive to the composition of waste feedstock together with OLR (Zuo et al. 2013; Sharma et al. 1999). An overload into the digester normally leads to the accumulation of VFAs or other inhibitors, which may finally terminate the methane production (Bouallagui et al. 2004; Mata-Alvarez et al. 2000). However, running the digester with too low organic loading (underloaded system) is not economically feasible since the capacity of the digester is not entirely utilized.

Another important parameter that controls the rate of bioconversion of substrate to biogas is the retention time. Retention time is usually expressed as hydraulic retention time (HRT), which regarded as the estimated time that the liquid sludge is present in the anaerobic digester, or solid retention time (SRT), which refers to the time that the microorganisms/solids spend in the digester (Appels et al. 2008). HRT is calculated based on the following formula;

$$\theta = V/Q \tag{6.1}$$

where
θ is hydraulic retention time (time),
V is the volume of the digester (m^3),
Q is fluid flow rate (volume/time)

Generally, HRT is more significant if the feedstock is complex and difficult to digest, whereas SRT is important for easily degradable biomass (Speece 1983; Forgács 2012). Shorter retention time is normally favorable to increase the efficiency of the process and reduce the capital investment costs (Chandra et al. 2012). However, there must be always a balance between OLR and HRT in order to optimize digestion efficiency. Therefore, at higher OLRs, retention times should be sufficiently longer to provide enough time for the microorganisms to degrade the substrates (Demirer and Chen 2005). HRT and SRT are equal when continuously stirred tank reactors (CSTR) are employed running a continuous or semi-continuous process. Nevertheless, in processes, when a part of the residues are recirculated back to the digester tank, SRT gets longer than HRT. In digestion of industrial sewage sludge, where the feedstock has a low total solid content, returning the thickened digestate sludge residue including the biomass, would allow longer retention time for the microorganisms to degrade the organic matter (Dererie et al. 2011). SRT can be also prolonged in proportion to HRT using high-rate processes, such as fluidized bed reactors and anaerobic expanded bed reactors where the microorganisms are attached to a certain carrier material, or UASB reactor in which the microorganisms are forming granules remaining in the system. New technologies for cell immobilization by using specific capsules made of a membrane which is permeable to nutrients and

metabolites retaining biomass (Cheng and Timilsina 2011; Youngsukkasem et al. 2012; Chaudhary 2008) are also in development to increase the efficiency of the process. An additional benefit with a longer SRT is to enable the viable biomass adapted to possible inhibitors, such as ammonia, sulfides, and other substances that might otherwise be toxic at high concentrations (Dererie et al. 2011).

6.4.2 Temperature

Temperature is also one of the most vital factors affecting the activity of anaerobic digestion microorganisms. Temperature fluctuations might be favorable to a certain group and unfavorable to other groups. Among the microorganism in AD system, methane-forming archaea are the most strongly affected by changes in temperature. For instance, an increase of 10 °C in temperature can terminate the methanogenic activity within 12 h; however, it increases the rate of production for acid-forming bacteria. Therefore, the system might suffer from accumulation of VFAs which cannot be utilized by the methane-formers, affecting the overall balance of the digestion process (Gerardi 2003) (Table 6.2).

The anaerobic digestion process can be operated at three different temperature ranges; the psychrophilic range, where the growth optima is around 10 °C, the mesophilic range with an optima at around 37 °C, and the thermophilic range with an optimum at above 50 °C (Mesbah and Wiegel 2008; Kashyap et al. 2003; Coelho et al. 2011). Psychrophilic temperatures can be used for small-scale digesters without heating. However, biogas production at psychrophil temperature is much slower compared to at higher that temperature conditions (Collins et al. 2006; Bohn et al. 2007; Hesselgren et al. 2005). The large-scale anaerobic digesters in Europe are mostly run at mesophilic or thermophilic conditions (Table 6.3).

Table 6.2 Temperature intervals for methane producers (based on Schnürer and Jarvis 2009; Gerardi 2003)

Temperature range	Temperature
Psychrophile	4–25
Mesophile	25–40
Thermophile	50–60
Hyperthermophile	>65

Table 6.3 Comparison of mesophilic and thermophilic digesters (adapted from Gerardi 2003)

Feature	Mesophilic digester	Thermophilic digester
Loading rate	Lower	Higher
Destruction of pathogens	Lower	Higher
Sensitivity to toxicants	Lower	Higher
Operational cost	Lower	Higher
Temperature control	Less difficult	More difficult

A greater diversity of methanogenic microorganisms are found in the mesophilic group (Sekiguchi et al. 1998; Sung and Santha 2003). At mesophilic conditions, the stability and growth conditions of the methanogens in the digester are more likely provided. Due to a greater diversity of the microorganisms at this range of temperature, the process is more robust and has more resistance to different process disturbances (e.g., accumulation of ammonia) which may occur (Zhao and Kugel 1996; Levén et al. 2007).

In general, under thermophilic conditions, methanogens have higher metabolic rates and higher specific growth rates (Lier 1995). Due to this fact, the digesters operated at thermophilic temperature may be constructed in smaller dimensions (which has lower capital costs), while maintaining high levels of biogas production (Duran and Speece 1997). However, in thermophilic range, a smaller group of methanogenic organisms are active. One of the drawbacks is therefore the high sensitivity of thermophilic methanogens to changes in process conditions, since even a small change of the operating parameters can negatively influence their activity (Hwu and Lettinga 1997; Duran and Speece 1997; Lier 1995). For example, a change in temperature with more than 1–2 °C causes a significant reduction in the amount of produced biogas (Chae et al. 2008) due to the fact that a sudden temperature alteration leads to a simultaneous rise in the concentration of all VFAs, particularly in acetic acid and propionic acids (Ahn and Forster 2002; Dohanyos et al. 1985).

Moreover, a range of substrates that can be processed in anaerobic mesophilic condition is higher than those at thermophilic conditions, mainly due to the chemical composition and the stronger influence of some inhibitors in the process (Braun et al. 1981). Several studies showed that anaerobic digestion of wastes with a high concentration of ammonia was less stable and more easily inhibited at thermophilic temperatures than at mesophilic temperatures (Parkin and Miller 1983).

6.4.3 pH and Alkalinity

pH is a vital factor in the anaerobic digestion system. The different microorganisms involved in the biogas process have widely varying requirements on pH for their best growth (Mittal 1996). Most of the microorganisms prefer a neutral pH range, i.e., between 7.0 and 8.5 (Kanokwan 2006). However, there are organisms which are active at both lower and higher pH values. Acid-forming microorganisms can survive in relatively acidic environments (pH 5.0). However, in favor of all the organisms in the digester, neutral pH needs to be maintained (Ferry 1993). The pH out of neutral range results in imbalances in the system by negatively affecting the microorganisms, especially the methanogens (Schnürer and Jarvis 2009; Dague 1968). Since the pH in the process directly depends on the production rates of intermediates, such as volatile fatty acids, during the digestion, in order to keep the pH in optimum range, the system needs to be fed at an optimal OLR. Generally, to

have a stable process, the concentration of volatile fatty acids, particularly acetic acid, should be below 2,000 mg/L (Jain and Mattiasson 1998).

Buffering capacity or alkalinity is referred to the equilibrium between carbon dioxide and bicarbonate, with ammonia as the major cation, which cause a significant resistance to pH changes. In order to preserve optimum pH in the digester, it is vital to have a high stable alkalinity. In AD process, the buffering capacity is mainly provided by few acid-base pairs including, carbon dioxide–bicarbonate, ammonium–ammonia, and dihydrogen phosphate–hydrogen phosphate. The major buffer, produced in anaerobic digesters, is bicarbonate (HCO_3^-), with a pKa of 6.3, and the main acids are VFAs, with an aggregate pKa around 4.8 (Kanokwan 2006). For the process stability, the recommended VFA: alkanity ratio should be maintained less than 0.3 (Ross et al. 1992). The higher the bicarbonate concentration in the digester medium, the greater the alkalinity and resistance to changes in pH (Alvarez et al. 2006). However, a sudden change in pH can occur, for instance, if the system is overloaded and the feed rate is significantly increased. Since the methanogens grow slower than the fermentative bacteria, VFA accumulations will result in a pH drop. In addition, feeding the digester with materials with low buffering capacity, such as lignocelluloses, can also lead to low pH in the digester (Banks and Humphreys 1998). Volatile fatty acid concentrations, specially propionic and acetic acid and butyric acids, are important intermediates to monitor the anaerobic digestion process (Björnsson et al. 1997). In order to maintain the pH in favor of fermentative bacteria and methanogenic archaea, the phase separation (two-staged and multi-staged digesters) is introduced, where the first phase can be optimized at optimal conditions for the growth of hydrolytic and acidogenic microorganisms, while the second phase can operate at conditions optimal for the acetate and methane formation (Ince 1998).

6.4.4 Nutritional Requirements

Nutrients are vital for synthesis and growth, enzymes, cofactors involved in biochemical and metabolic pathways of anaerobic digestion microorganisms. Methanogens have a wide range of mineral nutrient needs for robust metabolism (Blanchard 1992; Rowell and Young 1997). Nutrients are categorized into two types, the macronutrients and the micronutrients and to have a well-balanced system both macro- and micronutrients ought to be present in the digester in right ratios and concentrations. It is reported that in an ideal AD system, the nutrients should be found in excess in the digester as even small shortage may inhibit the overall process (Mara and Horan 2003).

Therefore, in case of feedstock nutrient deficiencies, supplementary nutrients must be added to stimulate the digestion process. However, it should be noted that the inhibition can also occur from the substrate fed to the reactor such as presence of heavy metals and other chemical compound, i.e., limonene in fruit such as citrus

waste, and toxic impurities from batteries and electronic waste mixed with organic fraction of municipal solid waste (OFMSW) (Nayono 2010).

Fundamental macronutrients such as carbon (C), nitrogen (N), phosphorus (P), and sulfur (S) are necessary for growth and multiplication of microorganism. The nitrogen content of a substrate also has a key role in this process since it results in neutral pH stability by liberating ammonium ions (Speece 1983; Gunnerson et al. 1986).

6.4.5 C/N Ratio

There is a vital connection between the utilization of carbon and nitrogen source within the biogas production process. Nitrogen is necessary for the growth of the microorganisms. In one hand, nitrogen deficiency results in insufficient consumption of the carbon source which prohibits the growth of the microorganisms which would accordingly decrease the biogas production (Resch et al. 2011). On the other hand, the degradation of the proteins and other nitrogenous materials would give rise to the high concentration of the nitrogen in the form of ammonium ion (NH_4^+) or ammonia (NH_3) in the system (Chandra et al. 2012; Hobson et al. 1981). Changes in temperature and pH are the main factors to control the chemical equilibrium between the ammonium and the ammonia. As the temperature or the pH increases, this equilibrium would shift more toward NH_3 resulting in ammonia inhibition (Chen et al. 2008). The free ammonia is a main source of inhibition as it can diffuse into the cell and cause proton imbalance in the AD systems (Chen et al. 2008). Therefore, the C/N ratio is considered as a vital parameter for the anaerobic digestion systems, which can be adjusted by feeding the digester with a proper substrate mixture (Chandra et al. 2012; Hobson et al. 1981).

6.4.6 Trace Elements

Among micronutrients, the elements which are known to be the most crucial ones are iron (Fe), nickel (Ni), cobalt (Co), molybdenum (Mo), and wolfram (W) (Zandvoort et al. 2006).

Micronutrients play an important role to form the active sites for several key enzymes; thus, several functions of anaerobic microorganism are dependent on the presence of sufficient micronutrients (Oleszkiewicz and Sharma 1990). The optimum micronutrient requirements in the digester have to be optimized based on the inherent micronutrient concentrations of the substrate, inocula, and the general process conditions within the digester (Jagadabhi 2011).

6.5 Lignocelluloses as Substrates for Anaerobic Digestion

Biogas today is mainly produced from the following: sewage sludge, the organic fraction of municipal solid waste (OFMSW), agricultural residues, energy crops, and waste from the food industry (Angelidaki et al. 2003). However, the current used feedstocks for anaerobic digestion are limited; therefore to reserve the growing needs to feed the digesters, the introduction of new substrates is highly demanded.

The abundant availability of lignocellulosic biomass worldwide with their high carbohydrate content makes them an attractive feedstock for biofuel production. Available lignocellulosic materials can be divided into two different groups: cultivated feedstocks, known as energy crops, and lignocellulosic residuals. Energy crops are mainly composed of cellulose, hemicellulose, and a smaller amount of lignin (Kabir et al. 2013). In addition to these compounds, they contain non-structural carbohydrates such as glucose, fructose, sucrose and fructans, extractives, and pectins (Kabir et al. 2014), which make them an ideal source for biomethane production. The utilization of the energy crops such as corn silage is already extensively common especially in Germany, where approximately 90 % of the digesters utilize crops as main or co-substrate (Weiland 2003; Braun et al. 2008).

Lignocellulosic residuals have a higher amount of lignin content, which is a major drawback regarding their application as a feedstock for anaerobic digestion. Currently, the utilization of lignocellulosic residues as feedstock for biomethane production is not widespread, due to the relatively low methane yield (Seppälä et al. 2007; Lehtomäki 2006). Generally, most lignocellulosic residuals such as straw and woody biomass are not degradable due to their native structure and composition (Hendriks and Zeeman 2009).

In organic wastes, VS are measured as total solids minus the ash content, as achieved by complete combustion of the wastes. The VS are referred to two groups, i.e., the biodegradable volatile solids (BVS) fraction and the refractory volatile solids (RVS). Only the BVS of the VS are potential for bioconversion during the anaerobic digestion. Therefore, knowing the BVS fraction of VS in individual fraction of any kind of heterogeneous waste streams allows a better estimation of the biodegradability, the organic loading, the C/N ratio, and lastly the biogas production (Golush 2008; Monnet 2003). The RVS in organic wastes are mainly lignin which is associated with cellulose and hemicelluloses in plant materials. Lignin is a complex polymer which is difficult to degrade and usually needs a long period of time for complete degradation (Golush 2008; Kayhanian 1995).

Thus, lignocellulosic waste, characterized by high VS and low RVS fraction, is more suitable for biogas production (Monnet 2003). For that reason, the inert fraction of the lignocellulosic waste is better to be removed prior to digestion, since in this case it will not increase the digester volume and slow down the digestion process. For example, in balanced condition in case of waste streams high in sewage and manure, the microorganisms thrive and hydrolyze the organic fraction rapidly while, for the more resistant waste materials, such as native lignocelluloses; i.e., forest residues and straw, the digestion is limited.

6.5.1 Specific Surface Area of Lignocelluloses

Specific surface area has been identified as a particularly important factor affecting enzymatic deconstruction rate and yield (Meng et al. 2013; Mansfield et al. 1999). To improve the biochemical reaction during the digestion process, the accessible surface area of the substrate needs to be increased (Deublein and Steinhauser 2008a). Therefore, in the case of lignocellulosic biomass, the main challenge is to enhance the susceptibility to biodegradation of the material (Bruni et al. 2010; Bruni 2010). The porosity of the lignocelluloses per gram of the substrate is found to be 600–800 m^2; however, the size of each pore is only about 5 nm due to the firm connection between the main three constituents; i.e., cellulose, hemicelluloses, and lignin (Bruni 2010).

Research in connection to biomass pore size and enzymatic hydrolysis propose that small pores with diameters smaller than the cellulase enzymes diameters can hinder, and conversely, large pores enhance enzymatic hydrolysis (Tanaka et al. 1988). When pores are small, only small cellulase components can slowly penetrate inside the pores and may become trapped there, causing a decrease in synergistic interactions, and eventually lowering the rate of cellulose deconstruction. This explains why enzymes with dimensions between 5 and 18 nm depending on the shape need long reaction times (Grethlein and Converse 1991; Schacht et al. 2008). However, if the pores are large, the enzyme accessibility to the substrate will increase and synergistic catalytic actions will take place, and subsequently, the enzymatic hydrolysis yield and rate will increase (Foston and Ragauskas 2010; Meng et al. 2013).

6.5.2 Microbial Degradation of Cellulose and Hemicellulose

Hydrolysis of cellulose necessitates the concerted action of three enzymes, including, endoglucanases, exoglucanases, and β-glucosidase. The function of endoglucanases is to randomly break intermonomer bonds, while exoglucanases are responsible for removing mono- and dimers from the end of the glucose chain; and finally, β-glucosidase hydrolyzes the glucose dimmers (Malherbe and Cloete 2002; Tomme et al. 1995). The rate-limiting factor in the hydrolysis step is due to the ability of endoglucanases to reach amorphous regions within the crystalline matrix of cellulose to create new chain ends, there exo-cellobiohydrolases can attack.

Similar types of enzymes are needed for the hydrolysis of hemicelluloses; however, other enzymes rather than cellulase are required for its complete degradation because of its greater complexity compared to cellulose.

Aerobic fungi and bacteria normally have non-complexed cellulase systems, which lead to the excretion of the cellulose hydrolyzing enzymes into the culture medium. The most reviewed is the fungi, *Trichoderma reesei*, which has been used industrially for production and extraction of cellulases (Wilson 2008). Nevertheless, anaerobic bacteria such as *Clostridium spp* and fungi including, genera

Neocallimastix, Piromonas, and *Sphaeromonas* comprise complexed cellulase systems, where the cellulose hydrolyzing enzymes are enclosed in membrane-bound enzyme complexes (called cellulosomes). The unique components that distinguish the cellulosome from free enzyme systems are the cohesion-containing scafoldin(s) and the dockerin-containing enzymes (hemicellulases, cellulases, and pectinases). Moreover, free non-cellulosomal enzymes usually contain a cellulose-binding domain, called carbohydrate-binding module (CBM), that is attached to the substrate (Fig. 6.4) (Shoham et al. 1999). In rumen and large intestine of herbivorous mammals, cellulose and hemicelluloses are anaerobically degraded by complex cellulase systems. These microorganisms produce short-chain fatty acids that are absorbed and used as energy sources by the mammals (Flint 2008). In anaerobic digester, the same microorganisms that perform cellulolytic and hemicellulolytic activities are present. The only difference between the rumen and anaerobic digester is that the short-chain fatty acids are further converted by methanogens into methane and carbon dioxide.

Generally, aerobic microorganisms utilize far more energy per degraded sugar than anaerobic microorganisms (38 mol ATP versus 2–4 mol ATP per mole of glucose) (Malherbe and Cloete 2002). Cellulose hydrolysis efficiency in anaerobic fungi and bacteria is higher than that in aerobic systems. The reason for that is the presence of cellulosome systems, which allow better coordination between the different cellulose hydrolyzing enzymes. Their close connection will limit the loss of degradation intermediates due to dynamic environmental conditions. Another reason is that the anaerobic microorganisms are more limited in the amount of produced enzymes; so they have a need for a more energy-efficient system (Bayer et al. 2008; Himmel 2009; Doi and Kosugi 2004).

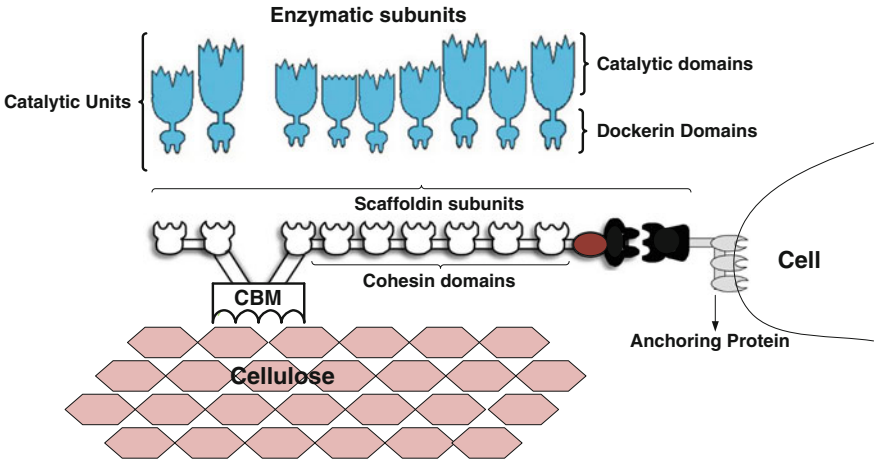

Fig. 6.4 Cellulosome complex structure, adapted from Shoham et al. (1999)

6.5.3 Microbial Degradation of Lignin

Lignin is the most recalcitrant constituent of the plant cell wall. The content of lignin and the biodegradability of the substrate are inversely proportional. The effect of lignin on the biodegradability of cellulose and hemicelluloses is considered to be largely a physical restriction, since the presence of lignin molecules will decrease the available surface area for enzymatic penetration and activity (Haug 1993). Lignin degradation is principally an aerobic process, and in anaerobic conditions, lignin is preserved for a very long period of time (Van Soest 1994). Lignin degradation by white-rot fungi is an oxidative process, and the key enzymes are phenol oxidases. Conditions which favor the lignin decomposition by white-rot fungi are adequate nitrogen level, moisture, temperature, all appear to be important in encouraging lignin decomposition, as does the composition of the lignocellulosic substrate itself (Kuhad et al. 1997; Leonowicz et al. 1999).

Laccase has broad substrate specificity and oxidizes lignin and phenols substructures with forming oxygen radicals. The other enzymes that contribute to the lignin degradation are H_2O_2-producing enzymes and oxidoreductases, which can act either intra- or extracellularly. Fungal and bacterial feruloyl and *p*-coumaroyl esterases are rather novel enzymes, and they are able to liberate feruloyl and *p*-coumaroyl which play a key role in biodegradation of recalcitrant cell wall in grasses (Kuhad et al. 1997). The above-mentioned enzymes can act synergistically with xylanases to disrupt the hemicellulose-lignin link, without mineralization of the lignin (Borneman et al. 1990).

6.6 Anaerobic Digestion of Energy Crops

Energy crops are plants which are dedicated for bioenergy production. Ideal crops for biogas production have the following characteristics: (1) high yield (maximum production of dry matter per hectare), (2) high methane yield (3) low energy input to produce, (4) low cost, (5) low content of contaminants and (6) low nutrient requirements (Koçar and Civaş 2013). Even though successful digestion of energy crops was demonstrated from 1930s, the practical application did not start due to economic reasons. In the 1990s, increasing oil prices and supportive European and National legal frameworks of eco-tariffs facilitated the spread of energy crop digestion (Braun et al. 2008). Moreover, crops digestion facilitates the growing activity in the agricultural sector due to the increasing demand for biomass.

6.6.1 Crops Used in Anaerobic Digestion

Various plant species and plant residues have been investigated for their biogas potential (Table 6.4) (Lehtomäki 2006; Amon et al. 2007). Many of them including

Table 6.4 Biomass and methane yield of various energy crops (Braun et al. 2008; Braun 2007)

Crop	Methane yield (m^3 CH_4/kg VS)	Crop yield (t TS/ha)	Calculated energy potential (GJ/ha)
Maize (whole crop)	205–405	9–30	59–435
Potatoes	276–400	10.7–50	95–644
Grass	298–467	10–15	96–226
Wheat (grain)	384–426	3.6–11.75	45–161
Oats (grain)	283–492	4.1–12.4	33–146
Triticale	337–555	3.3–11.9	36–213
Sorghum	295–372	8–25	76–300
Barley	353–658	3.6–4.1	41–87
Red clover	300–350	5–19	48–214
Alfalfa	340–500	7.5–16.5	82–266
Hemp	355–409	8–16	92–211
Flax	212	5.5–12.5	38–85
Nettle	120–420	5.6–10	22–135
Miscanthus	179–218	8–25	46–176
Sunflower	154–400	6–8	30–103
Oilseed rape	240–340	2.5–7.8	19–85
Jerusalem artichoke	300–370	9–16	87–191
Peas	390	3.7–4.7	47–59
Rhubarb	320–490	2–4	21–63
Turnip	314	5–7.5	51–76
Kale	6–45	240–334	46–484
Sugar beet	236–381	9.2–18.4	70–226

hemp, flax, potatoes, beets, kale, grass, and rape showed relatively high biodegradability and methane yield (Braun et al. 2008). Most of the successfully tested crops showed similar methane yields per VS. However, different crops have different biomass yield per hectare (Braun et al. 2008). Therefore, information regarding the overall energy methane yield per hectare of cultivated land is a more useful parameter from agricultural and economical point of view.

It is worth to mention that cultivation of energy crops has a certain energy requirement. This energy requirement includes the cultivation of the plant, harvesting and processing. Furthermore, significant energy is needed for the production and application of pesticides, herbicides, and fertilizers (Dalla Marta et al. 2011). Currently, maize and grass are the most common energy crops. Maize has high yield per hectare, while grass has relatively low energy requirement. Additionally, grass because of its perennial, it is associated with improved soil quality as well (Amon et al. 2007; Weiland 2006; Murphy and Power 2009). Both maize and grass are characterized by high net (energy yield/energy requirement) energy yield per hectare (Table 6.5).

Table 6.5 Energy calculation of net energy yield and energy output/input ratio for maize and grass, recalculated from Braun et al. (2008)

	Maize	Grass
Energy yield (GJ/ha)	247	161
Energy demand of cultivation (GJ/ha)	17	17
Energy requirement of digestion (GJ/ha)	33	24
Total energy requirement (GJ/ha)	50	41
Net energy yield (GJ/ha)	197	120
Energy output/input ratio	5.0	3.9

6.6.1.1 Stages of Crops Utilization in Anaerobic Digestion Process

Biogas production from crops can be divided into four district stages: (1) harvest, preprocessing and storage, (2) anaerobic digestion, (3) treatment and usage of biogas, and (4) treatment and usage of digestate. As Table 6.4 shows, various annual and perennial plants can be used as crops for AD. It is worth to mention that AD of crops as mono- substrate is not common, in practice crops are co-digested with liquid manure or other liquid substrates to obtain homogenous mixture in the digester and/or providing a more balanced C/N ratio in the system (Giuliano et al. 2013). Germany and Austria are the market leaders regarding to crop digestion with ca 7,800 and 290 digesters, respectively, utilizing mainly crops as feedstock. Other countries including Sweden, Finland, and France use crops as co-substrate (IEA Bioenergy 2014).

6.6.1.2 Harvest, Preprocessing and Storage

Crops can be used in the digestion process straight after harvest. However, for year-round availability of the feedstock, crops are usually stored in silage clamps. The time of the harvest is significantly influence the biomass composition, thus the biodegradability. Late harvest typically leads to higher lignin content, which results in lower methane yield in the subsequent AD process. Therefore, early harvest is recommended to maximize the methane yield. Ensiled biomass has a dry solid content between 20 and 40 %. During the ensiling, a rapid lactic acid and acetic acid fermentation take place, causing a sharp pH decrease to between 4 and 4.5 within a few days (Herrmann et al. 2011). Due to the low pH, the butyric acid fermentation is hindered. Furthermore, the acetic acid formation improves the aerobic stability of the silage and protects it from the growth of specific species of yeasts that are responsible for heating upon exposure to oxygen (Driehuis et al. 1999). Under these conditions, the ensiled crops can be stored for months (Weiland 2003). The harvesting and ensiling processes result in energy losses between 8 and 20 % which are mainly the results of the undesirable aerobic degradation process (Weiland 2010).

6.6.1.3 Anaerobic Digestion Process of Crops

Numerous technical solutions exist for anaerobic digestion of crops. These solutions can be divided into two groups, based on the solid content. Wet digesters operate with solid content less than 15 %; therefore, dilution of the feedstock with other liquid substrates or with process water is usually necessary (Redman 2008). According to Weiland (2010), a majority of the crop digestion plants uses wet processes. The most common reactor configuration applies single-stage digestion using a vertical continuously stirred tank reactor (CSTR) as digester; however, many plants have two-stage processes (Fig. 6.5) (Cirne et al. 2007; Parawira et al. 2008). In these two-stage systems, the second digester is often combined with a membrane type gas holder. Typically, the loading rate of wet crop digestion system is between 1.2 and 4.3 kg VS m^{-3} day^{-1} and the retention time varies between 50 and 150 days, although digesters with retention time longer than 200 days are also exist (Braun et al. 2008).

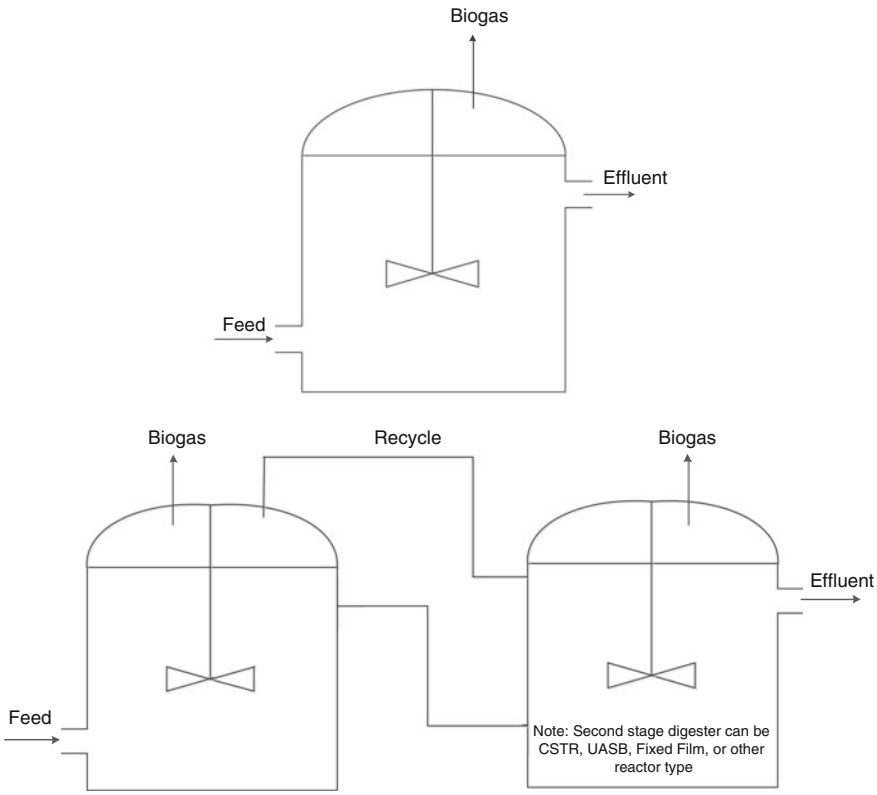

Fig. 6.5 Schematic figure of one-stage CSTR and two-stage wet anaerobic digesters

The other type of digestion is called dry digestion. The solid content in dry digestion systems is between 20 and 40 % (Karthikeyan and Visvanathan 2013). Minority of the crop digestion plants utilizes the crops through dry digestion. For dry digestion of crops, both batch and continuous processes are applied. Batch operations are mainly vertical reactors with or without mixing. During batch process, the feedstock is placed in the reactor followed by the addition of microbes from the inoculum (percolate and or digestate). The gas production starts, reaches the maximum rate then decreases, and finally stops. After the biogas production is stopped or nearly stopped, half/major part of the feedstock is removed and the remainder part acts as inoculum for the next batch. Figure 6.6 shows the schematic set-up of a simple dry batch digestion system

However, gas engine and turbines, there the produced gas is utilized, require relatively stable gas quality and quantity, and the production rate and composition of the gas vary during the batch operation. Therefore, numerous batch digesters coupled in series are used and fed sequentially to be able to produce gas with a stable quality and quantity.

For continuous dry digestion, the vertical and horizontal reactor designs are equally common (Fig. 6.7). The horizontal design has the advantage over the vertical design that the retention time of the feedstock is more controlled, but the construction and operation costs are higher than those for the vertical design, because vertical design always contains mixing devices (Karthikeyan and Visvanathan 2013). During continuous dry digestion, the feedstock is mixed with the digestate to ensure the inoculation, but in many cases, the process water is also recycled.

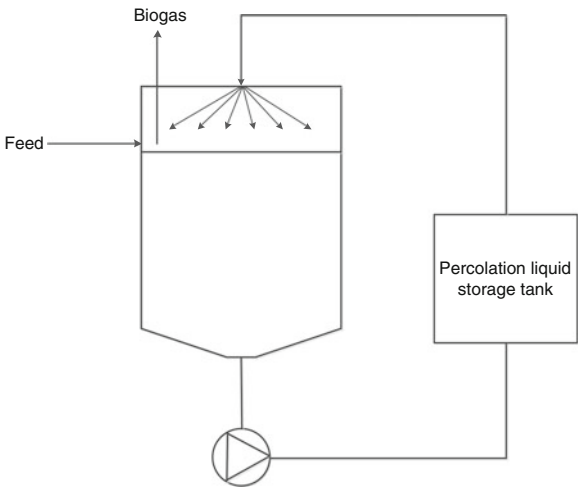

Fig. 6.6 Schematic figure of a dry batch digestion system

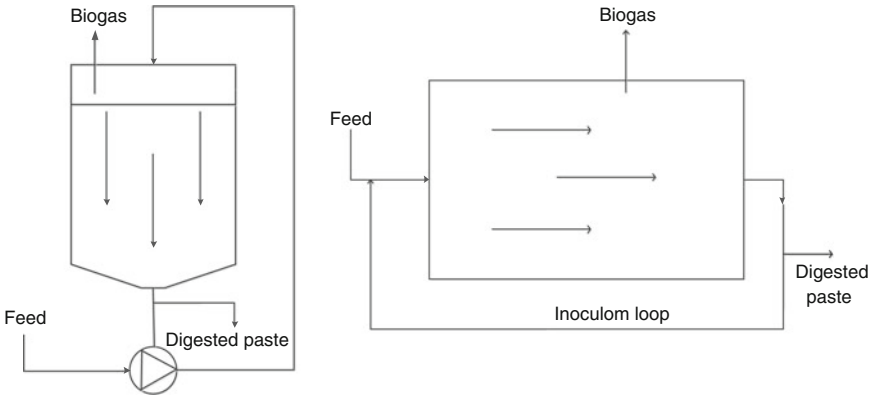

Fig. 6.7 Schematic figure of dry continuous digestion systems

6.6.1.4 Treatment and Usage of Biogas

Biogas collected from digestion can be used directly in a gas boiler for generating heat or burned in a combined heat and power plant (CHP) to produce heat and electricity. Currently, biogas utilization in CHP units dominates in Europe. The produced electricity is usually distributed through the public electricity net. The heat is used to provide energy for the process, and the remaining part can be sold for central and district heating. However, since during the summer, heat is not required in rural areas, an other possibility to utilize the biogas is to upgrade it to biomethane (Ryckebosch et al. 2011). Biomethane can be used as vehicle fuel or injected to the national gas grid. Several existing upgrading techniques are available, including water scrubbing, pressure swing adsorption, chemical absorption as well as cryogenic and membrane separation (De Hullu et al. 2008).

6.6.1.5 Treatment and Usage of the Digestate Residue

The digestate residue is the secondary product of anaerobic digestion. Approximately 80 % of the volume of the feedstock fed to the digester ends up as digestate residue. The solid content of digestate depends on the process, but generally varies between 5 and 30 %. Regardless of the applied process, the digestate residue contains almost the same quantities of macronutrients (nitrogen, potassium, phosphorous), micronutrients (Fe, Ni, Co, etc.), and trace elements as the original feedstock. Therefore, digestate can be used as natural fertilizer that recycles the organic matter and nutrients to the soil. In most cases, digestate can be directly applied to agricultural lands.

6.7 Anaerobic Digestion of Lignocellulosic Residues and Waste

Lignocellulosic residues and waste can be divided into four main groups: agricultural residues (straw), fruit and vegetable waste, forestry residues (woody biomass), and paper waste. These wastes are generated in a huge amount; however, the utilization is not always resolved. Anaerobic digestion is a possible solution, but the methane yield of these kinds of wastes is low and their degradation requires a very long process. Research was focused therefore during the last decades on suitable pretreatment methods that can increase the degradation rate of lignocelluloses, leading to increased methane yields (Yang and Wyman 2008; Taherzadeh and Karimi 2008).

6.7.1 Pretreatment Affecting Anaerobic Digestion of Lignocelluloses

Several pretreatment technologies are available in the literature on lignocellulosic materials. An ideal pretreatment would aim to complete or partial decomposition of the feedstock into fermentable sugars, thus increasing the rate of hydrolysis. The final goal of the pretreatment is to eliminate the resistance of lignin and decrease the crystalline structure of cellulose, and subsequently make the substrate more accessible for the microorganisms in the anaerobic digestion system.

So far numbers of promising pretreatment methods (discussed in detailed in Chap. 3) have been suggested for enhancing the biogas production from lignocellulosic biomass, such as physical, physicochemical, chemical, and biological pretreatments (Taherzadeh and Karimi 2008; Yang and Wyman 2008; Hendriks and Zeeman 2009; Chandra et al. 2007). Milling, among the physical pretreatments, was proven to be effective for increasing the specific surface area, reducing the degree of polymerization (DP), and also causes the shearing, thus improving the hydrolysis yield by 5–25 %. This improvement depends on type of biomass, duration and type of milling (Zeng et al. 2007; Jin and Chen 2006). Additionally, it is repeatedly shown that the smaller particle size of the lignocelluloses results in higher yield in biofuel production (Jin and Chen 2006; Monavari et al. 2009; Teghammar et al. 2012; Lennartsson et al. 2011). That is why the physical pretreatment is often carried out in combination with other pretreatment methods.

According to Hendrik and Zeeman (2009), the pretreatment methods such as steam, lime, liquid-hot-water and ammonia-based steam explosion, thermal hydrolysis, wet oxidation, and ultrasound and radiation are offering potential for improving biogas yield from lignocelluloses (Hashimoto 1986; Fox and Noike 2004). However, methods that result in a very high methane yield, such as steam explosion, wet explosion, and ammonia fiber explosion (AFEX), are energy-intensive pretreatments. Hence, the energy cost of applying these pretreatments is high and the net energy gain of these techniques is required to be clearly evaluated.

Furthermore, using these methods there is also a risk for production of inhibitory products such as furfural, HMF, and soluble phenolic compounds. Although the methane-producing bacteria are capable of adapting to a very low concentration of such compounds, the methane production rate would decrease at the beginning of the digestion (Fox et al. 2003).

Apart from the pretreatment methods, the results of anaerobic digestion are influenced by many different other factors, including inoculum, substrate to inoculum ratio, OLR, and process conditions (Angelidaki et al. 2009). Therefore, distinction between the methane productions of the same substrates, described in the next part of this chapter, do not necessarily show differences between the effects of pretreatments.

6.7.2 The Inhibition Effect of Pretreatment on the Digestion Process

As it was discussed previously, due to the recalcitrant structure and the high lignin content of the lignocellulosic biomass, the rate of anaerobic digestion of these materials is relatively slow. Therefore, pretreatments are performed to increase the rate of degradation and to improve the methane yield. However, in some cases the chemical agent used for pretreatment can act as a potential inhibitor for the microbial community of the anaerobic digestion. It was found that after pretreatment with the organic solvent *N*-methylmorpholine-*N*-oxide, the remaining solvent affected the digestion process negatively even though it was present in as low concentrations as 1 % (Kabir et al. 2013a). Besides, pretreatment might lead to the production of inhibitory products, such as furans in dilute acid and steam explosion pretreatments, furfural from alkaline pretreatments (Ahring et al. 1996; Taherzadeh and Karimi 2008). The problem of inhibitory by-products might be solved after a long hydraulic retention time since the microorganisms may adapt or degrade these by-products after a while, although, the kinetic of the process might be affected.

6.7.3 Anaerobic Digestion of Woody Biomass

Methane yield of woody biomass have been found to be not economically feasible without pretreatment. There are many factors influencing anaerobic digestion of wood, such as low moisture content, high lignin content, cellulose crystallinity, and degree of association between lignin and carbohydrates. Additionally, certain plants produce resin acid extracts for protection from microbial attack and biological damages, which might be inhibitory to the microorganisms carrying out the anaerobic digestion. Therefore, several pretreatment methods have been investigated aiming to improve the biogas production from this group of biomass (Tong et al. 1990; Cowling 1975; Chandler and Jewell 1980; Jerger et al. 1982; Kenney et al. 1990).

Generally, there is an inverse linear relationship between VS reduction and lignin content in anaerobic degradation of woody biomass (Chandler and Jewell 1980). Biodegradability of several woody species was investigated for biogas production by using biomethane potential (BMP) assay. Some of the results found in the literature presenting the methane potential from woody biomass before and after pretreatment are discussed in this section and summarized in Table 6.6.

Salehian et al. (2013) investigated the effect of alkaline pretreatment on pine (softwood) using 8 % NaOH. The pretreatment was performed in different conditions: at two temperatures (0 and 100 °C) in different duration times (10, 30, and 60 min). The results of anaerobic digestion in batch mode showed that while 0.065 m^3/kg VS CH_4 was produced from the untreated pine, methane yield of 0.178 m^3 CH_4/kg VS could be achieved after the most successful pretreatment (8 % NaOH, 10 min and 100 °C). This corresponds to 181 % improvement comparing to that of the untreated assay. Further analyses of pretreated assays with scanning electron microscopic (SEM) and Fourier transform infrared (FTIR) spectroscopy revealed that alkaline conditions at higher temperature resulted in the disintegration of the biomass structure, while the pretreatment at low temperature led to decrease in cellulose crystallinity. Mirahmadi et al. (2010) have also examined the effect of alkaline pretreatment using 7 % w/w NaOH on two different wood species, milled spruce (softwood) and birch (hardwood), at different temperatures ranging between −15 and 100 °C. Batch anaerobic digestion assay was then carried out at thermophilic conditions (55 °C) for 30 days. Treatment of birch at 100 °C led to a methane yield of 0.46 m^3/kg VS, compared to 0.25 m^3/kg VS obtained from untreated birch. The best result for spruce was achieved with NaOH pretreatment at 5 °C, resulting in a 74 % improvement in the methane production compared to that from untreated spruce. Furthermore, it was concluded that there was roughly no destruction of lignin during the pretreatments neither for softwood nor for hardwood. However, applying alkaline treatment to improve the methane production was more successful for hardwood than that for softwood.

The pretreatment of forest residues (mixture of spruce, pine, bark, etc.) using N-methylmorpholine-N-oxide (NMMO) was carried out in another study. The pretreatment with NMMO could effectively decrease the cellulose crystallinity of the wood without leading to a loss in carbohydrates. The best methane yield of the forest residues was achieved using 85 % NMMO for 15 h at 120 °C which corresponds to 85 % of the expected theoretical yield, assuming that only the carbohydrate fraction present in forest residues is utilized for methane production (Kabir et al. 2013a). Similarly, Teghammar et al. (2012) studied the effect of NMMO-pretreatment on spruce (softwood) for biogas production. Pretreatments were carried out at 130 °C for 1–15 h followed by anaerobic batch digestions for six weeks. The NMMO-pretreatment significantly improved the methane yields counting up to improvements between 400 and 1,200 %. The anaerobic digestion of untreated spruce chips (10 mm) and milled (<1 mm) spruce resulted in methane yields of 0.011, 0.066, Nm^3/kg raw material, respectively. Hence, only milling resulted in sixfold improvement in the methane yield. Moreover, increasing the pretreatment time for NMMO treatment led to better results. After the pretreatments

Table 6.6 Methane potential of different woody biomass

Substrate/wood	Pretreatment condition	Digestion condition	Methane yield	Methane yield m^3/kg raw material	References
Untreated wood chips (Eucalyptus globules)	Untreated	Mesophilic	0.014 m^3/kg TS	NA	Nakamura and Mtui (2003)
	Extraction using hot water 125 °C in 20 min		0.124 m^3/kg TS	NA	Nakamura and Mtui (2003)
	Extraction using 1 % NaOH, 125 °C in 20 min		0.134 m^3/kg TS	NA	(Nakamura and Mtui 2003)
	Steam explosion at 25 atm and 3 min		0.194 m^3/kg TS	NA	Nakamura and Mtui (2003)
Japanese cedar chips	Untreated	Mesophilic	0	NA	Take et al. (2006)
	Steam Explosion 4.5 MPa and 258 °C, 5 min		0.180 m^3/kg TS	NA	Take et al. (2006)
	Fungal treatment (*Cyathus stercoreus AW 03*-72)		0.043 m^3/kg TS	NA	Take et al. (2006)
Japanese cedar wood chips	Untreated	Mesophilic	NA	0.002	Amirta et al. (2006)
	Fungal pretreatment *C. subvermispora ATCC 90467* + wheat bran media for 8 weeks		NA	0.0835	Amirta et al. (2006)
	Fungal pretreatment C. subvermispora CBS 347.63 for 8 weeks		NA	0.0265	Amirta et al. (2006)
Japanese beech (Fagus crenata)	Untreated	Thermophilic	0	0	Yoshida et al. (2010)
	Supercritical water treatment at 380 °C and pressure 30 MPa		NA	0.105	Yoshida et al. (2010)
	Supercritical water treatment at 380 °C and pressure 100 MPa		NA	0.068	Yoshida et al. (2010)

(continued)

Table 6.6 (continued)

Substrate/wood	Pretreatment condition	Digestion condition	Methane yield	Methane yield m^3/kg raw material	References
Spruce chips (*Picea abies*)	Untreated (10 mm chips)	Thermophilic	17 ± 69 ml/g CH	0.011	Teghammar et al. (2010)
	6 % spruce in the NMMO solution (85 %), at 130 °C and 1 atm 15 h		202 ± 88 ml/g CH	0.125	Teghammar et al. (2010)
Milled spruce	Untreated (less than 1 mm)		106 ± 80 ml/g CH	0.066	Teghammar et al. (2010)
	6 % spruce in the NMMO solution (85 %), at 130 °C and 1 atm 15 h		395 ± 88 ml/g CH	0.245	Teghammar et al. (2010)
Spruce	Untreated	Thermophilic	0.030 m^3/kg VS	NA	Mirahmadi et al. (2010)
	7 % (w/w) NaOH, at 5 °C, 2 h		0.050 m^3/kg VS	NA	Mirahmadi et al. (2010)
Birch	Untreated	Thermophilic	0.250 m^3/kg VS	NA	Mirahmadi et al. (2010)
	7 % (w/w) NaOH, at 100 °C, 2 h		0.469 m^3/kg VS	NA	Mirahmadi et al. (2010)

for 15 h, methane productions of 0.125 and 0.245 Nm^3 CH_4/kg raw materials were obtained from spruce chips and milled spruce, respectively.

Nakamura and Mtui (2003) applied steam explosion, pretreatment on wood chips (Eucalyptus globules) at pressure of 25 atm and steaming time of 3 min. The obtained methane yield after the steam explosion treatment was 0.194 m^3 CH_4/kg TS, while only 0.014 m^3/kg TS methane was produced from the untreated material. The improvement of the methane yield was due to the high decrease in Klason lignin. Moreover, the pretreatment led to conversion of 80 % of the holocellulose into methane. Similarly, a considerable improvement was observed in a study performed by Take et al. (2006) who applied steam explosion treatment on wood (Japanese cedar chips), prior to biogas production. The pretreatment was performed at 4.51 MPa (258 °C) for 5 min. The pretreated wood yielded to 0.180 m^3/kg TS methane, while the methane yield for untreated wood samples was almost zero.

Biological pretreatment of Japanese cedarwood was carried out by Amirta et al. (2006) prior to anaerobic digestion. Pretreatment was performed using two different strains of white-rot fungi, i.e., *Ceriporiopsis subvermispora*, CBS 347.63 and ATCC 90467. The wood chips were subjected to cultivation of these two strains with and without the addition of wheat bran during 4–8 weeks. The methane production obtained during the subsequent anaerobic digestion of treated Japanese cedar wood enhanced with increased cultivation time of the fungi on the material. The longest pretreatment time, i.e., 8 weeks with *C. subvermispora* ATCC 90467 in the presence of wheat bran led to the highest methane yield of 0.083 m^3/kg raw material, which corresponds to 35 % of the theoretical yield based on the holocellulose content in the decayed wood.

6.7.4 Anaerobic Digestion of Straw

The results of various studies on anaerobic digestion of straw showed that the gas production varied depending on what kind of cereals were being used in anaerobic digestion system. Besides, investigations on straw also reveal that the physical pretreatment such as milling is one of the significant factors for improving the anaerobic digestion yield. Some of the results found in the literature from straw are discussed in this section and summarized in Table 6.7.

Alkaline pretreatment using 96 % lime ($Ca(OH)_2$) containing 3 % $CaCO_3$ was applied on milled oat straw with particle size of 5–15 mm at 55 °C for 24 h. The treated samples were then subjected to anaerobic batch digestion for 35 days resulting in a methane yield of 0.287 m^3/kg VS. Other pretreatment methods applied on the same substrate, such as steam explosion and steam explosion with addition of acid, resulted in lower methane yields of 0.197 and 0.201 m^3/kg VS, respectively, comparing to that obtained after the lime pretreatment (Dererie et al. 2011).

Table 6.7 Methane potential of different kind of straw

Substrate/ Straw	Pretreatment condition	Digestion condition	Methane yield	Methane yield m^3/kg raw material	References
Wheat Straw	Untreated	Mesophilic	0.189 m^3/kg VS	NA	KTBL (2005; Bauer et al. 2009)
Wheat Straw	Milled (0.5–1.0 mm)		0.275 m^3/kg VS	0.235	Bauer et al. (2009)
	Steam explosion 180 °C, 15		0.331 m^3/kg VS	0.283	Bauer et al. (2009)
Oat Straw	Untreated	Mesophilic	No data	No data	Dererie et al. (2011)
	Lime pretreatment		0.287 m^3/kg VS	0.252	Dererie et al. (2011)
	Steam explosion		0.197 m^3/kg VS	0.173	Dererie et al. (2011)
	Acid + steam explosion		0.201 m^3/kg VS	0.1845	Dererie et al. (2011)
Rice Straw	Untreated (3–5 mm particle size)	psychrophilic	0.240 m^3/kg VS	0.214	Lei et al. (2010)
	Phosphate supplementation 155 mg-P/l		0.250 m^3/kg VS	0.223	Lei et al. (2010)
Straw	Untreated	Mesophilic HRT, 28 days	0.165 m^3/kg VS	0.140	Hjorth et al. (2011)
	Extruded straw		0.281 (+70 %) m3/kg VS	0.239	Hjorth et al. (2011)
	Untreated	Mesophilic HRT, 90 days	0.320 m^3/kg VS	0.272	Hjorth et al. (2011)
	Extruded straw		0.355 (+11 %) m^3/kg VS	0.301	Hjorth et al. (2011)
Corn Straw*	Untreated	Mesophilic	0.1537 m^3/kg VS	0.1185	Zhong et al. (2011)
	NaOH 8 % Wt		0.472 m^3/kg VS	0.364	Zhong et al. (2011)
	Ammonia 5 % Wt		0.316 m^3/kg VS	0.2435	Zhong et al. (2011)
	Urea 4 % Wt		0.178 m^3/kg VS	0.137	Zhong et al. (2011)

* The yield for corn straw, represents the total biogas production.

In another study, wheat straw was subjected to steam explosion pretreatment at 180 °C and 15 min [48]. Methane production from the pretreated assay was 0.331 Nm^3/kg VS, while the untreated wheat straw yielded 0.275 Nm^3/kg VS methane. This corresponds to 20 % increase in methane production comparing to that of the untreated substrate. From this study, it was concluded that the longer residence time and higher temperature did not considerably increased the methane yield. The optimum temperature for steam explosion pretreatment was suggested to be between 160 and 200 °C (Panagiotou and Olsson 2007).

Another study investigated biogas production from rice straw after different pretreatments, i.e., mechanical, thermal, and chemical using ammonia in high-rate anaerobic digestion system. The results of this study reveal that the combination of milling to 10 mm particle size, and thermal treatment at 110 °C with addition of 2 % ammonia was the most successful method, which led to about 25 % improvement in biogas production comparing to that of the untreated assay. Biogas obtained from untreated and pretreated assays were 0.38 and 0.47 m^3/kg VS, respectively (Zhang and Zhang 1999).

Zhong et al. (2011) investigated the effect of three different alkaline pretreatment including 8 % NaOH, 5 % ammonia, and 4 % urea on corn straw prior to anaerobic digestion. The pretreatments were carried out at an ambient temperature of (15 ± 2 °C) for 20 days. All the pretreatments caused significant degradation of lignin, hemicellulose, and also cellulose. However, the treatment with 8 % NaOH resulted in the highest methane yield of 0.472 m^3/kg VS, which corresponds to 207 % increase compared to that of the untreated assay.

Teghammar et al. (2012) studied the effect of an organic solvent, i.e., N-methylmorpholine-N-oxide on triticale straw and rice straw aiming to enhance the methane production. The pretreatments were carried out at 130 °C for 1–15 h prior to batch anaerobic digestion assays running at thermophilic conditions for 6 weeks. The digestion of untreated rice straw and triticale straw resulted in methane yields of 0.022 and 0.030 Nm^3/kg raw material, respectively. The NMMO-pretreatment significantly improved the yield of anaerobic digestion leading to methane productions of 0.157 and 0.203 Nm^3 CH_4/kg for the pretreated rice straw and triticale straw, respectively.

6.7.5 Anaerobic Digestion of Paper Waste

Derived from literature the BMP from paper is highly dependent on the type of the paper, i.e., pulp and paper sludge, paper tube residual, the pretreatment method applied and the inoculum used. Generally, the methane yield from untreated paper is found to be between 0.1 and 0.2 m^3/kg VS.

Some of the results found in the literature regarding anaerobic digestion of different fractions of paper wastes are presented in this section and summarized in Table 6.8.

Table 6.8 Methane potential of paper wastes

Substrate/ paper	Pretreatment	Digestion condition	Methane yield	Methane yield ml/g raw material	References
Newsprint	Untreated	Mesophilic	–	No data	Fox et al. (2003)
	Alkaline supercritical water treatment, 190 °C pH = 11		No data	327 ml/g. day	
Newsprint	Untreated	Mesophilic	80 ml/g COD	No data	Clarkson and Xiao (2000)
	NaOH 10 %, 1 day at 25 °C		120 ml/g COD	No data	
Office paper	Untreated	Mesophilic	360 ml/g VS	No data	Xiao and Clarkson (1997)
Paper tube residual	Untreated	Thermophilic	222 Nml/g VS	188	Teghammar et al. (2010)
	Non-exclusive pretreatment 100 ml suspension of 50 g/l dry milled paper + 2 % NaOH at 190 °C for 30 min		269 Nml/g VS	228	Teghammar et al. (2010)
	Steam explosion 3 liter suspension of 50 g/l dry milled + both 2 % NaOH and 2 % H_2O_2 at 220 °C for 10 min		493 Nml/g VS	419	
	Steam explosion 3 liter suspension of 50 g/l dry milled + 2 % NaOH at 220 °C for 30 min		405 Nml/g VS	344	
	Steam explosion 3 liter suspension of 50 g/l dry milled + 2 % NaOH at 220 °C for 10 min		403 Nml/g VS	342.5	
Pulp and paper sludge	Untreated	Mesophilic	190 ml/g VS	36.5	Lin et al. (2009)
	0.6 % NaOH at 37 °C for 6 h		320 ml/g VS	61.5	

Xiao and Clarkson (1997) applied acetic acid and nitric acid reagent targeting the lignin fraction of newsprint waste prior to anaerobic digestion. The results of their investigation showed that even though the pretreatment was carried out using high concentration of acetic acid (80 %) at elevated temperature (boiling water bath), it could not successfully dissolve lignin. On the other hand, 80 % lignin removal from newsprint residues was observed when using 35 % acetic acid together with the addition of 2 % nitric acid. These treatment conditions increased the methane production from 0.100 m^3/kg VS (obtained from untreated) to 0.270 m^3/kg VS as it was observed during the subsequent anaerobic digestion tests.

In another study, newsprints were subjected to alkaline pretreatment using 10 % NaOH which significantly improved the biodegradability of the substrate. The NaOH pretreatment was also performed with increased concentrations of 15 and 20 %; however, no significant differences in terms of methane production were observed. Newsprint undergone alkaline pretreatment with 10 % NaOH resulted in 0.120 m^3/kg COD methane production, while 0.08 m^3/kg COD methane was obtained from the untreated assay (Clarkson and Xiao 2000). Similarly, the alkaline pretreatment of pulp and paper sludge using NaOH (8 g NaOH /100 g TS sludge), resulted in 184 % increase in methane yield (0.32 m^3CH_4/kg VS pretreated sludge) compared to that from the untreated paper sludge (Lin et al. 2009).

Paper tube residuals were used as a substrate for biogas production in a study by Teghammar et al. (2010). Steam explosion treatment was applied with the addition of sodium hydroxide and/or hydrogen peroxide to improve the biogas production. The untreated assay resulted in 0.238 Nm^3/kg VS methane. While, using steam explosion at 220 °C for 10 min and with addition of both 2 % NaOH and 2 % H_2O_2, the methane production was enhanced by 107 %, i.e., 0.493 Nm^3/kg VS methane was obtained.

Wet oxidation was also investigated to enhance methane production from newspaper waste. Pretreatments were carried out at 170, 190, and 210 °C, with a retention time of 1 h. The highest lignin removal was achieved at 190 °C in which about 65 % was isolated. Furthermore, the batch anaerobic digestion tests showed that the highest methane yield could be achieved after pretreatment at 190 °C, which converted 59 % of the initial total COD to methane (Fox and Noike 2004).

6.8 Co-digestion

Simultaneous digestion of homogenous mixture of two or more substrates is called co-digestion. Recently, co-digestion has taken much attention since it is one of the interesting ways of improving the yield of anaerobic digestion. The co-digestion causes improvement in yield of anaerobic digestion due to its positive synergisms established in the digestion medium and supplying the missing nutrients and sometimes by addition of suitable moisture contents required in the digester (Mata-Alvarez et al. 2000).

As mentioned earlier in this chapter, C/N ratio of the feedstock has an important role for a well-balanced digestion system. According to the literature, the optimum level of the C/N ratio is between 20 and 30 (Sreekrishnan et al. 2004; Liu and Whitman 2008). But this is only an approximate suggestion, since in the case of lignocellulosic biomass the nitrogen can be also bound in lignin structure (Deublein and Steinhauser 2008a). The C/N ratio of the lignocellulosic substrates is too high therefore; mixing it with high nitrogen content substrates can be beneficial to acquire optimal nutritional conditions. For instance, the co-digestion of manure and plant materials provides a better nutritional balance in AD system, which reduces the risk for inhibition. The manure fraction supply a wide range of nutrients, and the addition of plant materials with high carbon content would balance the C/N ratio of the feedstock (Lehtomäki et al. 2007).

The viability of co-digestion of two or more organic waste streams (e.g., organic fraction of municipal solid waste (OFMSW), sewage sludge or biosolids, animal waste, and agricultural solid waste) has been investigated at both laboratory-scale (Rivard et al. 1990; Zhang et al. 2013; Pagés-Díaz et al. 2014) and full-scale level (Cecchi et al. 1988).

Lehtomäki et al. (2007) investigated anaerobic co-digestion of grass silage, sugar beet, and oat straw together with manure in semi-continuously fed CSTRs. The results showed that co-digestion of manure with 40 % VS loading coming from the crop feedstock was advantageous to improve the yield of methane production. The methane yield obtained from manure was 0.155 dm^3 CH_4/kg VS, while co-digestion of manure with grass, sugar beet tops, and straw resulted in 268, 229, and 213 dm^3 CH_4/kg VS, respectively.

In another study, different mixture ratios of straw and manure were subjected for anaerobic co-digestion. The digestions were performed in bath reactors for 28 days at mesophilic conditions (35 °C). The results of this investigation revealed that co-digestion of manure and straw with a mixing ratio of 1:1 (VS) led to significant decrease in methane yield (0.182 m^3 CH_4/kg VS) production compared to the methane production of only manure, which was 0.234 m^3/kg VS (Demirbas 2006).

Müller and Trösch (1986) examined the effects of biological treatment on a mixture of straw and manure on anaerobic digestion. Batch digestion assays were carried out with loading of 40 g/L solids in mesophilic digesters. The results showed that pre-treated straw/manure mixture using *Pleurotus florida* pretreatment in 60 and 90 days showed higher methane yields, i.e., 0.318 and 0.343 dm^3/g raw material, respectively, while the biogas yield from untreated straw/manure was 0.293 dm^3/g raw material.

6.9 Anaerobic Digestion Versus Thermochemical Biofuel Production

Thermochemical processes are the other alternatives to biochemical methods for converting lignocellulosic materials into energy (Verma et al. 2012; McKendry 2002) Thermochemical conversion technologies have certain advantages and

drawbacks over biochemical conversion technologies. This section briefly describes the main thermochemical processes including combustion, pyrolysis, and gasification and compares to the anaerobic digestion process.

6.9.1 Thermochemical Conversions

6.9.1.1 Combustion

During the combustion of lignocellulosic biomass, heat is produced by chemical reaction, where carbon, hydrogen, oxygen, combustible sulfur, and nitrogen contained in biomass react with air or oxygen (Demirbas 2004). Currently, combustion is the most common technology converting biomass to usable heat energy is through straightforward combustion, and it accounts for around 90 % of all energy attained from biomass (Bhaskar et al. 2011). Combustion of lignocellulosic material consists of five main steps: drying, pyrolysis, gasification, char combustion, and gas-phase oxidation (Nussbaumer 2003). During the drying, the biomass first loses its moisture at temperatures up to 100 °C. Followed by pyrolysis and gasification steps, where the solid biomass chemically converted into fuel gases, volatile liquids, and a carbon-rich solid residue called char (Bhaskar et al. 2011). After all volatiles are removed, char combustion stage starts producing the fuel gases including hydrogen and carbon monoxide. Finally, in the gas-phase oxidation, the produced gases burn with oxygen from the air producing water vapor and carbon dioxide. It is worth to mention that only burning of the fuel gases generates heat, and solids and liquids do not burn themselves, but consume heat and energy during the beginning of the process. Currently, combustion is widely used on various scales to convert biomass into bioenergy; however, its efficiencies are the lowest among thermochemical processes (McKendry 2002; Demirbaş 2001).

6.9.1.2 Gasification

Gasification is an environmental-friendly way to produce energy from lignocellulose. The gasification conversion is taken place at temperatures of 500–1,300 °C in an oxygen-deprived environment (Goyal et al. 2008). The result of the gasification process is an energy-rich combustible gas mixture called producer gas which mainly consists of H_2, CO, and CH_4; however, it also contains impurities such as nitrogen, CO_2, sulfur, alkali compounds, and tars (Damartzis and Zabaniotou 2011). Tar is a complex mixture of hydrocarbons, which can condensate and form tar aerosols and polymers causing problems in the process equipment as well as it damages engines and turbines (Meng et al. 2011; Chiang et al. 2013). Temperature has a significant role in the destruction and reforming of tar and it influences the gas yield (Kumar et al. 2009; Narvaez et al. 1996; González et al. 2008; Gupta and Cichonski 2007). Among all thermochemical processes, gasification is one of the

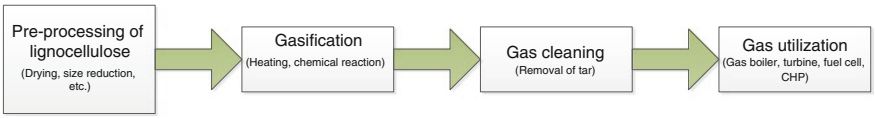

Fig. 6.8 Schematic figure of gasification of lignocellulosic biomass

promising, since the conversion efficiency is relatively high. Lignocellulosic biomass has an especially low sulfur content which is a major advantage when SO_2 emission is taken into account (Basu 2013). The main steps involved in the gasification process of lignocellulosic biomass are shown in Fig. 6.8.

6.9.1.3 Pyrolysis

Pyrolysis is the third basic thermochemical process for converting biomass to a more useful fuel. In respect of combustion and gasification during pyrolysis, biomass is heated in the absence of oxygen or with such a limited oxygen supply that gasification does not occur to an appreciable extent. The results of the pyrolysis are hydrocarbon-rich gas mixture, an oil-like liquid, and a carbon-rich solid residue. Usually, pyrolysis is optimized prior to maximize the liquid fuel yield. Fuel type, temperature, pressure, and heating rate affect the quality and quantity of the formed products. In the case of pyrolysis of lignocellulosic biomass, a considerable amount of carbon monoxide and carbon dioxide is formed due to the high oxygen content of the fuel. Fast pyrolysis conducted at temperatures between 400 and 550 °C and lasted for 0.5–3 s with small biomass particle size (up to 2 mm) results in high liquid production (Meier and Faix 1999). Pyrolysis at lower temperatures (250–350 °C) with long residence time (few minutes to hours) and larger particle size favors the production of solid char (Kersten and Garcia-Perez 2013; Verma et al. 2012). Among lignocellulosic materials forest residue, sawdust and straw are the most common feedstocks (Mohan et al. 2006). Pyrolysis produces energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion; however, because of some problems related to the conversion process and poor thermal stability and corrosively of the products, pyrolysis technology is currently still at pilot stage (Verma et al. 2012).

6.9.2 Comparison of Anaerobic Digestion and Thermochemical Conversion Processes

As it mentioned in the previous sections, the main products of AD process are biogas and digestate. Typically, the biogas used for generation of heat and electricity or it is upgraded to biomethane and used as a biofuel in the public transportation sector or

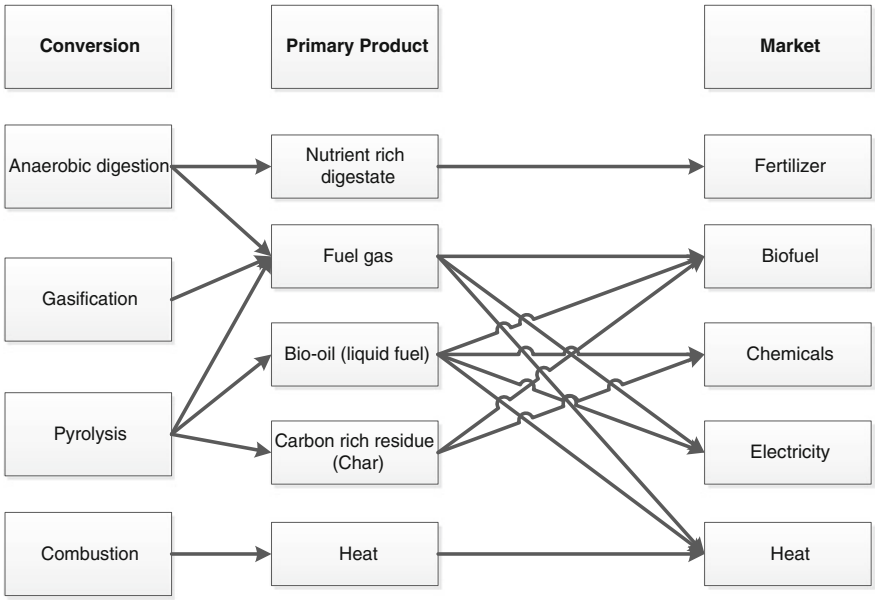

Fig. 6.9 Main conversion processes applied on lignocellulosic biomass together with their primary products and market

injected to the national gas grid, while the digestate is applied on farms as fertilizer (Kabir et al. 2013b; Forgács et al. 2014). Thermochemical conversion has multiple products including gases, liquids, and solids, which can be converted to a variety of fuels (H_2, Fischer-Tropsch (FT) diesels, and synthetic gasoline) and chemicals (methanol, urea). Figure 6.9 summarizes the main conversion processes applied on lignocellulosic materials including their primary products and market.

Anaerobic digestion of lignocellulosic biomass is a completely sustainable waste management technology which beside the production of biogas can considerably reduces the GHGs emission. It also allows almost complete nutrient and water recovery through the application of the digestate as fertilizer. However, the process efficiency greatly depends on the type of the lignocellulose, and in many cases, pretreatment is needed to improve the productivity. In contrast, thermochemical conversion can be effectively applied on any types of lignocellosic biomass, and generally it has a higher productivity due to the nature of the chemical reaction and the fact that it completely utilizes the lignocellulose except its inorganic fraction (ash). The major drawbacks are the high cost associated with cleaning of the product gas from the unwanted chemicals such as tar and alkali compounds and the inefficiency of the process due to the application of elevated temperature. Table 6.9 compares anaerobic digestion process with combustion, gasification, and pyrolysis.

Table 6.9 Comparison of AD process with combustion, gasification, and pyrolysis

	Anaerobic digestion	Combustion	Gasification	Pyrolysis
Technology status	Commercial	Commercial	Commercial	Demonstration
Preprocessing step	Not essential, but can help	Not essential	Necessary	Necessary
Temperature (°C)	Low 35–55	Very high 700–1,400	Very high 500–1,300	High 380–550
Sustainable	Yes carbon neutral	No fertilizer loss	No fertilizer loss	No fertilizer loss
Environmental impact	Positive GHGs mitigation	Negative toxic ash	Neutral pollutants locked in slag	Negative toxic ash
Energy recovery	Depends on the type of lignocellulose	High energy loss	High energy loss	High energy loss
Water recovery (%)	100	0	0	0
Nutrient recovery	All nutrients recovery possible	Some P and K N loss	Some P and K N loss	Some P and K N loss

6.10 Concluding Notes

Anaerobic digestion is an effective biological process for treating a broad range of biodegradable feedstocks for biogas production. However, the efficiency of the entire process is greatly dependent on the type of feedstock. For instance, digestion of manure is easier than digestion of other lignocellulosic biomass, such as wood and straw. Lignocelluloses are the building blocks of all plants with high carbohydrate content. Their worldwide availability makes them an attractive feedstock for biogas production. However, the arrangements of the components of lignocelluloses, i.e., cellulose, hemicellulose, and lignin, have a profound effect on lignocellulose tertiary structure. These complex associations create physical and chemical hindrances to lignocellulose biodegradation in natural and man-made environments.

Therefore, to achieve a stable and cost-efficient methane production from lignocelluloses, the following developments can be pursued:

1. Adjustment of the carbon/nitrogen ratio with co-digestion with other nitrogen-rich substrate
2. Addition of macronutrients and other trace metals
3. Integration of effective pretreatments on the feedstock prior to anaerobic digestion

Even though there have been so many studies available on investigations of the biodegradability of lignocelluloses for biogas production, more detailed research is needed in the future to emphasize on the following:

- Development of new and cost-effective pretreatments that are suitable for AD processes
- Collection of techno-economic data for AD systems that adopt biomass pretreatment processes
- Combination of AD with other biofuel processes such as bioethanol, biohydrogen, or biobutanol to obtain a more energy-efficient biorefinery process.

References

Aardenne Jv, Fernandez R (2010) Mitigating climate change, in The European Environment state and outlook. European Environment Agency, Copenhagen

Abbasi T, Abbasi SA (2010) Production of clean energy by anaerobic digestion of phytomass—new prospects for a global warming amelioration technology. Renew Sustain Energy Rev 14 (6):1653–1659

Ahn JH, Forster CF (2002) The effect of temperature variations on the performance of mesophilic and thermophilic anaerobic filters treating a simulated papermill wastewater. Process Biochem 37(6):589–594

Ahring BK, Jensen K, Nielsen P et al (1996) Pretreatment of wheat straw and conversion of xylose and xylan to ethanol by thermophilic anaerobic bacteria. Bioresour Technol 58(2):107–113

Alvarez R, Villca S, Liden G (2006) Biogas production from llama and cow manure at high altitude. Biomass Bioenerg 30(1):66–75

Amigun B, Sigamoney R, Von Blottnitz H (2008) Commercialisation of biofuel industry in Africa: a review. Renew Sustain Energy Rev 12(3):690–711

Amirta R, Tanabe T, Watanabe T et al (2006) Methane fermentation of Japanese cedar wood pretreated with a white rot fungus, Ceriporiopsis subvermispora. J Biotechnol 123(1):71–77

Amon T, Amon B, Kryvoruchko V et al (2007) Methane production through anaerobic digestion of various energy crops grown in sustainable crop rotations. Bioresour Technol 98(17):3204–3212

Angelidaki I, Alves MM, Bolzonella D et al (2009) Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays. Water Sci Technol 59(5):927–934

Angelidaki I, Ellegaard L, Ahring BK (2003) Applications of the anaerobic digestion process. In: Ahring BK (ed) Biomethanation II. Springer, New York, pp 1–33

Appels L, Baeyens J, Degrève J et al (2008) Principles and potential of the anaerobic digestion of waste-activated sludge. Prog Energy Combust Sci 34(6):755–781

Banks CJ, Humphreys PN (1998) The anaerobic treatment of a lignocellulosic substrate offering little natural pH buffering capacity. Water Sci Technol 38(4/5):29

Basu P (2013) Biomass gasification, pyrolysis and torrefaction: practical design and theory. Academic press, London

Batstone DJ, Keller J, Angelidaki I et al (2002) The IWA Anaerobic Digestion Model No 1 (ADM 1). Water Sci Technol 45(10):65–73

Bauer A, Bösch P, Friedl A et al (2009) Analysis of methane potentials of steam-exploded wheat straw and estimation of energy yields of combined ethanol and methane production. J Biotechnol 142(1):50–55

Bayer EA, Henrissat B, Lamed R (2008) The cellulosome: a natural bacterial strategy to combat biomass recalcitrance Biomass Recalcitrance: Deconstructing Plant Cell Wall Bioenergy:407–435

Bhaskar T, Bhavya B, Singh R et al (2011) Thermochemical conversion of biomass to biofuels. In: Pandey A, Larroche C, Ricke SC (eds) biofuels. Academic Press, Burlington, pp 51–77

Björnsson L, Mattiasson B, Henrysson T (1997) Effects of support material on the pattern of volatile fatty acid accumulation at overload in anaerobic digestion of semi-solid waste. Appl Microbiol Biotechnol 47(6):640–644

Blanchard PH (1992) Technology of corn wet milling and associated processes. Elsevier, Amsterdam

Bohn I, Björnsson L, Mattiasson B (2007) The energy balance in farm scale anaerobic digestion of crop residues at 11–37 C. Process Biochem 42(1):57–64

Borneman WS, Hartley RD, Morrison WH et al (1990) Feruloyl and p-coumaroyl esterase from anaerobic fungi in relation to plant cell wall degradation. Appl Microbiol Biotechnol 33 (3):345–351

Bouallagui H, Torrijos M, Godon JJ et al (2004) Two-phases anaerobic digestion of fruit and vegetable wastes: bioreactors performance. Biochem Eng J 21(2):193–197

Braun R (2007) Anaerobic digestion: a multi-faceted process for energy, environmental management and rural development. In: Ranalli P (ed) Improvement of crop plants for industrial end uses. Springer, New York, pp 335–416

Braun R, Huber P, Meyrath J (1981) Ammonia toxicity in liquid piggery manure digestion. Biotechnol Lett 3(4):159–164

Braun R, Weiland P, Wellinger A (2008) Biogas from energy crop digestion. Task 37. IEA Bioenergy

Bruni E (2010) Improved anaerobic digestion of energy crops and agricultural residues. Dissertation, Technical University of Denmark

Bruni E, Jensen AP, Angelidaki I (2010) Steam treatment of digested biofibers for increasing biogas production. Bioresour Technol 101(19):7668–7671

Bryant MP (1979) Microbial methane production—theoretical aspects. J Anim Sci 48(1):193–201

Börjesson P, Mattiasson B (2008) Biogas as a resource-efficient vehicle fuel. Trends Biotechnol 26 (1):7–13

Cecchi F, Traverso PG, Mata-Alvarez J et al (1988) State of the art of R&D in the anaerobic digestion process of municipal solid waste in Europe. Biomass 16(4):257–284

Chae KJ, Jang A, Yim SK et al (2008) The effects of digestion temperature and temperature shock on the biogas yields from the mesophilic anaerobic digestion of swine manure. Bioresour Technol 99(1):1–6

Chandler JA, Jewell WJ (1980) Predicting methane fermentation biodegradability: final report. Dissertation, Cornell University

Chandra R, Takeuchi H, Hasegawa T (2012) Methane production from lignocellulosic agricultural crop wastes: a review in context to second generation of biofuel production. Renew Sustain Energy Rev 16(3):1462–1476

Chandra RP, Bura R, Mabee WE et al (2007) Substrate pretreatment: the key to effective enzymatic hydrolysis of lignocellulosics? In: Olsson L (ed) Biofuels. Springer, Berlin, pp 67–93

Chaudhary BK (2008) Dry continuous anaerobic digestion of municipal solid waste in thermophilic conditions. Asian Institute of Technology, Bangkok

Chen Y, Cheng JJ, Creamer KS (2008) Inhibition of anaerobic digestion process: a review. Bioresour Technol 99(10):4044–4064

Cheng JJ, Timilsina GR (2011) Status and barriers of advanced biofuel technologies: A review. Renew Energy 36(12):3541–3549

Chiang K-Y, Lu C-H, Lin M-H et al (2013) Reducing tar yield in gasification of paper-reject sludge by using a hot-gas cleaning system. Energy 50:47–53

Cirne DG, Lehtomäki A, Björnsson L et al (2007) Hydrolysis and microbial community analyses in two-stage anaerobic digestion of energy crops. J Appl Microbiol 103(3):516–527

Claassen PAM, Van Lier JB, Contreras AML et al (1999) Utilisation of biomass for the supply of energy carriers. Appl Microbiol Biotechnol 52(6):741–755

Clarkson WW, Xiao X (2000) Bench-scale anaerobic bioconversion of newsprint and office paper. Water Sci Technol 41(3):93–100

Coelho NMG, Droste RL, Kennedy KJ (2011) Evaluation of continuous mesophilic, thermophilic and temperature phased anaerobic digestion of microwaved activated sludge. Water Res 45 (9):2822–2834
Collins G, McHugh S, Connaughton S et al (2006) New low-temperature applications of anaerobic wastewater treatment. J Environ Sci Health Part A 41(5):881–895
Cowling EB (1975) Physical and chemical constraints in the hydrolysis of cellulose and lignocellulosic materials. In: Biotechnology and Bioengineering Symposium, p 163
Dague RR (1968) Application of digestion theory to digester control. J (Water Pollut Control Fed):2021–2032
Dalla Marta A, Natali F, Mancini M et al (2011) Energy and water use related to the cultivation of energy crops: a case study in the Tuscany region. Ecol Soc 16(2):2
Damartzis T, Zabaniotou A (2011) Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review. Renew Sustain Energy Rev 15(1):366–378
De Hullu J, Maassen JIW, Van Meel PA et al (2008) Comparing different biogas upgrading techniques. Eindhoven University of Technology, The Netherlands
Demirbas A (2004) Combustion characteristics of different biomass fuels. Prog Energy Combust Sci 30(2):219–230
Demirbas A (2006) Biogas Potential of Manure and Straw Mixtures. Energy Sources Part A Recovery, Utilization, Environ Eff 28(1):71–78
Demirbaş A (2001) Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energy Convers Manage 42(11):1357–1378
Demirer GN, Chen S (2005) Two-phase anaerobic digestion of unscreened dairy manure. Process Biochem 40(11):3542–3549
Dererie DY, Trobro S, Momeni MH et al (2011) Improved bio-energy yields via sequential ethanol fermentation and biogas digestion of steam exploded oat straw. Bioresour Technol 102 (6):4449–4455
Deublein D, Steinhauser A (2008a) Biogas from waste and renewable resources: an introduction. Wiley-VCH Verlag GmbH & Co, Mörlenbach
Deublein D, Steinhauser A (2008b) Energy Supply in the Future-Scenarios. In: Deublein D, Steinhauser A (eds) Biogas from Waste and Renewable Resources. Wiley-VCH Verlag GmbH & Co, Mörlenbach, pp 7–10
Deublein D, Steinhauser A (2008c) History and status to date in other countries. In: Deublein D, Steinhauser A (eds) Biogas from waste and renewable resources. Wiley-VCH Verlag GmbH & Co, Mörlenbach, pp 35–42
Dohanyos M, Kosova B, Zabranska J et al (1985) Production and utilization of volatile fatty acids in various types of anaerobic reactors. Water Sci Technol 17(1):191–205
Doi RH, Kosugi A (2004) Cellulosomes: plant-cell-wall-degrading enzyme complexes. Nat Rev Microbiol 2(7):541–551
Dolan T, Cook MB, Angus AJ (2011) Financial appraisal of wet mesophilic AD technology as a renewable energy and waste management technology. Sci Total Environ 409(13):2460–2466
Driehuis F, Elferink S, Spoelstra SF (1999) Anaerobic lactic acid degradation during ensilage of whole crop maize inoculated with Lactobacillus buchneri inhibits yeast growth and improves aerobic stability. J Appl Microbiol 87(4):583–594
Duran M, Speece RE (1997) Temperature-staged anaerobic processes. Environ Technol 18 (7):747–753
Fernandes TV, Klaasse Bos GJ, Zeeman G et al (2009) Effects of thermo-chemical pre-treatment on anaerobic biodegradability and hydrolysis of lignocellulosic biomass. Bioresour Technol 100 (9):2575–2579
Ferry JG (1993) Methanogenesis: ecology, physiology, biochemistry & genetics. Springer, Berlin
Flint HJ (2008) Cellulase systems of anaerobic microorganisms from the rumen and large intestine. Biomass Recalcitrance: Deconstructing Plant Cell Wall for Bioenergy:393–406
Forgács G (2012) Biogas production from citrus wastes and chicken feather: pretreatment and co-digestion. Dissertation, Chalmers University of Technology

Forgács G, Niklasson C, Sárvári Horváth I et al (2014) Methane production from feather waste pretreated with Ca (OH) 2: process development and economical analysis. Waste Biomass Valorization 5(1):65–73
Foston M, Ragauskas AJ (2010) Changes in the structure of the cellulose fiber wall during dilute acid pretreatment in Populus studied by 1H and 2H NMR. Energy Fuels 24(10):5677–5685
Fox M, Noike T (2004) Wet oxidation pretreatment for the increase in anaerobic biodegradability of newspaper waste. Bioresour Technol 91(3):273–281
Fox MH, Noike T, Ohki T (2003) Alkaline subcritical-water treatment and alkaline heat treatment for the increase in biodegradability of newsprint waste. Water Sci Technol 48(4):77–84
Frigon JC, Guiot SR (2010) Biomethane production from starch and lignocellulosic crops: a comparative review. Biofuels Bioprod Biorefin 4(4):447–458
Gerardi MH (2003) The microbiology of anaerobic digesters. Wiley, New Jersey
Giuliano A, Bolzonella D, Pavan P et al (2013) Co-digestion of livestock effluents, energy crops and agro-waste: feeding and process optimization in mesophilic and thermophilic conditions. Bioresour Technol 128:612–618
Golush TV (2008) Waste management research trends. Nova Publishers
González JF, Román S, Bragado D et al (2008) Investigation on the reactions influencing biomass air and air/steam gasification for hydrogen production. Fuel Process Technol 89(8):764–772
Goyal HB, Seal D, Saxena RC (2008) Bio-fuels from thermochemical conversion of renewable resources: a review. Renew Sustain Energy Rev 12(2):504–517
Grethlein HE, Converse AO (1991) Common aspects of acid prehydrolysis and steam explosion for pretreating wood. Bioresour Technol 36(1):77–82
Gunnerson CG, Stuckey DC, Greeley M et al (1986) Anaerobic digestion: principles and practices for biogas systems, vol 49. World Bank
Gupta AK, Cichonski W (2007) Ultra-high temperature steam gasification of biomass and solid wastes. Environ Eng Sci 24(8):1179–1189
Hashimoto AG (1986) Pretreatment of wheat straw for fermentation to methane. Biotechnol Bioeng 28(12):1857–1866
Haug RT (1993) The practical handbook of compost engineering. CRC Press, Boca Raton
Hendriks ATWM, Zeeman G (2009) Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour Technol 100(1):10–18
Herrmann C, Heiermann M, Idler C (2011) Effects of ensiling, silage additives and storage period on methane formation of biogas crops. Bioresour Technol 102(8):5153–5161
Hesselgren F, Hellström D, Nordberg Å (2005) Anaerob behandling av hushållsavloppsvatten vid låga temperaturer. JTI-rapport Kretslopp och avfall (35)
Himmel ME (2009) Biomass recalcitrance: deconstructing the plant cell wall for bioenergy. Wiley, New York
Hjorth M, Gränitz K, Adamsen APS et al (2011) Extrusion as a pretreatment to increase biogas production. Bioresour Technol 102(8):4989–4994
Hobson PN, Bousfield S, Summers R (1981) Methane production from agricultural and domestic wastes. Methane production from agricultural and domestic wastes
Hwu C-S, Lettinga G (1997) Acute toxicity of oleate to acetate-utilizing methanogens in mesophilic and thermophilic anaerobic sludges. Enzyme Microb Technol 21(4):297–301
IEA BIoenergy (2013) Key world energy statistics. Paris
IEA Bioenergy (2014) Biogas Country Overview (Country Reports) Task 37
Ince O (1998) Performance of a two-phase anaerobic digestion system when treating dairy wastewater. Water Res 32(9):2707–2713
Jagadabhi PS (2011) Methods to enhance hydrolysis during one and two-stage anaerobic digestion of energy crops and crop residues
Jain SR, Mattiasson B (1998) Acclimatization of methanogenic consortia for low pH biomethanation process. Biotechnol Lett 20(8):771–775
Jerger DE, Dolenc DA, Chynoweth DP (1982) Bioconversion of woody biomass as a renewable source of energy. Institute of Gas Technology, Chicago

Jiang X, Sommer SG, Christensen KV (2011) A review of the biogas industry in China. Energy Policy 39(10):6073–6081
Jin S, Chen H (2006) Superfine grinding of steam-exploded rice straw and its enzymatic hydrolysis. Biochem Eng J 30(3):225–230
Kabir MM, del Pilar Castillo M, Taherzadeh MJ et al (2013) Enhanced methane production from forest residues by N-methylmorpholine-N-oxide (NMMO) pretreatment. BioResources 8 (4):5409–5423
Kabir MM, Niklasson C, Taherzadeh MJ, Sárvári Horváth I (2014) Biogas production from lignocelluloses by N-methylmorpholine-N-oxide (NMMO) pretreatment: Effects of recovery and reuse of NMMO. Bioresour Technol 161(0):446–450
Kanokwan B (2006) Online monitoring and control of the biogas process. Dissertation, Technical University of Denmark
Karthikeyan OP, Visvanathan C (2013) Bio-energy recovery from high-solid organic substrates by dry anaerobic bio-conversion processes: a review. Rev Environ Sci Bio/Technol 12(3):257–284
Kashyap DR, Dadhich KS, Sharma SK (2003) Biomethanation under psychrophilic conditions: a review. Bioresour Technol 87(2):147–153
Kayhanian M (1995) Biodegradability of the organic fraction of municipal solid waste in a high-solids anaerobic digester. Waste Manage Res 13(2):123–136
Kenney WA, Sennerby-Forsse L, Layton P (1990) A review of biomass quality research relevant to the use of poplar and willow for energy conversion. Biomass 21(3):163–188
Kersten S, Garcia-Perez M (2013) Recent developments in fast pyrolysis of ligno-cellulosic materials. Curr Opin Biotechnol 24(3):414–420
Klass DL (1984) Methane from anaerobic fermentation. Science 223(4640):1021–1028
Koçar G, Civaş N (2013) An overview of biofuels from energy crops: Current status and future prospects. Renew Sustain Energy Rev 28:900–916
KTBL (2005) Faustzahlen für die Landwirtschaft. Kuratorium für Bauwesen in der Landwirtschaft e.V, Darmstadt
Kuhad RC, Singh A, Eriksson K-EL (1997) Microorganisms and enzymes involved in the degradation of plant fiber cell walls. In: Biotechnology in the pulp and paper industry. Springer, New York, p 45–125
Kumar A, Jones DD, Hanna MA (2009) Thermochemical biomass gasification: a review of the current status of the technology. Energies 2(3):556–581
Lehtomäki A (2006) Biogas production from energy crops and crop residues. University of Jyväskylä
Lehtomäki A, Huttunen S, Rintala JA (2007) Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: effect of crop to manure ratio. Resour Conserv Recycl 51(3):591–609. doi:10.1016/j.resconrec.2006.11.004
Lei Z, Chen J, Zhang Z et al (2010) Methane production from rice straw with acclimated anaerobic sludge: effect of phosphate supplementation. Bioresour Technol 101(12):4343–4348
Lennartsson PR, Niklasson C, Taherzadeh MJ (2011) A pilot study on lignocelluloses to ethanol and fish feed using NMMO pretreatment and cultivation with zygomycetes in an air-lift reactor. Bioresour Technol 102(6):4425–4432
Leonowicz A, Matuszewska A, Luterek J et al (1999) Biodegradation of lignin by white rot fungi. Fungal Genet Biol 27(2):175–185
Lettinga G (2005) The anaerobic treatment approach towards a more sustainable and robust environmental protection. Water Sci Technol 52(1–2):1–11
Levén L, Eriksson ARB, Schnürer A (2007) Effect of process temperature on bacterial and archaeal communities in two methanogenic bioreactors treating organic household waste. FEMS Microbiol Ecol 59(3):683–693
Lier JBv (1995) Thermophilic anaerobic wastewater treatment, temperature aspects and process stability. Ph D Thesis, Department of Environmental Technology, Wageningen University, The Netherlands
Lin Y, Wang D, Wu S et al (2009) Alkali pretreatment enhances biogas production in the anaerobic digestion of pulp and paper sludge. J Hazard Mater 170(1):366–373

Liu Y, Whitman WB (2008) Metabolic, phylogenetic, and ecological diversity of the methanogenic archaea. Ann N Y Acad Sci 1125(1):171–189
Malherbe S, Cloete TE (2002) Lignocellulose biodegradation: Fundamentals and applications. Rev Environ Sci Biotechnol 1(2):105–114
Mansfield SD, Mooney C, Saddler JN (1999) Substrate and enzyme characteristics that limit cellulose hydrolysis. Biotechnol Prog 15(5):804–816
Mara D, Horan NJ (2003) Handbook of water and wastewater microbiology. Academic press, New York
Mata-Alvarez J, Mace S, Llabres P (2000) Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. Bioresour Technol 74(1):3–16
McKendry P (2002) Energy production from biomass (part 2): conversion technologies. Bioresour Technol 83(1):47–54
Meier D, Faix O (1999) State of the art of applied fast pyrolysis of lignocellulosic materials—a review. Bioresour Technol 68(1):71–77
Meng X, de Jong W, Fu N et al (2011) Biomass gasification in a 100 kWth steam-oxygen blown circulating fluidized bed gasifier: Effects of operational conditions on product gas distribution and tar formation. Biomass Bioenerg 35(7):2910–2924
Meng X, Foston M, Leisen J et al (2013) Determination of porosity of lignocellulosic biomass before and after pretreatment by using Simons' stain and NMR techniques. Bioresour Technol 144:467–476
Mesbah NM, Wiegel J (2008) Life at Extreme Limits. Ann N Y Acad Sci 1125(1):44–57
Mirahmadi K, Kabir MM, Jeihanipour A et al (2010) Alkaline pretreatment of spruce and birch to improve bioethanol and biogas production. BioResources 5(2):928–938
Mittal KM (1996) Biogas systems: principles and applications. New Age International Limited Publishers, New Delhi
Mohan D, Pittman CU, Steele PH (2006) Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 20(3):848–889
Monavari S, Galbe M, Zacchi G (2009) Impact of impregnation time and chip size on sugar yield in pretreatment of softwood for ethanol production. Bioresour Technol 100(24):6312–6316
Monnet F (2003) An introduction to anaerobic digestion of organic wastes. Final Report, pp 1–43
Montoneri E, Savarino P, Bottigliengo S et al (2009) Biomass wastes as renewable source of energy and chemicals for the industry with friendly environmental impact. In: Fresenius Environmental Bulletin. Parlar Scientific Publications, Freising, pp 219–223
Murphy JD, Power NM (2009) An argument for using biomethane generated from grass as a biofuel in Ireland. Biomass Bioenerg 33(3):504–512
Müller HW, Trösch W (1986) Screening of white-rot fungi for biological pretreatment of wheat straw for biogas production. Appl Microbiol Biotechnol 24(2):180–185
Naik SN, Goud VV, Rout PK et al (2010) Production of first and second generation biofuels: a comprehensive review. Renew Sustain Energy Rev 14(2):578–597
Nakamura Y, Mtui G (2003) Anaerobic fermentation of woody biomass treated by various methods. Biotechnol Bioprocess Eng 8(3):179–182
Narvaez I, Orio A, Aznar MP et al (1996) Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas. Ind Eng Chem Res 35(7):2110–2120
Nayono SE (2010) Anaerobic digestion of organic solid waste for energy production. Karlsruher Institut für Technologie Karlsruher, Germany
Nussbaumer T (2003) Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction. Energy Fuels 17(6):1510–1521
Odlare M (2005) Organic residues-A resource for arable soils, vol 2005
Oleszkiewicz JA, Sharma VK (1990) Stimulation and inhibition of anaerobic processes by heavy metals—a review. Biol Wastes 31(1):45–67

Pagés-Díaz J, Pereda-Reyes I, Taherzadeh MJ et al (2014) Anaerobic co-digestion of solid slaughterhouse wastes with agro-residues: synergistic and antagonistic interactions determined in batch digestion assays. Chem Eng J 245:89–98
Panagiotou G, Olsson L (2007) Effect of compounds released during pretreatment of wheat straw on microbial growth and enzymatic hydrolysis rates. Biotechnol Bioeng 96(2):250–258
Parawira W, Read JS, Mattiasson B et al (2008) Energy production from agricultural residues: high methane yields in pilot-scale two-stage anaerobic digestion. Biomass Bioenerg 32(1):44–50
Parkin GF, Miller SW (1983) Response of methane fermentation to continuous addition of selected industrial toxicants. In: Proceedings industrial wastes conference, Purdue University, West Lafayette
Rajendran K, Aslanzadeh S, Taherzadeh MJ (2012) Household biogas digesters—a review. Energies 5(8):2911–2942
Redman G (2008) A detailed economic assessment of anaerobic digestion technology and its suitability to UK farming and waste systems. The Andersons Centre for the National Non-Food Crops Centre, Melton Mowbray
Resch C, Wörl A, Waltenberger R et al (2011) Enhancement options for the utilisation of nitrogen rich animal by-products in anaerobic digestion. Bioresour Technol 102(3):2503–2510
Rivard CJ, Vinzant TB, Adney WS et al (1990) Anaerobic digestibility of two processed municipal-solid-waste materials. Biomass 23(3):201–214
Ross WR, Novella PH, Pitt AJ et al (1992) Anaerobic digestion of waste-water sludge: Operating guide TT 55/92 vol TT 55/92. Water Institute of Southern Africa (WISA), Midrand
Rowell RM, Young RA (1997) Paper and composites from agro-based resources. CRC press, Boca Raton
Ryckebosch E, Drouillon M, Vervaeren H (2011) Techniques for transformation of biogas to biomethane. Biomass Bioenerg 35(5):1633–1645
Salehian P, Karimi K, Zilouei H et al (2013) Improvement of biogas production from pine wood by alkali pretreatment. Fuel 106:484–489
Schacht C, Zetzl C, Brunner G (2008) From plant materials to ethanol by means of supercritical fluid technology. J Supercrit Fluids 46(3):299–321
Schink B (1997) Energetics of syntrophic cooperation in methanogenic degradation. Microbiol Mol Biol Rev 61(2):262–280
Schnürer A, Jarvis Å (2009) Mikrobiologisk handbok för biogas anläggningar. Rapport U2009, vol 3
Sekiguchi Y, Kamagata Y, Syutsubo K et al (1998) Phylogenetic diversity of mesophilic and thermophilic granular sludges determined by 16S rRNA gene analysis. Microbiology 144 (9):2655–2665
Seppälä M, Paavola T, Rintala J (2007) Methane yields of different grass species on the second and third harvest in boreal conditions. In: 11th IWA World Congress on Anaerobic Digestion, Brisbane, Australia, pp 23–27
Sharma A, Unni BG, Singh HD (1999) A novel fed-batch digestion system for biomethanation of plant biomasses. J Biosci Bioeng 87(5):678–682
Shoham Y, Lamed R, Bayer EA (1999) The cellulosome concept as an efficient microbial strategy for the degradation of insoluble polysaccharides. Trends Microbiol 7(7):275–281
Speece RE (1983) Anaerobic biotechnology for industrial wastewater treatment. Environ Sci Technol 17(9):416A–427A
Sreekrishnan TR, Kohli S, Rana V (2004) Enhancement of biogas production from solid substrates using different techniques—a review. Bioresour Technol 95(1):1–10
Sung S, Santha H (2003) Performance of temperature-phased anaerobic digestion (TPAD) system treating dairy cattle wastes. Water Res 37(7):1628–1636
Taherzadeh M, Karimi K (2008) Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review. Int J Mol Sci 9(9):1621–1651

Take H, Andou Y, Nakamura Y et al (2006) Production of methane gas from Japanese cedar chips pretreated by various delignification methods. Biochem Eng J 28(1):30–35
Tanaka M, Ikesaka M, Matsuno R et al (1988) Effect of pore size in substrate and diffusion of enzyme on hydrolysis of cellulosic materials with cellulases. Biotechnol Bioeng 32(5):698–706
Teghammar A, Karimi K, Sárvári Horváth I et al (2012) Enhanced biogas production from rice straw, triticale straw and softwood spruce by NMMO pretreatment. Biomass Bioenerg 36:116–120
Teghammar A, Yngvesson J, Lundin M et al (2010) Pretreatment of paper tube residuals for improved biogas production. Bioresour Technol 101(4):1206–1212
Tippayawong N, Thanompongchart P (2010) Biogas quality upgrade by simultaneous removal of CO_2 and H_2S in a packed column reactor. Energy 35(12):4531–4535
Tomme P, Warren RAJ, Gilkes NR (1995) Cellulose hydrolysis by bacteria and fungi. Adv Microb Physiol 37:1–81
Tong X, Smith LH, McCarty PL (1990) Methane fermentation of selected lignocellulosic materials. Biomass 21(4):239–255
Van Soest PJ (1994) Nutritional ecology of the ruminant. Cornell University Press, New York
Vandevivere P, De Baere L, Verstraete W (2003) Types of anaerobic digester for solid wastes. Biomethanization of the organic fraction of municipal solid wastes 111–140
Verma M, Godbout S, Brar SK et al (2012) Biofuels production from biomass by thermochemical conversion technologies. Int J Chem Eng 2012:18
Ward AJ, Hobbs PJ, Holliman PJ et al (2008) Optimisation of the anaerobic digestion of agricultural resources. Bioresour Technol 99(17):7928–7940
Weiland P (2003) Production and energetic use of biogas from energy crops and wastes in Germany. Appl Biochem Biotechnol 109(1–3):263–274
Weiland P (2006) Biomass digestion in agriculture: a successful pathway for the energy production and waste treatment in Germany. Eng Life Sci 6(3):302–309
Weiland P (2010) Biogas production: current state and perspectives. Appl Microbiol Biotechnol 85 (4):849–860
Wilson DB (2008) Aerobic microbial cellulase systems. Biomass Recalcitrance Deconstructing Plant Cell Wall Bioenergy:374–392
Xiao W, Clarkson WW (1997) Acid solubilization of lignin and bioconversion of treated newsprint to methane. Biodegradation 8(1):61–66
Yang B, Wyman CE (2008) Pretreatment: the key to unlocking low-cost cellulosic ethanol. Biofuels, Bioprod Biorefin 2(1):26–40
Yoshida K, Miyafuji H, Saka S (2010) Methane production from organic acids obtained by supercritical water treatment of Japanese beech. J Wood Sci 56(2):160–165
Youngsukkasem S, Rakshit SK, Taherzadeh MJ (2012) Biogas production by encapsulated methane-producing bacteria. BioResources 7(1):56–65
Zandvoort MH, Van Hullebusch ED, Fermoso FG et al (2006) Trace metals in anaerobic granular sludge reactors: bioavailability and dosing strategies. Eng Life Sci 6(3):293–301
Zeng M, Mosier NS, Huang CP et al (2007) Microscopic examination of changes of plant cell structure in corn stover due to hot water pretreatment and enzymatic hydrolysis. Biotechnol Bioeng 97(2):265–278
Zhang C, Li J, Liu C et al (2013) Alkaline pretreatment for enhancement of biogas production from banana stem and swine manure by anaerobic codigestion. Bioresour Technol 149:353–358
Zhang R, Zhang Z (1999) Biogasification of rice straw with an anaerobic-phased solids digester system. Bioresour Technol 68(3):235–245
Zhang YHP (2008) Reviving the carbohydrate economy via multi-product lignocellulose biorefineries. J Ind Microbiol Biotechnol 35(5):367–375
Zhao Q, Kugel G (1996) Thermophilic/mesophilic digestion of sewage sludge and organic wastes. J Environ Sci Health Part A 31(9):2211–2231
Zhong W, Zhang Z, Qiao W et al (2011) Comparison of chemical and biological pretreatment of corn straw for biogas production by anaerobic digestion. Renew Energy 36(6):1875–1879

Ziemiński K, Frąc M (2012) Methane fermentation process as anaerobic digestion of biomass: Transformations, stages and microorganisms. Afr J Biotechnol 11(18):4127–4139

Zuo Z, Wu S, Zhang W et al (2013) Effects of organic loading rate and effluent recirculation on the performance of two-stage anaerobic digestion of vegetable waste. Bioresour Technol 146:556–561