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Review

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Innovative Pretreatment Strategies for Biogas Production

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ABSTRACT:

Biogas or biomethane is traditionally produced via anaerobic digestion, or recently by thermochemical or a combination of thermochemical and biological processes via syngas (CO and H₂) fermentation. However, many of the substrates feedstocks have recalcitrant structure and difficult to digest (e.g., lignocelluloses or keratins), or they have toxic compounds (such as fruit flavors or high ammonia content), or not digestible at all (e.g., plastics). To overcome these challenges, innovative strategies for enhanced and economically favorable biogas production were proposed in this review. The strategies considered are commonly known physical pretreatment, rapid decompression, autohydrolysis, acid- or alkali pretreatments, solvents (e.g. for lignin or cellulose) pretreatments or leaching, supercritical, oxidative or biological pretreatments, as well as combined gasification and fermentation, integrated biogas production and pretreatment, innovative biogas digester design, co-digestion, and bio-augmentation.

Keywords:

Biogas; Pretreatment strategies; Lignocellulosic residue; Syngas; Fruit and Food waste; Keratin waste

1. Introduction

Biogas production through anaerobic digestion technology has advanced tremendously over the years. Presently, due to high energy demand and environmental concerns as the world's population increases, the drive for anaerobic digestion processes is gaining momentum within research and the industry for sustainable energy generation. In this vein, there is an increasing focus on better feedstock utilization for improved biogas production. Nevertheless, the challenges of low biogas yield, high retention time, and high investment cost impede the maximum performance of biogas production in anaerobic digestion systems. These bottlenecks are highly dependent upon the availability, composition, and degradability of the feedstock used for biogas production. Great potential lies in biogas production from various feedstocks such as crop residues, livestock residues, municipal waste, landfill waste, food waste, aquatic biomass, keratin waste, and lignocellulosic feedstocks because of their availability and abundance. However, most of these feedstocks have slow degradation rates and as such require longer retention times. In addition, some of these feedstocks form toxic intermediates or contain toxic compounds, which inhibit the biogas production process. Nevertheless, the abundance and thus low cost of these feedstocks confirm that there is a need for new strategies for a better utilization of such kinds of waste streams.

Theoretically, biogas can be produced from the organic fraction of any material, such as wood, crop residue, textile wool, chicken feathers, lignocellulosic waste, industrial food waste, fruit waste, etc. However, today, biogas is typically produced only from feedstocks that are easily utilizable by the microbial community responsible for transforming these feedstocks into biogas. However, these easily digestible feedstocks,

i.e., crop and livestock residues, source sorted municipal waste, food waste, waste water with high organic content, etc., are not as abundant or readily available for biogas production, thereby, limiting the amount of biogas that can be produced. Nevertheless, the development of innovative technologies aiming for the utilization of feedstocks that are readily available but not easily degradable would result in an increase in biogas production.

The major reasons why some feedstocks are not ideal for biogas production are: (a) they cannot be digested by microorganisms, (b) digestion by microorganisms is very difficult to achieve, (c) digestion could be achieved but in a very slow way, and (d) the presence of inhibitors in the feedstock or the production of inhibitory compounds during microbial degradation. The goal of the “pretreatment” is to facilitate the digestion process by removing these barriers and to make the organic content of the substrate easily accessible and utilizable by the microbial community. There have been several approaches toward pretreatment, which can be classified as physical, chemical, physicochemical, and biological (Taherzadeh & Karimi, 2008). This review considers some innovative strategies, helping the utilization of indigestible, slow, hard to digest, and inhibitory feedstocks for biogas production. The ideal pretreatment to be employed for processing these feedstocks should be cost-effective, increase feedstock accessibility to microorganisms, should not use or produce substances that inhibit biogas production, should not demand high energy, and should not generate by-products that are harmful to the environment. A short review on the biochemistry of biogas production, theoretical yield, available potential feedstocks, and the challenges associated with these feedstocks

will help in understanding how innovative strategies toward pretreatment can be implemented.

1.1 Biochemistry of biogas production

1.1.1 Biological Route

Feedstock for biogas production is prepared prior to digestion by removing contaminants such as grits, metals, and other debris depending on the source of feedstock. Moreover, the size of the feedstock may be reduced (for feedstock whose available surface area is not accessible by hydrolyzing bacteria), and inhibitors from feedstocks such as fruit flavors and the oil from palm oil mill effluent (POME) can be removed.

Organic feedstocks undergo different degradation steps during the anaerobic digestion (AD) process (Fig. 1), and they are briefly discussed as follows. Step one is hydrolysis, here the feedstock is disintegrated by the action of a diverse community of hydrolytic bacteria producing exoenzymes. The products of this first step are simple sugars, amino acids, and fatty acids. This step has been reported as being the rate limiting step for hard-to-digest biomass (Fernandes et al., 2009) such as lignocellulose and keratin-rich wastes. Moreover, some toxic by-products can be formed during this step (Neves et al., 2006). Step two is acidogenesis, in this step monomers from the hydrolysis are converted into short chain organic acids, alcohols, a few organic-nitrogen and organic-sulfur compounds, together with hydrogen and carbon dioxide. This step has been reported to be the fastest step in the AD process (Vavilin et al., 1996). If the feedstock has a low buffering capacity and the organic loading rate is high, the accumulation of volatile fatty acids can result in a pH drop, which would inhibit the methanogens that

produce methane in the final step. Step three is the acetogenesis, here the homoacetogenic microorganisms reduce hydrogen and carbon dioxide to acetic acid (Deublein & Steinhauser, 2011). In this step, the acetogenic bacteria can only survive at a very low hydrogen concentration, so excessive production of hydrogen from the acidogenesis step can inhibit these bacteria (Deublein & Steinhauser, 2011). Step four is methanogenesis, where methane production takes place under strict anaerobic conditions. This step has been reported as the rate limiting step for easily degraded and those with low buffering capacity feedstocks (Rozzi & Remigi, 2004). There are mainly two groups of methanogenic bacteria that can be distinguished, i.e., hydrogenotrophic methanogens and acetotrophic methanogens converting hydrogen and carbon dioxide, and acetic acid, respectively, to methane. The balance between the hydrogen-forming and hydrogen-consuming microorganisms is very important, since anaerobic oxidation, i.e., acetate formation can only take place at a low partial pressure of hydrogen because of thermodynamic reasons.

1.1.2 Combined Thermochemical and Biological Route

The increasing generation of indigestible organic waste increases the interest in the combination of thermochemical and biochemical processes such as gasification and fermentation. Both gasification and fermentation consist of several process steps. Initially, the feedstock is fed to the gasifier in which temperature increases to approx. 1200 °C. As the temperature rises, the feedstock's water evaporates (at 100 °C), tar and char are produced, and pyrolysis gases are generated. The main reaction steps at this point are the water gas and the Boudouard reaction (equation 1 and 2). Moreover, gases

react with each other (gas-phase reactions) and with the carbon (gas-solid reactions).

Methane can also be produced by the reaction of carbon and hydrogen.

The gas produced from the gasification contains fermentable hydrogen, carbon monoxide, and carbon dioxide. This gas mixture is fed into a fermenter where it is converted into methane. More specifically, carbon dioxide and hydrogen are converted into methane and water by hydrogenotrophic methanogens, while acetotrophic methanogens convert carbon monoxide and water into methane and carbon dioxide.

1.1.3 Theoretical yield

The organic content of a feedstock determines the theoretical yield of biogas production. When the elemental composition is known, the theoretical methane production can be calculated using equation 3 (Symons & Buswell, 1933):

$$\text{Moles of methane produced (x)} = 1/8 (4c + h - 2o - 3n - 2s) \quad (3b)$$

If carbohydrates ($\text{C}_6\text{H}_{10}\text{O}_5$), protein ($\text{C}_5\text{H}_7\text{O}_2\text{N}$), or fat ($\text{C}_{57}\text{H}_{104}\text{O}_6$) are used as substrates, the theoretical yield will be 0.42, 0.50, and 1.01 $\text{Nm}^3\text{-CH}_4/\text{kgVS}$ respectively (Schnürer & Jarvis, 2010). When both the elemental composition and the proportion of carbohydrates, proteins, and fats are not known, the theoretical methane yield can also be calculated from the chemical oxygen demand of the feedstock using equation 4:

From this equation, 2-kmols of O_2 (or 64 kg COD) are needed for the complete oxidation of 1-kmol of methane, so 1 kg COD is equivalent to 1/64-kmol of methane or

0.35 m³ CH₄ at standard temperature and pressure. Using the calculations from equations 3 and 4, the theoretical methane yields of some substrates are summarized in Table 1.

2. Digestion of potential feedstocks for biogas production and their challenges

As discussed earlier, biomass that is easily processed is mainly used as feedstock for anaerobic digestion process. Common, easily processed, feedstocks include livestock manure, food-processing wastes, and sewage sludge. On the other hand, biomass that is difficult to process is in high abundance and accumulates tremendously. This biomass, when properly pretreated, can be a valuable feedstock for biogas production, thereby reducing environmental pollution and enhancing the recovery of renewable energy. For instance, lignocellulosic wastes have about 40–60 % cellulose and 20–40 % hemicellulose (Kang et al., 2014), which is a good potential carbon source for biogas production if made accessible to the microorganisms. In addition, keratin-rich wastes (e.g., feathers) are composed of about 91–93 % crude protein (Patinvoh et al., 2016; Salminen et al., 2003), which is an insoluble protein and when converted into soluble oligomers will be of great potential for biogas production. Moreover, approximately 91% of the volatile solids of fruit wastes are degradable, depending on the fruit species (Schnürer & Jarvis, 2010), and food processing wastes also have good potentials for biogas production. The biogas production potential of these feedstocks varies depending on their composition, pretreatment process, and concentration of biodegradable material. Therefore, some of these feedstocks which are indigestible, hard to digest, slow to digest, or contain inhibitors are discussed as potential feedstocks for anaerobic digestion. Challenges associated with these feedstocks are discussed as well.

2.1 Indigestible feedstocks

A large fraction of the globally produced waste is composed of organic indigestible materials, which are not biologically degradable or their degradation is extremely slow and cost-inefficient. Landfills contain many indigestible compounds such as processed paper and impregnated wood. Because of the indigestible and heterogeneous nature of these wastes, their volumes increase exponentially posing an environmental threat. According to the world bank, these materials make up the highest proportion of municipal solid waste in high income countries, while they accounted for 27 % of the global solid waste generated in 2009 (TheWorldBank, 2010).

Indigestible wastes contain components that can be used by microbial catalysts during the biogas production. Recently, some studies were conducted on the biological degradation of traditionally indigestible feedstock for biogas production. For example, a novel bacterium, *Ideonella sakaiensis* 201-F6, was proven to degrade polyethylene tetraphthalate (PET) (Yoshida et al., 2016). Furthermore, the digestion of cotton/polyester textiles was investigated in another study (Jeihanipour et al., 2013). However, these processes are premature, and more research is required for scaling up. One way to convert indigestible waste into fermentable feedstock is to apply gasification step before AD. During gasification, the feedstock is converted into a gas mix called syngas, which is thereafter converted into methane by anaerobic microbes. The combination of two already industrial processes gathers many advantages such as efficient know-how and existing infrastructures. However, the main bottleneck of syngas AD or fermentation is the low gas-liquid mass transfer, especially of hydrogen and carbon monoxide. However, the use of a gas dispenser such as an innovative hollow

fiber membrane can drastically increase the gas diffusion rate (Shen et al., 2014). In addition, the diffusion of syngas in a more economical way would be a very positive step for scaling up the process.

2.2 Hard-to-digest feedstocks

The recalcitrant nature of some feedstocks limits their biological degradation for biogas production. This recalcitrant nature is a result of several properties such as the crystalline structure of the feedstock, different layers of the plant cell wall, and their interactions with other polymers (Taherzadeh & Jeihanipour, 2012). These complex polymers are tightly packed and highly crosslinked with hydrogen bonds, disulfide bonds (for keratin wastes), and hydrophobic interactions (Daroit et al., 2009). Hydrolysis is the rate-limiting step for these feedstocks; therefore, it is necessary to overcome the recalcitrant nature and make them accessible to the microorganisms for effective biogas production. Some of these feedstocks and their challenges as well as how to overcome these challenges are discussed below in order to ascribe value to them.

2.2.1 Lignocellulosic wastes

Lignocellulosic wastes are one of the most abundant renewable organic resources on earth with a yearly production of approximately 200 billion tons (Zhang, 2008). The increasing expansion of the agricultural industry and its activities has led to an increase in the production and the consequent accumulation of a large volume of these wastes. Forestry by-products, woody crops, and municipal solid waste also contribute to an enormous amount of these waste streams. About 60 % of the dry weight of the average municipal solid waste is composed of lignocelluloses (Holtzapple et al., 1992). The abundance of lignocellulosic wastes makes them a potential feedstock for biogas

production, and it has been reported that these kinds of wastes can add up to a significant energy value of approximately 1500 MJ/year (Kang et al., 2014) depending on the yield from the biomass, total cultivable area, and the technology used. Although these wastes are rich in fibers, readily available, and have a significant energy value, they have a low biogas yield due to their resistance to microbial attack.

Lignocellulosic wastes are difficult to digest as a result of matrix polymers (hemicellulose, pectins, and lignin) surrounding the cellulosic microfibrils in the plant cell wall (Himmel & Picataggio, 2009). The degree of resistance of these wastes to microbial attack varies depending on the type of lignocellulose, various compartments of the cell wall, and cell age, while it is also affected by processing phenomena such as drying and heating (Taherzadeh & Jeihanipour, 2012). However, effective use of lignocellulosic biomass for biogas production requires a hydrolysis step in order to open up the structure and increase the accessibility for cellulose degrading microorganisms. It is only after this step that the material will be ready for conversion. The rate and extent to which cellulose can be hydrolyzed depends on the connection between the lignin, hemicellulose, and cellulose and also the degree of crystallinity in the cellulose itself. A potential solution is an innovative pretreatment method to increase the digestibility and ascribe value to the lignocellulosic wastes.

2.2.2 Keratin-rich Wastes

Keratin-rich wastes such as chicken feather, wool, hair, nails, horns, hooves, and claws are produced worldwide by the poultry, wool, meat, and fish industries. For instance, the world's average stock of chicken is about 22 billion (FAOSTAT, 2013); thus, the poultry industries produce a tremendous amount of feathers yearly. Moreover, the

global production of wool amounts to 2.1 million tons per year (IWTO, 2015). Assuming that all the insoluble protein (keratin) are converted into soluble protein, the methane potential of keratin wastes is as high as 0.496 Nm³/kgVS (Angelidaki & Sanders, 2004). However, the methane yield obtained is usually low due to the recalcitrant structure of keratin. Keratin is an insoluble structural protein where the polypeptides chain is tightly packed and highly cross-linked with disulfide bonds, hydrogen bonds, and hydrophobic interactions (Daroit et al., 2009). This structure makes the protein insoluble and resistant to enzymatic attack, which is a major hindrance in the biological processing of these wastes. The keratin in hair, wool, and horn is tightly packed in an α -helix, and it is different from the keratin in the chicken feathers (β -helix) because it contains a higher amount of cysteine (Moreira et al., 2007), which makes α -keratins even more difficult to hydrolyze than β -keratins. An appropriate pretreatment is required, therefore, prior to biogas production for keratin-rich wastes to be utilized for biogas production.

2.3 Feedstock with inhibitors

Inhibitors are compounds or substances that slow down or stop the ability of enzymes, catalysts, or microorganisms to transform reactants to desired products. From the biogas pretreatment perspective, inhibitors could be classified based on their biodegradability or the point at which they enter the biogas production process. Based on the biodegradability, some inhibitors such as furfural, long chain fatty acids, and organic pollutants are biodegradable, while others such as heavy metals are non-biodegradable (Chen et al., 2008). Under optimal conditions, microbes in the digesters can digest feedstocks containing low concentrations of biodegradable inhibitors, while the

accumulation of non-biodegradable inhibitors can lead to the death of microbes in the digester (Chen et al., 2008). The other categories of inhibitors either come into the digester as part of the feed (such as fruit flavors, aromatic compounds) or are released during digestion or pretreatment (such as NH_3 , long chain fatty acids). Feedstocks with inhibition based on point of entry or release are discussed in the following subsections.

2.3.1 Inhibitors as part of the feedstock-fruit wastes

The Food and Agricultural Organization (FAO) of the United Nations 2013 statistics showed that the global fruit production has increased by 3 % annually in the past decade, with 804.4 million tons produced in 2012 (FAO, 2013). The FAO also reported that 36–56 % of the produced fruits end up as waste (FAO, 2011). Fruit waste could be generated as a result of poor management or storage, diseases or infestation as well as mechanical damage during harvesting or fruit processing. Fruit processing generates two types of waste: solid waste that consists of peels, skin, seed, stones, etc., and liquid waste from juice and wash-waters (Gustavsson et al., 2011). The average VS of fruit waste consists of 78.3 % carbohydrates, 8.5 % protein, and 6 % fat (Schnürer & Jarvis, 2010), so the theoretical yield of methane from fruit waste is $0.43 \text{ Nm}^3\text{-CH}_4/\text{kg-VS}$ or $0.04 \text{ Nm}^3\text{-CH}_4/\text{kg}$ fruit waste. Using the estimated global fruit production for the past decade, the estimated fruit production in 2016 would be 905.4 million tons, and if 46 % ends up as waste, $16.7 \times 10^9 \text{ Nm}^3$ of methane could be produced from the fruit waste. However, the actual methane production from fruit waste is much less than this theoretical yield because of the presence of inhibitory flavor compounds affecting the AD process negatively (Wikandari et al., 2013).

These flavor compounds can be classified into esters, alcohols, aldehydes, ketones, lactones, and terpenoids. Compounds like geraniol, thymol, carvacrol, etc. belonging to the terpenes family have been reported as cytotoxic (Rosato et al., 2007). Wikandari et al. (2013) found that 0.5 % of terpenoids, aldehydes, and alcohols in an AD feedstock can reduce the methane production by 99 %. Limonene, a terpenoid and a major component of peel oil from citrus fruits, has been reported to cause failure in a continuous mesophilic AD process at a concentration of 400 $\mu\text{L/L}$ (Mizuki et al., 1990), while at a concentration of 450 $\mu\text{L/L}$ it can lead to the failure of a thermophilic AD process (Forgács, 2012). Due to these flavor compounds, it is essential for fruit waste to be pretreated before it is used for biogas production.

2.3.2 Inhibitors released during digestion - wastes from food processing

Wastes from the food processing industries are a good choice for biogas production because the waste produced consists mostly of the organic fraction of the raw materials used by the industry. These wastes usually have a high biological oxygen demand (BOD) and a high chemical oxygen demand (COD), with varying contents of suspended solids depending on their source (Russ & Meyer-Pittroff, 2004). The wastes from food processing are either solid or liquid, and most of the solid part can be classified as a lignocellulosic residue (Table 1). As lignocellulosic wastes have been discussed in section 2.2.1, in this section only the liquid fraction of the waste from food processing which is associated with a high volume of production and negative environmental effects, will be discussed. More specifically, the liquid waste from the oil industry has attracted a lot of attention because of its potential for biogas production and its negative effect on the environment.

Global vegetable oil production increased from 90.5×10^6 MT in 2000 to 160.59×10^6 MT in 2012 (Statista, 2016) with oil-palm, soybean, rapeseed, and sunflower accounting for 75 % of the global oil production (FAO, 2013). Over this period, the palm oil production increased from 21.75×10^6 MT to 51.74×10^6 MT making palm oil to be the most produced vegetable oil in the world. The production of vegetable oil is usually associated with the production of wastewater. Taking palm oil as an example, for every ton of crude palm oil produced, 2.5–3.75 tons of palm oil wastewater called palm oil mill effluent (POME) is produced (Chin et al., 2013). POME is a thick brownish liquid generated from the clarification and sterilization of palm oil during the oil extraction process in the palm oil mills. It is considered to be one of the most polluting effluents from the agricultural industry because of its properties such as high COD (15–100 g/L), high BOD (10.25–43.75 g/L), and acidic pH (3.4–5.2) (Ahmad et al., 2011). Biogas production from POME could solve the problem of treating POME for the environment and also generating an additional valuable product (biogas) for the oil-palm industries. Using 50 g/L as an average COD of POME, every 1 m³ of POME can produce 18.78 Nm³ of CH₄ or 37.56 Nm³ of biogas. Taking into account the production of 3.125 tons of POME per ton of the palm oil, theoretically 2.9×10^{15} Nm³ of CH₄ or 5.8×10^{15} Nm³ of biogas could have been produced from the palm oil produced globally in 2012. With this tremendous potential, it is important both from energy and environmental perspectives that POME is properly utilized.

Despite the tremendous potential of producing biogas from POME or other waste water from oil production, in reality most AD digesters fail when fed continuously with daily COD load of between 35–65 g/L (Zinatizadeh et al., 2007), which is challenging as the

COD of these feedstocks could be as high as 100 g/L (Ahmad et al., 2011). One of the reasons for this failure is that POME or other waste water from the oil production contains polymeric fat, which are broken down during hydrolysis to long chain fatty acids such as stearic acid, oleic acid, and arachidic acid, and long chain fatty acid accumulation has been shown to inhibit the AD process (Angelidaki & Ahring, 1992). Another reason for the failure when using POME is the accumulation of volatile fatty acids (VFAs) in the digester. Thus, to fully harness the potential of waste water from the oil production, such as POME, for biogas production, it is important to come up with innovative strategies.

2.3.3 Inhibitors released during digestion – ammonia inhibition from protein wastes

Presently, about 1 million tons of protein-rich wastes are produced annually (Kovács et al., 2013), and about 30 % of the weight of animals processed for food ends up as slaughterhouse waste (Kovács et al., 2015). These wastes mainly contain manure and blood; they are highly rich in protein, readily available, and can be easily digested, which makes them a potential feedstock for biogas production. The theoretical methane potential of protein wastes is 0.496 Nm³/kgVS (Angelidaki & Sanders, 2004), and slaughterhouse wastes have a theoretical potential of about 0.70 Nm³ CH₄/kgVS (Schnürer & Jarvis, 2010); however, since they have a low C/N ratio, digestion of these feedstocks as a single substrate is usually unsuccessful due to the accumulation of ammonia during digestion. During the breakdown of protein-rich wastes, depending on the pH and temperature, free ammonia (NH₃) or ammonium ion (NH₄⁺) are produced, which at higher concentrations inhibit the anaerobic digestion process (Yenigün & Demirel, 2013). Studies have shown that inhibition is due to the presence of free

ammonia rather than ammonium ion (Kayhanian, 1999), with a free ammonia nitrogen (FAN) concentration of 150 mg/L causing complete inhibition (Yenigün & Demirel, 2013). Therefore, proper treatment of these feedstocks before digestion and control of ammonia concentration during the digestion process is necessary to maximize the potential of these wastes for biogas production.

2.3.4 Inhibitors released during gasification

During feedstock gasification, several inhibitors can be generated mainly because of the feedstock composition and the operating conditions. Some of these inhibitors are char, H_2S , NH_3 , NO_x , ethane, ethylene, and acetylene as well as heavy metals and particles. A high concentration of these components is known to cause cell dormancy, enzyme inhibition, low cell growth, and limited hydrogen uptake. The amounts of these components can be limited by cleaning the syngas with cyclones, reforming, and by controlling the operating conditions and the feedstock composition.

3. Pretreatment methods

3.1 Gasification of indigestible feedstock

During gasification, the feedstock is gasified by exposure to high temperatures (1000–1200 °C) and an oxidizing agent. Steam, oxygen, and air are mainly used as oxidizing streams. The produced gas (syngas) is mainly composed of H_2 , CO, and CO_2 , which can thereafter be fermented for biogas production. In addition, at the end of the gasification, a residual ash, in the form of slag, is left in the gasifier. The composition of the syngas and the ash is affected greatly by the feedstock composition and the process temperature. For example, feedstocks with high amount of carbon generate syngas with high CO content. Furthermore, at lower operating temperatures below 1000 °C, the gas

produced contains higher amounts of impurities. The remaining ashes, from thermochemical processes, have been mainly used as building material in road construction. However, ashes consist of toxic components such as heavy metals, which pose an environmental threat. Therefore, alternative uses have been considered. For example, it has been reported that the addition of ash enhanced the biogas production and benefitted the alkalinity, and pH of anaerobic digesters (Banks & Lo, 2003).

One of the main advantages of gasification as a pretreatment process is that it can treat a wide variety of heterogeneous feedstocks. Furthermore, gasification has a high conversion rate, and both syngas and the remaining ash can be used for biogas production (Banks & Lo, 2003). In addition, syngas production can be economically efficient if parameters such as pressure, gasification agent, syngas and feedstock composition are taken into consideration. More specifically, an economic assessment showed that it is possible to produce syngas with an approximate cost of \$ 0.25/Nm³ based only on biomass feedstock. Moreover, the production costs can almost be reduced by half when considering co-gasification of biomass and coal (Trippe et al., 2011). On the other hand, another study argues that challenges such as high operational costs should be addressed in order to upgrade the combined gasification and fermentation process to a commercial scale (Richter et al., 2013).

3.2 Hard-to-digest feedstocks and feedstocks with inhibitors

Due to the recalcitrant nature and strong elasticity, recalcitrant feedstock can only result in a low biogas yield. Furthermore, feedstocks such as fruit wastes are easily degraded but also result in low yield due to the presence of inhibitors. Therefore, these wastes are pretreated prior to the biogas production. The main purpose of pretreatment for

lignocellulosic wastes is to break the lignin layer that protects the cellulose and hemicellulose, in order to make the feedstock more accessible for digestion. Pretreatment also helps to decrease the crystallinity of cellulose and to increase the porosity. For other feedstocks like keratin-rich wastes, if the crosslinking between the polypeptides chain breaks, the keratin is more accessible and easier to digest. Another purpose of pretreatment is to remove the inhibitors, which are present in potential feedstocks. Several pretreatment methods have been reported in detail aiming to make these feedstocks viable to digestion by microorganisms, thereby increasing the biogas yield (Table 2). Some pretreatments lead to changes in the feedstock composition by dissolving the hemicellulose or lignin or both, while some other pretreatments result in changes in the cellulose crystallinity, molecular weight, biomass porosity, and particle size (Johnson & Elander, 2009). Specific pretreatment methods suitable for (i) increasing accessible surface area, (ii) decrystallization of cellulose, (iii) hydrolysis of hemicellulose, (iv) removal of lignin, (v) hydrolysis of keratin, and (vi) removal of inhibitory compounds are discussed in the following subsections.

3.2.1 Accessible surface area and decrystallization

Comminution, such as ball milling, is a physical pretreatment method that increases the feedstock surface area and decrystallizes cellulose. Silva *et al.* (Silva *et al.*, 2012) investigated the effect of grinding on wheat straw. The results showed that ball milling samples yield 46 % total carbohydrates and 72 % glucose as a result of the reduction in the cellulose crystallinity from 22 % to 13 %. Ball milling was also applied to non-degraded digestate in order to feed it back into the digestion process (Lindner *et al.*, 2015). Enhanced methane production by 9 % was reported in the case of two-stage

maize silage digestate, and an increase of 17 % was detected when using two-stage hay/straw digestate. Irradiation is also an effective pretreatment method that disrupts the structure of the biomass cell wall and decreases the crystallinity of the cellulose (Johnson & Elander, 2009). The effect of microwave pretreatment was evaluated on the solubilization of microalgae as a substrate for biogas production, and it was determined that at a specific energy of 21.8, 43.6, and 65.4 MJ/kgTS, the pretreatment increased the biogas production rate by 27–75 % and the biogas yield by 12–78 %, according to the results applied from the BMP assays. These pretreatments are suitable methods for increasing the surface area and decrystallizing recalcitrant feedstocks; however, they are not economically feasible due to the high energy consumption. Therefore, they are not viable as stand-alone pretreatments for industrial applications but can be combined with other pretreatments that are cost effective.

3.2.2 Hydrolysis of hemicellulose

Dilute acid pretreatment at controlled conditions can solubilize almost all the hemicellulose from a biomass and thereby increase the accessibility of microorganisms to cellulose. This method breaks the intramolecular bonds between the lignin, hemicellulose, and cellulose in the cell wall and hydrolyzes the hemicellulose (Taherzadeh & Jeihanipour, 2012). However, at a high temperature and acid concentration, undesirable dehydration occurs resulting in the hemicellulose and cellulose being degraded into different types of inhibitory compounds, such as furfural (Taherzadeh et al., 1997). Hence, it is necessary to carry out the pretreatment at mild conditions to prevent excessive sugar degradation. Un-catalyzed steam explosion is also an alternative pretreatment method for the hydrolysis of hemicellulose. However, the

xylose yield from the hemicellulose is usually not higher than 65 % of the theoretical yield due to the excessive sugar degradation (Brownell & Saddler, 1987). Liquid hot water pretreatment at a lower temperature (200–230 °C) has also been reported as an effective method for the hydrolysis of hemicellulose (Johnson & Elander, 2009). A higher yield of soluble sugars is possible with this method compared to the un-catalyzed steam explosion method. However, the liquid hot water pretreatment method liberates the sugars in the oligometric form (Johnson & Elander, 2009).

3.2.3 Lignin removal

Alkaline pretreatment is a suitable method for solubilizing the lignin; it can be carried out at different concentrations of lime, sodium hydroxide, or ammonia. This method causes swelling of the fibers, which results in an increased accessible surface area, reduced degree of polymerization, and decrystallization of the cellulose. Alkaline treatment breaks the intramolecular bonds between the lignin, hemicellulose, and cellulose and disrupts the lignin structure (Hsu, 1996). Lime (Ca(OH)_2) pretreatment in the presence of water (9 ml/g dry biomass) was investigated for 2 h on switchgrass at 100–120 °C with 0.1 g Ca(OH)_2 /g dry biomass loading (Chang et al., 1997). The results showed that 29 % lignin was solubilized. Moreover, Sambusiti et al. (2013) investigated the effect of alkaline (NaOH) pretreatment on ensiled sorghum forage in semi-continuous digesters. It was observed that pretreatment with 10g NaOH/100gTS increased the methane yield by 25 % compared to untreated sorghum and did not cause any inhibition of the process. Organic or organic-aqueous solvent mixtures utilizing ethanol, benzene, ethylene glycol, or butanol have also been reported as being effective for lignin removal (Taherzadeh & Karimi, 2008). Studies have also shown that white-

rot fungi produce enzymes that are capable of extensive degradation of lignin. As a result, the biomass digestibility is increased (Adney et al., 2009), although there is a loss of cellulose and hemicellulose during this process (Hatakka, 1983).

3.2.4 Hydrolysis of keratin

Pretreatment of keratin-rich waste using a strong acid, alkaline hydrolysis, and other physicochemical methods results in severe degradation and destruction of the keratin (Barone et al., 2006). Hence, recent research focuses on the biological pretreatment methods, which have been reported as successful for keratin degradation. Microorganisms (bacteria and fungi) produce enzymes that can break down the keratin and make it soluble. The keratin-rich feedstock is inoculated with appropriate bacteria or fungi cultures and incubated for days or weeks depending on the activity of the microorganism used and the properties of the substrate. Several microorganisms such as *Bacillus* sp. (Cai et al., 2008; Fellahi et al., 2014; Forgács et al., 2011a; Patinvoh et al., 2016; Zaghloul et al., 2011) and *Aspergillus* sp. (Mazotto et al., 2013) have been investigated and reported as being effective for hydrolyzing keratin.

3.2.5 Removal of inhibitors present in the feedstocks-fruit flavors

Inhibitory compounds that are part of the feedstocks used for the biogas production such as flavor compounds present in fruits have been shown to be adversely affecting the anaerobic digestion process even at low concentrations. Steam explosion has been reported to successfully remove these types of inhibitors from citrus waste, while also breaking up the lignocellulose structure in the feedstock (Forgács et al., 2011b). Steam explosion is a thermal pretreatment method that requires a very high pressure of up to 60 bar and a temperature of up to 150 °C. Combined chemical and steam explosion

pretreatment methods have been found to reduce the required temperature and residence time of the pretreatment, while also increasing the degradation rate in contrast to when chemical or steam explosion methods are used separately (Forgács et al., 2011b).

4. Innovative non-pretreatment strategies

Although several pretreatment methods have emerged over the past few years, certain challenges such as high cost, harmful environmental by-products, low biogas yield, and high energy requirement still persist. To address these challenges, some innovative non-pretreatment strategies aiming to improve the use of the readily available and low cost feedstocks for biogas production are discussed in this section. The strategies discussed include integrated biogas production, innovative digester design, co-digestion, and bio-augmentation. An integrated biogas production strategy addresses the cost challenge, the innovative digester design strategy addresses the inhibition challenge, and the co-digestion strategy addresses both the challenge of low yield and inhibitors, while the bio-augmentation strategy addresses the challenge of inhibitors.

4.1 Integrated biogas production strategy

Process integration refers to combining production systems either at the level of individual processes or whole factories with the goal of efficient utilization of resources, while reducing the cost and environmental emissions (Hallale, 2001). Although researchers agree that having biofuel production facilities close to each other can reduce the costs associated with the waste treatment, energy utilization, and shared logistics, the economics of integrating different biofuel production facilities have not been fully explored. Despite this, there have been successful instances where integrating an additional process route into an already established biofuel production facility resulted

in better economics for the biofuel production company. As an example, Dererie et al. (2011) used thermochemically pretreated oat straw for ethanol production and after the removal of ethanol, the residue was used for biogas production. The results showed that sequential ethanol and biogas production resulted in 28–34 % higher energy yield than direct biogas digestion. Biogas production was also faster with fermentation residues compared to direct digestion, showing that enzymatic saccharification and ethanol fermentation make the feedstock more digestible.

Detailed techno-economic analysis of this kind of integration has not been investigated, however a brief understanding of how integration affects the economics can be investigated by comparing the production cost with the revenue. The cost of methane production from wheat straw using steam pretreatment was estimated as \$ 0.85/m³, with the cost from pretreatment as \$ 0.11/m³ CH₄ (13 % of the total cost) (Shafiei et al., 2013). The cost of ethanol production from lignocellulose residue in California was estimated as \$ 0.43/L ethanol (Williams et al., 2007), excluding pretreatment (as the pretreatment cost has been factored into the biogas production cost), the cost could drop to \$ 0.33/L ethanol. Using the current selling price of ethanol (\$ 0.4/L) (USEIA, 2016) and the experimental results from Dererie et al. (2011), integrating ethanol and biogas production facility could increase the profitability of the biogas facility by \$ 0.014/kg-dry matter of wheat straw than when pretreated wheat straw is used to produce only biogas. This shows that the ethanol production process can be used for pretreating biogas feedstocks, while also bringing the benefits of process integration such as increased productivity.

Considering citrus waste as an example of fruit waste, the high costs associated with the pretreatment could be a deterrent from using it for biogas production. However, integrating pretreated citrus waste into already established ethanol and biogas production facilities could make the process more economically attractive, because in addition to ethanol and biogas, limonene and pectin would be valuable products that could generate additional revenue to offset the cost of pretreatment. Pourbafrani et al. (2010) found that from a ton of citrus waste at 20 % dry weight, 39.64 L of ethanol, 45 m³ of methane, 8.9 L of limonene, and 38.8 kg of pectin can be produced. Furthermore, oranges, a type of citrus waste, accounted for 8.5 % of the total global fruit waste in 2012 (FAO, 2013). Putting this amount of orange waste into the results found by Pourbafrani et al. (2010) would result in the production of 2.7×10^6 m³ of ethanol, 3.1×10^9 Nm³ of biogas, 6.1×10^5 m³ of limonene, and 2.7×10^6 tons of pectin.

Apart from the fruit waste, the integration concept can be applied to the other readily available feedstocks. From the biorefinery principles, diverse valuable products or energy can be generated from these feedstocks. For example, lignocellulosic waste conversion into ethanol and biogas has gained a lot of attention from researchers, but in addition to this, the US Department of Energy (DOE) identified fifteen high value building block chemicals that can be attained from lignocellulosic sugar conversion (Werpy et al., 2004). Integrating any of the identified high value chemicals production with biogas production could enhance the economics of biogas production from lignocellulosic waste. A similar analogy applies to other easily available feedstocks. Thus, process integration could be vital in making the economics of biogas production more favorable.

4.2 Innovative digester design strategy

Conventionally, a biogas digester design could be simple or detailed depending on the scale of application, the nature of the feedstock as well as the microorganisms involved. The design usually aims for the digester to provide a good environment that enables efficient contact between the microorganisms and the substrate. However, in case of some pretreatment methods or the use of certain chemicals, the AD process can be inhibited, even though these methods can successfully release dissolved intermediates for the AD process (Bolado-Rodríguez et al., 2016). To make these methods beneficial for methane production, it is important to develop a new digester concept that shields the microorganisms from the inhibitors, and in this way allow for a higher biogas yield to be achieved.

One way for this is to allow for a good contact between the microorganisms and the substrate, while selectively removing the inhibitors. In a recent study (Ezeji et al., 2013), a bioreactor design was applied, called continuous bioreactors with simultaneous product recovery and bleeding, to overcome the inhibition challenges in the bio-butanol production. This design allowed for a good contact between the microorganisms and the substrate, while bleeding away the inhibitory materials and recovering the bio-butanol to prevent an inhibitory concentration. With this design, 25 times higher production of butanol was achieved than in the traditional bioreactor used as a control (Ezeji et al., 2013). Apart from the inhibitory by-products or chemicals, feedstock such as POME could be inhibitory to the AD process. POME is produced in large volumes, so to minimize the costs associated with a large digester volume, a digester design that can allow for a short hydraulic retention time (HRT) is necessary. Najafpour et al. (2006)

used a modified form of an up-flow anaerobic sludge blanket (UASB) reactor called an up-flow anaerobic sludge fixed film (UASFF) digester and in this way they were able to achieve 90 % reduction in the COD of POME at an organic loading rate (OLR) of 23.15 g-COD/d and HRT of 1.5 days. This modification of the UASB concept was essential since POME contains suspended and colloidal components. Furthermore, these components consist of fat, protein, or cellulose, which can lead to bed failure and washout of microorganisms from the traditional UASB system (Zinatizadeh et al., 2007). Hence, an innovative digester design can be helpful, both in overcoming inhibition challenge and for reducing the retention time needed for the biogas production.

Another innovative design is the use of two- or multi-stage digesters. Separating the methanogenesis step from the acidogenesis step during the AD process has been found to give optimal conditions to the different microorganisms involved in the AD processes. Moreover, it has achieved a better process control and ability to handle higher OLRs than that in the single digesters (Demirel & Yenigün, 2002). This is due to the difference in the nutritional needs, environmental sensitivity, and the growth rate of the acidogenesis microorganism from those of the methanogens. Theoretically, using the two-stage AD system means that optimal conditions can be provided to the rate limiting steps within the AD process, leading to a better methane yield or shorter retention time, especially for the difficult-to-digest substrates. Using 20 g/L cellulose loading, Jeihanipour et al. (2013) found that a two-stage digester system resulted in 80 % increase in the maximum methane production and a decrease in the lag phase from 15 to 4 days. However, the cost and the added complexities of the two-stage AD systems

have been hindering the wide scale establishment of commercial two-stage AD facilities (Blumensaat & Keller, 2005).

The use of membranes for biological processes, referred to as membrane bioreactor, is another interesting application of the innovative digester strategy for biogas production. Membrane bioreactor applications have been reported to be effective in protecting the microorganisms from the toxic effect of substrate and product inhibition (Youngsukkasem et al., 2013). Youngsukkasem et al. (2013) reported that using a membrane bioreactor enabled biogas production from a substrate with 3 % D-limonene at a loading rate of 15 g-COD/L, while the control digester with free cells failed at 7.5 g-COD/L loading. The use of a membrane is also a suitable option for handling inhibition caused by ammonia accumulation. The use of a hollow fiber membrane was reported to successfully reduce the free ammonia nitrogen concentration by about 70 % (Lauterböck et al., 2012). The ability of the membrane bioreactors to shield the microorganisms from inhibitors means that the pretreatment of inhibitory feedstock and the costs associated with it could be avoided.

4.3 Co-digestion strategy

Mono-digestion of the recalcitrant feedstocks, highly protein-rich substrates, or feedstocks with harmful compounds often results in a slow process and a low biogas yield. These restrictions can be overcome by the co-digestion of different feedstocks with an appropriate mixing ratio, considering the C/N ratio, inhibitors, feedstock biodegradability, and total solid content. This is an effective strategy for reducing the ammonia inhibition during the digestion process since it aims at favoring synergisms, dilutes harmful compounds, optimizes the biogas production, and increases the digestate

quality (Mata-Alvarez et al., 2014). Comino et al. (2010) investigated the co-digestion of chopped crop silage with cow manure at different feeding rates. It was observed that feeding with 70 % VS of crop in the feedstock increased the methane yield by 109 % compared to manure mono-culture. Co-digestion of various substrates (manure, slaughterhouse wastes, municipal solid wastes, and crop residues) at different mixing ratios was investigated by Pagés Díaz et al. (2011). Synergetic effects were reported, giving rise to up to 43 % more methane yield, compared to that calculated from the methane yields of individual feedstocks. Paper tube residuals added to a nitrogen-rich substrate mixture used in an industrial digestion plant was also reported as having stabilizing effects on the digestion process (Teghammar et al., 2013). Paper addition prevented the accumulation of VFAs, increased the methane yield by 15–34 %, and decreased the hydraulic retention time by five days. Considering the fact that easily degraded feedstocks are not highly available and the problems associated with pretreatments, co-digestion is a good strategy to increase the amount of produced biogas, while avoiding the costs and challenges associated with the pretreatments. Nevertheless, more research is necessary in this area for a better understanding of the appropriate mixing ratios, interaction effects, and the impact of co-digestion.

Another benefit of co-digestion is the reduction of ammonia accumulation when feedstocks with high protein content are being digested. Zeshan et al. (2012) reported that adjustment of the C/N ratio to 32 resulted in 30 % less ammonia formation when food wastes, fruit and vegetable wastes, garden and paper wastes were co-digested in a dry digestion process.

4.4 Bio-augmentation strategy

Biological pretreatment of lignocellulose biomass and keratin-rich wastes has been reported to be successful thereby, improving the biogas production (Forgács et al., 2011a; Patinvoh et al., 2016; Rouches et al., 2016). Nevertheless, the need for two-stage processes or for pretreatment makes these options unfeasible for industrial applications. A promising option is bio-augmentation with anaerobic cellulolytic bacteria and with keratinase enzymes to enhance hydrolysis and improve the biogas yield, which has previously been demonstrated by several researchers. Peng et al. (2014) applied the bio-augmentation strategy to improve the hydrolysis of wheat straw using *Clostridium cellulolyticum*. According to the results, the biochemical methane potential of wheat straw was improved. Bio-augmentation with 10 % inoculation of *Acetobacteroides hydrogenigenes* on the anaerobic digestion of corn straw has also been reported (Zhang et al., 2015) leading to an increase of 19–23 % of the methane yield. Forgács et al. (2013) investigated the co-digestion of the organic fraction of municipal solid waste (OFMSW) with chicken feathers bio-augmented with savinase, an alkaline endopeptidase (0.53 ml/gVS_{feathers}). The addition of this anaerobic enzyme resulted in a methane yield of 0.485 Nm³/kgVS/d with stable reactor performance, while the process without bio-augmentation resulted in a low yield and accumulation of un-degraded feathers.

Another bio-augmentation strategy that could be helpful in handling the inhibitory feedstocks and some inhibitory by-products formed during the pretreatment is the use of flocculating bacteria (flocs). Flocculation has been shown as an effective way for yeast cells to overcome the inhibitory effect of some by-products (e.g., furfural), which are

formed during the pretreatment of lignocellulosic biomass (Westman et al., 2014). The formation of the local high cell density by flocs allows the outer cells to shield the cells inside the flocs from the inhibitory surrounding, thus, allowing the flocs to utilize the biodegradable content of the feedstock. In another similar work, flocculating cells were used by Najafpour et al. (2006) to treat POME with a pH of between 3.8–4.4, which could otherwise be lethal to methanogens. Apart from pH, ammonia toxicity can also be handled by using flocs. Koster and Lettinga (1988) studied the anaerobic digestion of potato juice at extreme ammonia concentrations using flocs, showing that methanogenesis can occur even at 11.8 g ammonia-nitrogen/L concentration. The flocs were adapted to a high concentration of ammonia nitrogen, and after the adaptation processes the maximum tolerable ammonia concentration was 6.2 times higher than the initial toxicity threshold level. Bio-augmentation, either in the form of addition of new microbial community or the formation of high local cell density (flocs), is a promising strategy for possible industrial applications utilizing recalcitrant and inhibitory feedstocks for biogas production.

5. Conclusion

The feedstock for biogas production may contain indigestible, hard-to-digest, and inhibitory compounds. Therefore, there is a need for pretreatment or other innovative methods in order to facilitate the biological digestion. The indigestible materials can be treated by a combined gasification-fermentation process. Moreover, hard-to-digest compounds such as recalcitrant lignocelluloses or keratin can be pretreated by thermal, chemical, physicochemical, or biological methods. In addition, feedstock with inhibitors can be pretreated by several methods such as steam explosion, or non-pretreatment

methods developed to facilitate their digestion, such as innovative digesters and/or bio-augmentation.

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Table 1

Wastes from food processing industries (Russ & Meyer-Pittroff, 2004) and theoretical methane yield from the different substrates (Schnürer & Jarvis, 2010)

Industry	Application	Waste
Diary	Diary processing	Diluted whole milk, whey, separated milk, cleaning water
	Yoghurt processing	Diluted milk, cleaning water, whey
	Cheese processing	Dry milk particle, whey, cleaning water
	Palm oil processing	Palm kernel shell, empty fruit bunches, palm oil mill effluent
Oil	Olive oil processing	Vegetable water, olive husk and skin
	Vegetable oil processing	Oil seed cake
	Coconut oil processing	Outer coat fiber (coir), desiccated coconut meat (copra)
Meat	Slaughterhouse	Slaughterhouse waste water, slaughterhouse blood
Brewery	Beer making	Malt dust, spent grain, kieselguhr sludge, yeast
Grain	Grist or flour mill	Bran, middlings, shells, husk, broken grain, ergot
	Oat husking	Bran, husk
	Rice mill	Rice bran, brown rice waste
	Malt processing	Malt dust, grain separator waste
Sugar		Bagasse, molasses
	Sugar cane processing Sugar beet processing	Molasses, exhausted beet pulp, carbonation sludge
Substrate	Methane yield (m ³ /ton-vs)	
Food waste	400 – 600	
Fruit waste	200 – 500	
Grass	200 – 400	
Straw	100 – 320	
Municipal sludge	160 – 350	
Protein wastes	496	
Manure (pigs, cattle, chickens)	100 – 300	
Slaughterhouse waste	700	
Cereals	300 – 400	

Table 2

Conventional Pretreatment Processes for Biogas Production

Pretreatment	Processes	Function	Economic challenges
Physical pretreatment ^{1,2,3}	Milling, irradiation, pyrolysis, ultrasonic	Increase of surface area and pore size	Consumes high electric energy ¹⁶ Equipment repairs can be very expensive
		Disruption of biomass structure and decrease of crystallinity	
		Reduction of degree of polymerization	
Rapid decompression pretreatment ^{4,5}	High pressure steaming, steam explosion ammonia fibre explosion (AFEX) CO ₂ explosion, SO ₂ explosion	Partial hydrolyzation of hemicellulose	Effective recovery of ammonia can be expensive ³
		Disruption and defibration of biomass	
		Partial decrystallization	
		Partial lignin solubilization	
		Increase of hydrolysis rate	
Autohydrolysis pretreatment ⁵	Liquid hot water batch, liquid hot water percolation	Hydrolyzation of cellulose at very high and lower temperature	Energy cost is relatively moderate ³
		High removal of hemicellulose and lignin	
Acid pretreatment ^{5,6}	Sulfuric, hydrochloric, phosphoric, nitric and carbonic acid	Enhancement of hemicellulose hydrolysis	Recovery of acid is expensive ¹⁷
			Corrosion-resistant equipment is costly ¹⁸
Alkaline pretreatment ^{1,5}	Sodium hydroxide, ammonia, lime, potassium hydroxide	Increase of internal surface area	High cost of bases
		Reduction in degree of polymerization, Decrystallization	
		Disruption of lignin structure	
		Breaking of structural linkages between lignin and Carbohydrates	

Table 2 (continue)

Conventional Pretreatment Processes for Biogas Production

Pretreatment	Processes	Function	Economic challenges
Solvent pretreatment ^{7,8}	Organic solvents e.g. methanol, ethanol, acetone, ethylene glycol and hydrofurfuryl alcohol	Solubilization of lignin	High cost of solvent ¹⁹
	Cellulose-dissolving solvents e.g. cadozen, concentrated mineral acids, DMSO*, NMMO** and zinc chloride		Effective recovery of solvent is costly
Leaching ⁹	Organic solvents e.g. hexane, diethyl ether, dichloromethane or ethyl acetate	Removal of inhibitors in citrus waste	
Supercritical fluid pretreatment ¹⁰	Utilizing water, CO ₂ or ammonia	Removal of lignin Increase of biomass digestibility	Highly expensive ³
Oxidative pretreatment ⁴	Oxidizing compounds e.g. hydrogen peroxide or peracetic acid	Removal of hemicellulose and lignin	High cost of chemical ²⁰
		Increase of cellulose accessibility	
Biological pretreatment ^{7,8,11,12,13,14,15}	White rot fungi, brown rot fungi, Enzyme products (cellulase, hemicellulase and β -glucosidase)	Degradation of lignin, degradation of cellulose and hemicellulose	High cost of enzymes ¹⁸
	<i>Bacillus</i> sp., <i>Aspergillus</i> sp. and alkaline endopeptidase	Hydrolyzation of keratin	

* Dimethyl sulfoxide ** N-Methylmorpholine N-oxide

1:(Bochmann et al., 2013), 2:(Onyeche et al., 2002), 3:(Taherzadeh & Karimi, 2008), 4:(Hendriks & Zeeman, 2009), 5:(Johnson & Elander, 2009), 6:(Singh et al., 2014), 7:(Hsu, 1996), 8:(Sun & Cheng, 2002), 9:(Wikandari et al., 2015), 10:(Li & Kiran, 1988), 11:(Fellahi et al., 2014), 12:(Forgács et al., 2011a), 13:(Mazotto et al., 2013), 14:(Patinvoh et al., 2016), 15:(Zaghloul et al., 2011), 16:(Wang et al., 2016), 17:(Xiao & Clarkson, 1997), 18:(Kumar & Murthy, 2011), 19:(Kabir et al., 2015), 20:(Li et al., 2013)

Fig. 1

Biochemistry of Anaerobic Digestion Processes (Modified from (Mkoma & Mabiki, 2011))

Highlights:

- Substrates for biogas might be indigestible, hard to digest, toxic materials
- Indigestible materials can be gasified to syngas and then fermented to biogas
- Recalcitrant biomass can go through a variety of pretreatments
- Toxic substrate can be digested with or without a pretreatment
- Right choice of digesting reactor and criteria can resolve some of these challenges

ACCEPTED MANUSCRIPT