Critical review

Yield improvements in anaerobic digestion of lignocellulosic feedstocks

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**ABSTRACT**

The new EU bioenergy sustainability criteria demonstrate that bioenergy sustainability can be a challenge (Schlegel and Kaphengst, 2007). In 1990s, the energy crops were the main source for biogas production in Europe; however, their competition with food production led these sources to be phased out as sustainable renewables. This makes alternative abundant bioenergy resources such as lignocellulosic materials increasingly interesting. Anaerobic digestion (AD) is a suitable waste management method in which renewable bioenergy can be produced from different feedstocks including lignocellulosic material. Even though the lignocellulose is a biomass with high energy content, it has rigid structure to be used in AD. To overcome this, a pre-treatment method is needed for the complete extraction of the energy in AD. Several pre-treatment methods have shown to be very effective independent of the type of lignocellulose in the biomass. Apart from assessing physical characteristics of lignocellulosic materials and their biogas production potential before and after pre-treatment, this review assesses the developed pre-treatment methods for lignocellulosic feedstocks for AD, and highlights the effectiveness, limitations and challenges of these techniques. This review discusses the possible strategies to implement a lignocellulosic-based biogas plant with optimised net cost and energy consumption through improving process design. Even though high energy yields from the harvested biomass is economically desirable, the solutions with the highest possible energy yield are not necessarily the ecologically best ones. Thermal pre-treatment appears to give the highest increases in methane yields, but the proper balance between high yields and the ecological fate of non-digested carbon containing materials (i.e. lignin in the AD digestate) needs to be further studied. Heat recovery and process integration will be needed to reduce inherent energy consumption in thermal pre-treatment.

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1. Introduction

Biogas production through anaerobic digestion (AD) is a reliable source that replaced 36 Mtoe fossil fuel consumption in 2018 (IEA, 2020). Biogas is a mixture of mainly methane and carbon dioxide that provides a broad range of applications, such as thermal energy production, electricity generation and transportation with reduced pollution effects (Kothari et al., 2010). Biomethane (i.e., the methane component of the raw biogas) production in Europe has increased from 2.5 × 10^11 m³ in 2000 to over 18 × 10^11 m³ in 2015 (Scarlat et al., 2018). Wastewater treatment plants and landfills have produced one-fouth of this biomethane, while the rest has originated from AD plants, due to the increasing potential for biomethane production from different feedstocks through the AD process (Meyer et al., 2018).

AD feedstocks have been divided into three main categories: energy crops (first-generation feedstocks); plant- and seed-residues and livestock wastes including manure (second-generation feedstocks); and, aquaculture products and wastes (third-generation feedstocks) (Allen et al., 2016). In the 1990s, first generation biomass was the main source for biogas production in Europe (Seadi et al., 2013). Despite high biogas production rates, the first generation feedstocks compete with food production making them an undesirable biomass source (Allen et al., 2016). It has been crucial to find alternative sources for biogas production in recent decades, with lignocellulosic materials becoming highly interesting (Schlegel and Kaphengst, 2007). Lignocellulosic biomass can be seen as a suitable feedstock for bioenergy production as it is an available source and does not compete with food production; however, its rigid structure prevents the complete use of these energy sources (Paul and Dutta, 2018). Various methods exist (including physical, chemical, thermal, biological, electrochemical and combined methods), and in some cases have been observed to increase the biogas production when used as biomass pre-treatments (Hassan et al., 2018).

Residues from forest industries and agriculture that contain...
The lignocellulosic-based materials in this paper have been categorized in 5 main classes as:

- agricultural by-products and wastes (i.e., including different types of straws, stovers, bagasse and residues);
- forestry by-products and wastes of hard and soft woods (i.e., branches, roots, bark, wood chips, residues from wood chipping);
- residues from woody industry (i.e., sawdust, wood chips and residues of timber), by-products from pulp and papering industry and residues of oil seeds;
- livestock-based lignocellulosic materials (mainly manure); and,
- grasses, leaves, local plants and flowers, fruit skins and shells.

The purpose of this review can be split into two parts: to give an overview of the various pre-treatment methods available for lignocellulosic biomasses to investigate their potential in biogas production after a pre-treatment step; to assess how these methods can be integrated into existing and new AD plants in terms of economic cost, energy balance, digestibility of the pre-treated feedstock and storage. This review intends to provide valuable economic information and possible technical upgrading methods that can moderate the net cost and energy required for a pre-treatment method. Unlike other recently published review papers that have been focused mainly on challenges and opportunities of pre-treatment techniques (Table 1), the current review paper in addition to dealing with the different pre-treatment methods, temped to comparing large number of experimental results in this field in order to give an overview of biogas production potential of different lignocellulosic materials before and after pre-treatment as well as selecting the most effective pre-treatment method for various feedstock categories.

2. Anaerobic digestion

Anaerobic digestion is a biological process including four main steps (i.e., hydrolysis, acidogenesis, acetogenesis and methanogenesis), which converts organic and inorganic substrates (i.e., ranging from complex to easily-degradable components) to biogas through biological pathways (Steffen et al., 1998). Biogas mainly contain 30–50% carbon dioxide (CO₂) and 50–70% methane (CH₄); however, depending on feedstocks and operational condition, it may also contain hydrogen (H₂), hydrogen sulfide (H₂S) and nitrogen (N₂) (Metcalfe et al., 2014). The methane content in the biogas not only depends on organic biomass sources, but also varies with operational conditions (Zhang et al., 2014).

Enzymatic hydrolysis is the first step of AD, where complex organic polymers including protein, lipid and carbohydrates are produced from complex materials as a result of intracellular enzymatic activity of cells (Jain et al., 2015). Then acidoferment bacteria (Li et al., 2019) decompose components from hydrolysis step and converts them to volatile fatty acids, CO₂ and hydrogen (Ziganshin et al., 2013). Acidogenesis products (e.g., butyrate, valerate and propionate) are further fermented by acetogenic microorganisms to acetate, CO₂ and hydrogen (Aryal et al., 2018). These final products of fermentation steps (acetate, CO₂, H₂) are used by the methanogenesis step to produce methane, carried out with a group of Archaea organisms known as methanogens (Ziganshin et al., 2013). Two main types of methanogens are active in the final step of AD process. The first group, called acetoclastic methanogens produce methane from acetates, while the second group, hydrogenotrophic methanogens, produce methane from hydrogen and CO₂. Hydrogenotrophic methanogens use hydrogen as the electron donor and CO₂ as electron acceptor to produce methane in a strict anaerobic condition (Metcalfe et al., 2014).

Table 1
The Main Focus Area of Recently Published Review Paper for Biogas Production from Lignocellulosic Materials and The Novelty of The Current study.

| Area of Focus and Achievements | Studies |
|--------------------------------|---------|
| Overview of different pre-treatment methods in order to increase the biogas production rate from lignocellulosic materials in AD. Challenges and opportunities of using lignocellulos as a substrate in AD. Physical characteristic of lignocellulosic biomass. | Current study and Refs. (Dahadha et al., 2017; Hassan et al., 2018; Hernández-Beltrán et al., 2019; Hosseini Koupaei et al., 2019; Kainthola et al., 2019a; Mishra et al., 2018; Solarte-Toro et al., 2019; Zheng et al., 2014a) |
| Pre-treatment severity and operational condition. | Current study and Refs. (Dahadha et al., 2017; Hassan et al., 2018; Hernández-Beltrán et al., 2019; Hosseini Koupaei et al., 2019; Mishra et al., 2018; Solarte-Toro et al., 2019; Usmani et al., 2020; Van Fan et al., 2018) |
| Considering electrochemical methods as a potential pre-treatment method for lignocellulosic biomass. Assessing hybrid pre-treatment methods. | Current study |
| Overall biogas production yield improvement through applying different pre-treatment methods. Comparison of biogas production potential of lignocellulosic-based materials before and after a pre-treatment process from experimental data. Gathering a large number of lab- and full-scale research results in order to select the most efficient pre-treatment technique. Techno-economic assessment of various pre-treatment techniques. Economic and energy-based analysis of the pre-treatment processes. Environmental concerns associated with the utilisation of different lignocellulosic-based biomass for AD. Implementation and integration approaches for moderate cost and energy consumption in AD. Kinetic modelling of lignocellulose-based AD | Current study |
| Current study and Refs. (Hassan et al., 2018; Hernández-Beltrán et al., 2019; Solarte-Toro et al., 2019) |
| Refs. (Solarte-Toro et al., 2019; Usmani et al., 2020; Van Fan et al., 2018) |
| Current study and Refs. (Dahadha et al., 2017; Mishra et al., 2018; Van Fan et al., 2018) |
| Current study and Refs. (Hernández-Beltrán et al., 2019; Kainthola et al., 2019a) |
| Refs. (Kainthola et al., 2019a; Solarte-Toro et al., 2019; Yu and Wensel, 2013) |
3. Lignocellulosic feedstocks

Lignocellulose is the main component of plants and is considered as one of the most abundant biomasses in the world. The forestry industry, agricultural by-products, pulp and paper industry, livestock manure and the residues from the wood industry are examples of lignocellulosic sources (Dashtban et al., 2010; Hernández-Beltrán et al., 2019). In addition, the pulp and paper mill sludge contains lignocellulosic materials and can be served as a substrate for biomethane production (Pan et al., 2015). Lignocellulosic biomass mainly consists of cellulose, hemicellulose and lignin. The interaction of these components results in a highly resistant material, making hydrolysis the rate-limiting step during AD (Jain et al., 2015). Lignocellulosic materials have a limited degradability under AD condition without pre-treatment (Hosseini Koupaei et al., 2019), resulting in a reduced methane yield in terms of their energy content. This is due to some fractions of the materials not being easily degradable (Sarker et al., 2019). The size and proportion of individual structural components of the substrate play an essential role in the rate of the hydrolysis process (F. Ödner, I. Horváth, M. Kabir, 2012), and lignocellulosic feedstocks must be broken down into smaller constituents to maximise their hydrolysis potential during AD.

3.1. Characteristics of lignocellulose

Lignocellulose mainly consists of two hydrocarbon polymers known as cellulose and hemicellulose, and one aromatic polymer called lignin that has a rigid structure (Kanthola et al., 2019a; Sánchez, 2009). The composition of the cellulose, hemicellulose and lignin components varies based on its source (Table 2). Cellulose is a stable polymer of linear chains of up to 12,000 D-glucose units attached by β-1,4-glycosidic bonds with an average molecular weight of 100 kDa (Anwar et al., 2014; Sánchez, 2009). The fundamental shape of cellulose (also called elementary fibrils), is created from hydrogen bonding of 60–70 cellulose polymers, which results in fibril crystals. As a result of its strong crystalline structure, cellulose has high tensile strength and is insoluble in water (Dashtban et al., 2010; Menon and Rao, 2012). Cellulose is also difficult to degrade biologically, unless enough hydrated area is provided for hydrolysis enzymes such as cellulase (Dashtban et al., 2010; Menon and Rao, 2012).

Hemicellulose is a randomly branched polymer (Anwar et al., 2014; Dashtban et al., 2010) of different polysaccharides including xylose, arabinose, glucose, galactose, mannose and sugar acids (Sánchez, 2009; Tian et al., 2018). The average molecular weight of the hemicellulose is less than 30 kDa and its abundancy in lignocellulosic biomass varies depending on the source (Anwar et al., 2014). Hemicellulose is connected to cellulose through hydrogen bonds, and is also linked to lignin. In order to degrade hemicellulose biologically, multiple enzymes such as cellulase, hemicellulase and xylanase are required to break its structural heterogeneity (Menon and Rao, 2012; Wagner et al., 2018). Process monitoring and adaption are essential in order to reduce the concentration of AD inhibitors such as furfurals and hydroxymethyl furfurals that mostly originate from hemicellulose at high temperature (Haghighi Mood et al., 2013).

Lignin is an amorphous heteropolymer that is non-soluble in water (Dashtban et al., 2010). It is composed of phenolic components including guaiacyl propanol, p-hydroxyphenyl propanol and syringyl propanol (Sánchez, 2009). Lignin is connected to both cellulose and hemicellulose, and acts as a barrier against all solutions and enzymatic attack. In order to hydrolyse biodegradable materials of plant biomass, an effective method for degrading lignin is essential (Anwar et al., 2014; Menon and Rao, 2012).

3.2. Lignocellulose-based carbon cycle

When considering lignocellulosic biomass as a source of energy, it is important to consider their carbon cycle. It can take decades to regenerate a given volume of plant biomass through the growth of new plants. During this rotation period, emitted CO₂ from the biomass consumption can contribute to global warming (coined “carbon debt”) (Holtsmark, 2012; Lien, 2013). It is beneficial to use biomass sources that have short rotation times for biofuel production to minimise the carbon debt. This means that the harvesting of trees with long rotation times may lead to CO₂ accumulation in the atmosphere, as the transfer of CO₂ into the soil is reduced when there are less trees (Holtsmark, 2012; Lien, 2013).

Plants have a crucial role in CO₂ transfer from the atmosphere to the soil through carbon fixation by photosynthesis (Holtsmark, 2012; Lien, 2013). During photosynthesis, CO₂ from the atmosphere is converted to the organic compounds. This can be used as an energy source or building block in the plant (Fleischman, 2012). It is estimated that each year approximately 250 × 10⁸ Tonnes CO₂ can be stored in biomass (Geider et al., 2001). The soil organic matter (SOM) is composed of carbon-rich materials such as plant residues, animal tissue and highly recalcitrant materials with long residence time in soil (known as humus) (Oglesby et al., 1968). Soil organic carbon (SOC) level is directly affected by the SOM through

**Table 2**

Polymeric composition of different types of lignocellulosic biomass.

| Lignocellulosic material | Composition % | References |
|--------------------------|--------------|-----------|
|                          | Lignin | Hemicellulose | Cellulose |
| Newspaper | 21 | 21.7 | 64.4 | TNO (2019) |
| Paper mixed waste | 33.55–40.9 | 13.24–16.3 | 45.12–46 | TNO (2019) |
| Banana waste | 14 | 14.8 | 13.2 | John et al. (2006) |
| Olive cake | 28.13 | 20.28 | 28.4 | TNO (2019) |
| Olive husk | 45–48.5 | 21–33 | 22–24 | TNO (2019) |
| Olive pit | 25.3–31.2 | 37.2 | 28.1 | TNO (2019) |
| Wheat straw | 16–21 | 26–32 | 29–35 | McMendry (2002) |
| Rice straw | 17–19 | 25–25.9 | 28.2–34.7 | Prasad et al. (2007) |
| Corn cobs | 15 | 35 | 45 | Chandra et al. (2012a) |
| Corn Stover | 11–10.1 | 20.7–24.6 | 35.1–39.5 | Mosier et al. (2005a) |
| Sweet sorghum | 21 | 27 | 45 | Kim and Day (2011) |
| Hardwood | 18–25 | 24–40 | 40–55 | Chandra et al. (2012a); Malherbe and Cloete, 2002 |
| Softwood | 25–35 | 25–35 | 45–50 | Chandra et al. (2012a); Malherbe and Cloete, 2002 |
| Leaves | 0 | 80–85 | 15–20 | Chandra et al. (2012a) |
| Grasses | 10–30 | 25–50 | 25–40 | Malherbe and Cloete (2002) |
several ecosystem processes including photosynthesis, respiration and decomposition (Miltner et al., 2005). Plant growth, death and transfer of carbon-enriched compounds from roots to soil microbes affects the soil carbon (Ontil, 2012). As long as the carbon inputs (e.g., plant root, leave and branches) and outputs (CO₂ loss due to biomass decomposition by microbes) are in balance, the SOC level remains unchanged. When carbon inputs from photosynthesis increases, the SOC level may increases over time (Ontil, 2012).

Lignin has a significant role in transferring atmospheric carbon to the soil (Oglesby et al., 1968). Lignin is considered as one of the main components of soil organic matter (SOM) due to its aromatic structure. Due to its complex structure, Lignin can only be degraded by a few bacteria (e.g., Streptomyces sp. or Nocardia sp.), and some fungi (especially white- and brown-rot fungi). Lignin is transferred to the soil through aboveground and underground structures (e.g., leaves and roots) (Thevenot et al., 2010). As an example of the underground carbon transfer system, the Arbuscular mycorrhizal fungi (AMF) creates a symbiotic mutualism with roots of terrestrial plants and trades carbon from the plant for nitrogen and phosphor. AMF fungi can secrete long carbon chain glycoproteins (i.e., gloculin), which accumulate in the soil through adhesion of soil particles and increases carbon storage due to its natural cross-linking (H. Yang et al., 2019). The brief description is necessarily quite simplified and there are many aspects of the fate of lignin in soil that are still not well understood, in particular related to how local environmental factors such as temperature and humidity (rainfall) will affect the rate of lignin decomposition.

3.3. Available lignocellulosic feedstock for AD

Lignocellulosic biomass have broad applications ranging from building material to producing bioenergy. Since wood is a renewable resource, there is a tremendous potential for its utilisation in producing significant amounts of energy. The wood industry can provide raw materials such as hardwood, bark, branches and sawdust for biogas production (Ballesteros et al., 2018; Ministry of Agriculture and Food, 2014). According to Klitkou et al. (2019), two-thirds of a tree is utilised as sawn timber, with the rest as sawdust and fine particles. Wood mill wastes (e.g., wood chips, pulpwood and forest waste) are useable as sources for biogas production that can have a significant impact on profitability throughout the forest-based value chain (Klitkou et al., 2019; Treindustrien, 2016).

Some of the by-products such as wood chips, bark, wood pulp and sawdust can be used in the pulp and paper industry (Ghose and Chinga-Carrasco, 2013). The wastewater from the pulp and paper industry contains around 1 m³ of sludge per ton of paper produced (Veluchamy and Kalamdhad, 2017), which can be employed as a substrate for biogas production. Veluchamy and Kalamdhad (2017), reported 254 ml biogas production from pulp and paper sludge within 45 days through batch AD, where the feed-to-microorganism ratio was 2:1. Although the sludge from pulp and paper can be used as a substrate in AD, it needs some pre-treatment due to the presence of highly resistant components such as lignocellulose in the feedstock (Priadi et al., 2014; Veluchamy and Kalamdhad, 2017).

Another example of a lignocellulosic biomass is herbivore manure, which has a large unutilised potential for use in biogas production (Bruni et al., 2010). Livestock manure is readily degradable, and the bacteria that drive the biogas process are already present in the substrate, ensuring stable reactor function and biogas production. The disadvantage is that readily degradable organics have already been partially broken down in the digestion tract, leaving majority of the obstinate compounds in the manure (Miaik et al., 2019). As a result, appropriate pre-treatment processes are required to increase the biogas production yield (Zieliński et al., 2019b).

4. Pre-treatment methods

The methane share of raw biogas obtained from untreated plant-based lignocellulosic substrates can be as low as 20% (Alizadeh et al., 2005). Pre-treatment methods (Fig. 1) for lignocellulosic biomass are used in order to increase the methane content and enhance biogas production (Hernández-Beltrán et al., 2019). Various factors affect the digestibility of lignocellulose. These including the degree of crystallinity of the cellulose, lignin and hemicellulose content (Hendriks and Zeeman, 2009). The moisture content and the accessible surface area for enzymatic hydrolysis affect the digestibility (Sun et al., 2016). The pre-treatment methods for different substrates vary because of the characteristic variations of the biomass (Taherzadeh and Karimi, 2008; Han Zhang et al., 2018). The most effective pre-treatment methods would need to address the following requirements (Bochmann and Montgomery, 2013):

• providing a water soluble substrate for AD (Fig. 2) (Hernández-Beltrán et al., 2019);
• providing low crystallinity of cellulose (Mancini et al., 2016a);
• increasing the accessible surface area for enzymatic attack and boosting the hydrolysis rate in AD process ( Hosseini Koupai et al., 2019);
• breaking hydrogen bonds between cellulose and hemicellulose (Taherzadeh and Karimi, 2008);
• low concentrations of AD inhibitors in the feedstock (Ravindran and Jaiswal, 2016); and,
• diminishing requirements for utilisation of chemicals and energy (Carlsson et al., 2012).

4.1. Physical pre-treatment

Physical pre-treatment (also known as mechanical pre-treatment) of lignocellulosic materials counts as the first step of substrate preparation for the biogas production process (Kratký and Jirout, 2011). The particle size is significantly reduced through physical pre-treatment, which leads to an increased accessible surface area for enzymes. These methods are not capable of removing or degrading lignin (Kratký and Jirout, 2011; Tedesco et al., 2014). Since mechanical pre-treatment can be an energy-intensive process (Hu et al., 2005), it is not economical to use it for particle sizes smaller than 0.4 mm as it does not have further effect on biogas production improvement (Kang et al., 2019; Sharma et al., 1988). According to previous studies (Kang et al., 2019; Pommier et al., 2010), excessive size reduction can also increase the concentration of inhibitors, leading to VFA accumulation in the system. Table 3 gives the methane yield enhancement by different physical pre-treatment methods for lignocellulosic materials.

4.1.1. Grinding

Grinding processes are methods that can be used for biomass size reduction (Kratký and Jirout, 2011). These processes increase the ability of the particles to dissolve. Grinding is an energy-intensive process, and the energy consumption of the grinding technologies varies with the type of feedstock, moisture content and biomass composition. The energy required for the hammer mill can vary between 5 and 60 kWh/ton of pre-treated biomass (Sharma et al., 1988a; Tumuluru and Heikila, 2019). The grinding process is capable of reducing particle size as small as 0.02 mm (Masa Cater et al., 2014), leading to the high amount of surface area accessible for hydrolysis. It can also reduce the crystallinity of the cellulose, which can increase the biogas production rate during AD (Dumas et al., 2015; Ziemiński and Kowalska-Wentel, 2017).
4.1.2. Chipping

The chipping process is widely used for physical size reduction of enormous waste biomasses such as timber, straw residues and corn stover (Rodriguez et al., 2018). The main application of

| Treatment method | Substrate            | Particle size | Methane yield (untreated) | Methane yield (treated) | Increased biomethane mL/g VS | Treatment condition                        | Ref.                                  |
|------------------|----------------------|---------------|---------------------------|-------------------------|-----------------------------|------------------------------------------|---------------------------------------|
| Grinding         | Wheat straw          | 0.088 mm      | 235 mL/g TS               | 362 mL/g TS             | 127                         | 5 L batch AD bottle, 37 °C               | Sharma et al. (1988)                  |
|                  | Rice straw           | 0.4 mm        | 320 mL/g TS               | 487 mL/g TS             | 167                         | 5 L batch AD bottle, 37 °C               | Sharma et al. (1988)                  |
|                  | Mirabilis leaves     | 0.4 mm        | 355 mL/g TS               | 418 mL/g TS             | 63                          | 5 L batch AD bottle, 37 °C               | Sharma et al. (1988)                  |
|                  | Sugar beet pulp      | 2.5 mm        | 351.4 mL/g VS             | 452.1 mL/g VS           | 100.7                       | Lab-scale batch AD                      | Ziemiński and Kowalska-Wentel (2017) |
| Cavitation       | Cauliflower leaves   | 0.088 mm      | 440 mL/g TS               | 520 mL/g TS             | 80 mL/g TS                  | 5 L batch AD bottle, 37 °C               | Sharma et al. (1988)                  |
|                  | Birch wood           | 0.4 mm        | 170 mL/g TS               | 282 mL/g TS             | 112 mL/g TS                 | 5 L batch AD bottle, 37 °C               | Sharma et al. (1988)                  |
|                  | Spruce               | Alkaline ball mill, < 0.8 mm | 30 mL/g TS | 50 mL/g TS | 20 mL/g TS | Lab-scale AD | Mirahmadi et al. (2010) |
|                  | Banana peeling       | 0.04 mm       | 460 mL/g TS               | 510 mL/g TS             | 50 mL/g TS                  | 5 L batch AD bottle, 37 °C               | Garuti et al. (2018)                  |
|                  | Wheat straw          | --            | 60 mL/g TS                | 77.9 mL/g TS            | 17.9 mL/g TS                | Batch AD, 37 °C, hydrothermal cavitation | Patil et al. (2016)                   |
|                  | Agricultural residue | --            | --                        | --                      | 10% increased               | Full-scale biogas plant, 42–43 °C        | Zieliński et al. (2019a)            |
|                  | Cattle manure/ wheat straw | -- | 193 mL/g VS | 227.9 mL/g VS | 34.9 | Full-scale AD, mesophilic cavitation | Zieliński et al. (2019a) |
|                  | Cattle manure/ wheat straw | -- | 193 mL/g VS | 249 mL/g VS | 56 | Full-scale AD, ultrasonic cavitation | Zieliński et al. (2019a) |
|                  | Grubben deflaker and a Krina disperser | -- | 151 mL/g VS | 255 mL/g VS | 104 | Batch lab-scale AD, 37 °C, 36 days | Lindmark et al. (2012) |
|                  | Lay silage           | <2 mm         | 151 mL/g VS               | 235 mL/g VS             | 84                          | Batch lab-scale AD, 37 °C, 36 days        | Lindmark et al. (2012)               |
|                  | Lay silage           | <2 mm         | 210 mL/g VS               | 254 mL/g VS             | 44                          | Batch AD, 0.5 L batch, 37 °C             | (C. Rodriguez et al., 2017)          |

Fig. 1. Different pre-treatment methods for lignocellulosic biomass.
chipping is to reduce the size of biomass in order to increase heat and mass transfer. The chipping processes are less effective compared to grinding and milling processes, and the final particle sizes from chipping varies between 10 and 30 mm. Although chipping methods provide uniform wood chips, the final biomass form does not affect the biogas production yield (Kumar and Sharma, 2017; Cristina Rodriguez et al., 2017).

4.1.5. Grubben de

When compared to grinding and milling processes, and the chipping is to reduce the size of biomass in order to increase heat (B. Hashemi, S. Sarker, J.J. Lamb et al. Journal of Cleaner Production 288 (2021) 125447).

form does not affect the biogas production yield (Kumar and chipping methods provide uniform wood chips, the sizes from chipping varies between 10 and 30 mm. Although concentration of potential inhibitors (Corbett et al., 2018; Park et al., 2016). The mechanical refining process can decrease the severity of the thermal and chemical pre-treatment processes and reduce pre-treatment cost and energy requirements (Batalha et al., 2015). Due to the low severity condition, the final products contain a lower concentration of potential inhibitors (Corbett et al., 2018; Park et al., 2016). It has been reported that mechanical refining can enhance the sugar yield from the biomass and improve the conversion of up to 8% of sugars to the fermentable sugars (Cheng et al., 2019). It has been observed that the liquid hot water process has a 5–15% higher sugar yield compare to the mechanical refining (Cheng et al., 2019).

4.1.4. Cavitation

Cavitation occurs by rapid formation, growth and collapse of gas- or vapour-filled bubbles. Ultrasonic and hydrodynamic methods are the main types of cavitation processes. Cavitation bubbles provide shock waves that lead to mechanical effects like particle erosion resulting in size reduction and recrystallisation of cellulose (Patil et al., 2016). The cavitation pre-treatment processes increase the accessible surface area, and some recrystallisation has been reported (Garutti et al., 2018). The presence of the AD inhibitors has been detected after cavitation pre-treatment (Terán Hilares et al., 2018). Among different types of cavitation, the ultrasonic cavitation has shown better results in terms of biomass production (Islam et al., 2019; Lamb et al., 2019). The process efficiency has been significantly improved when it is integrated with chemical pre-treatment (Zielinski et al., 2019a).

4.1.5. Grubben deflaker and Krima disperser

During physical pre-treatment by the deflaker method the substrate structure changes into a pulp-like material. In the disperser system, watery substrates pass through a narrow entrance between rotary discs and then travel along a screw that reduces the particle size (Lindmark et al., 2012). The deflaker has a positive energy balance, while disperser systems have a break-even energy balance. Digestion time for final products is quite long (>25 days), which increases the total cost of the system (Lindmark et al., 2012; Cristina Rodriguez et al., 2017).

4.1.6. Hollander beater

The Hollander beater is used in the pulp industry to break down the structure of cellulose. It consists of circular or oval metal blades to cut and chop suspension (Rodriguez et al., 2018). The final products usually contain metal contaminants originating from the blade materials (Tedesco et al., 2013, 2014). This method increases available surface area for enzymatic hydrolysis and reduces the cellulose crystallinity without providing inhibitors for the AD process (Zhou et al., 2018).

From Table 3 it can be concluded that cavitation is the least effective physical pre-treatment with average biomethane yield improvements of 21.7 ± 8%. The grinding with deflaker and disperser are more effective with an average biomethane yield improvement of 62.2 ± 6%. The agricultural by-products and wastes (i.e., ley silage, grasses and straws), can be converted to a useable source for biogas production in mesophilic conditions (i.e., operating temperature between 35 and 45 °C), after physical structure disruption.

4.2. Thermal pre-treatment

Thermal pre-treatment employs elevated temperatures (between 150 and 240 °C) and pressures (up to 35 bar) to break the structure of the lignocellulosic material (Masa Cater et al., 2014). Depending on several factors such as temperature, pressure, residence time and moisture content, thermal pre-treatment processes can reduce the particle size and increase the available surface area for enzymes. This method not only reduces cellulose crystallinity but also facilitates the depolymerisation of hemicellulose (Paul and Dutta, 2018; Yan et al., 2009).

The end products of thermally pre-treated lignocellulosic materials do not have adverse environmental effects, which is considered as an advantage compared to chemical pre-treatments (Digman et al., 2010; Kaldís et al., 2017). Thermally treated biomass contains some inhibitory products (such as furfural and hydroxyl methyl furfural) due to the higher solubility of hemicellulose in the elevated temperatures; however, culture adaptation can reduce the inhibitory effects (Masa Cater et al., 2014; Paul and Dutta, 2018). Recent studies have shown that the energy efficiency and biogas yield from lignocellulosic biomass can significantly increase if thermal pre-treatment methods are integrated with chemical or biological processes (Shi et al., 2019; Y. Wang et al., 2019). Table 4 summarises the effect of different thermal pre-treatment methods on methane yield from lignocellulosic material.

4.2.1. Hydrothermal, liquid hot water extraction

Pressure is employed to maintain water in the liquid phase at a temperature range between 120 and 260 °C to penetrate the biomass (Mlaik et al., 2019). At elevated temperatures (around 200 °C), water and organic acids from hemicellulose boost the hemicellulose degradation into the monomeric sugars. Depending on the operational temperature, it can also cause acid accumulation and subsequently an acidic environment. This results in improved access to the cellulose for enzymatic hydrolysis as well as providing organic-rich liquid for further degradation (2019; Pérez et al., 2008; Wan and Li, 2011). Presence of hydroxymethyl-furfural (HMF), furfural, formic acid and levulinic acid in the liquid fraction can act as an AD inhibitor in high temperatures and can reduce the pH (Jiang et al., 2016). In order to control the concentration of acidic components, utilisation of some base chemicals or a combination of hydrothermal pre-treatment with other types of pre-treatment processes is recommended. By including liquid hot water, hydrothermal processes increase the accessible surface area and can enhance the degradability of hemicellulose; however, generally the net energy gained from the methane yield enhancement is lower than the energy input to the liquid hot water process (Chandra et al., 2012c; Wang et al., 2018).

4.2.2. Microwave heating

Electromagnetic energy is converted to thermal energy inside the particle volume leading to one or more changes in lignocellulose (Sapci, 2013). High temperature can reduce the crystallinity of the cellulose, disruption of polar bonds, depolymerisation of lignin, and increase the accessible surface area for enzymatic hydrolysis. It has been reported (Sapci, 2013; B. Zhao et al., 2017) that biogas production from several types of straws is reduced after microwave
heating in elevated temperatures (between 200 and 300 °C). The main advantages of this method are the uniform and controllable heating, short process times, fast heat transfer, easy operation and low concentration of hazardous products (Kainthola et al., 2019b; Zieliński et al., 2019b).

### 4.2.3. Extrusion

Extrusion is a thermal-mechanical pre-treatment method that employs one or two screw conveyors inside a tube (Panejunto and Genon, 2016). The temperature and pressure inside the tube rises due to high shear forces between raw materials, tube surfaces and the screw conveyors (Duque et al., 2017; Hjorth et al., 2011). At the outlet point, the pressure drops suddenly, which may further break down the substrate structure. Extrusion pre-treatment reduces the particle size and improves the biomethane yield; however, the substrate type has a significant effect on energy consumption and methane yield. Presence of impurities like stone or metallic materials can significantly affect the screw lifetime (Chen et al., 2014; Lamsal et al., 2010).

### 4.2.4. Torrefaction

Torrefaction (or low-temperature pyrolysis) is a thermal process where the biomass is converted to coal-like particles with a higher energy content than the original biomass (Biomass Technology Group, 2017). The torrefaction process changes the physical and chemical composition of the biomass through heating the biomass in the temperature range between 200 and 400 °C in the absence of the oxygen (Ribeiro et al., 2018; Uemura et al., 2015). The final product of torrefaction is brittle and is a material that is easily ground to smaller particles. The significant reactions of torrefaction are related to the decomposition of the hemicellulose. The products from the torrefaction process cannot directly be used for biogas production; however, biochar produced after grinding can increase the biogas production rate and methane yield in the AD compared to the untreated biomass (Mumme et al., 2014; Pan et al., 2019).

### 4.2.5. Steam explosion

Steam explosion is considered as the most cost-effective and most straightforward thermal-based pre-treatment process (Lizasoain et al., 2016; Vivekanand et al., 2013). Lignocellulosic biomass is exposed to saturated steam for a specific retention time (Pielhlop et al., 2016). The steam penetrates the inner structure of lignocellulose, and then a sudden pressure drop leads to vapour explosion (Fig. 2). This phenomenon not only disrupts the lignocellulose structure by size reduction of particles, but also hydrolyses hemicellulose into sugars. The biogas production and methane yield from steam-exploded biomass is increased significantly through this method (Horn et al., 2011; Shi et al., 2019). Vivekanand et al. (2013) has reported that in hardwoods, the steam explosion yield can increase the biogas yield up to 1.8 times compared to untreated biomass. They have also claimed that in high severity factors (4.5), lignin can also be converted into biomethane (Vivekanand et al., 2013). More furfural is formed in the steam explosion compared to hydrothermal and microwave heating processes; however, unlike ethanol production processes, in the case of biogas production, adapted cultures can solve inhibition issues (Horn et al., 2011; Shi et al., 2019).
industry, and thermal pre-treatment methods could improve the methane content of these substrates even more, although a high standard deviation in the percentage improvement is observed from the different methods.

4.3. Chemical pre-treatment

Commonly used chemical pre-treatment methods are based on the application of acid, base or ionic liquids in order to disrupt the structure of the lignocellulosic material with an acceptable pre-treatment rate (Kucharska et al., 2018; Tu and Hallett, 2019). The major effects of chemicals on lignocellulose are:

- removing lignin (i.e., alkaline based methods) and hemicellulose (i.e., acidic pre-treatment methods), which leads to an increase in the accessible surface area for enzymatic hydrolysis (Je;drzejczyk et al., 2019); and,
- reducing the crystallinity of cellulose (Baruah et al., 2018).

Although chemical pre-treatment methods are efficient methods for lignocellulose pre-treatment with short substrate retention time, some concerns such as the high cost, effectiveness of chemical recovery and chemical discharge into the environment are the most critical barriers in large scale applications. Table 5 gives an overview of methane yield enhancement due to the chemical pre-treatment methods.

4.3.1. Acidic pre-treatment

Acidic chemicals such as H2O2, HCl, H2SO4 and other organic acids (e.g., H3PO4 and HNO3) are used to break down the polymeric bonds of the hemicellulose to release xylose. The cellulose is then exposed to enzymes and degraded to monomeric sugars (Tu and Hallett, 2019; Yao and Chen, 2016). The severity of the acidic pre-treatment can increase the concentration of inhibitors in the biomass, and diluted acid solution can be favourable over concentrated acids (Chen et al., 2015; Keskin et al., 2019). Apart from the high efficiency and high treatment rate of the acidic pre-treatment, it introduces some operational problems (Kristiani et al., 2013). For instance, the acidic reject water from this process is challenging to handle. Moreover, due to the low pH of the pre-treatment process, specific corrosion-resistant materials are needed for the pre-treatment reactors. These factors increase both implementation and operation costs (Jaffar et al., 2016; Jiang et al., 2017).

4.3.2. Alkaline pre-treatment

Several types of bases (e.g., NaOH, Ca(OH)2, ammonia solution, alkaline H2O2, KOH and urea) have been investigated in for enhancing biogas production from lignocellulosic biomass via solubilization of hemicellulose (Yao and Chen, 2016). Alkaline pre-treatment methods have superiority over other chemical pre-treatment methods in depolymerisation of the lignin and providing accessible surface area for enzymatic activities. These methods generally are conducted in moderate temperature and pressure and of all chemicals used for alkaline pre-treatment, NaOH and Ca(OH)2 are preferred and provide a better substrate for the AD process (Chandra et al., 2012c; Zheng et al., 2018). Alkaline pre-treatment can enhance the buffering capacity of the AD system and prevent inhibition of the AD process due to acid accumulation, but in high dosages, it can increase methanogen inhibitors such as furfural, vanillin and lignin polymers (Jiang et al., 2017). The ammonia based pre-treated substrates may imbalance the carbon: nitrogen ratio, resulting in inhibitory effects for many bacteria, especially acetotrophic methanogens. Free ammonia can disrupt potassium and proton balance inside the cell by diffusing into the cell membrane (Zhang et al., 2014). NaOH is an expensive chemical for industrial-scale applications, and less expensive chemicals such as Ca(OH)2, urea or ammonia can prove to be a useful alternative for lignocellulose pre-treatment (Sajad Hashemi et al., 2019). Alkaline solvent recovery can be an additional option to reduce the operational costs of the system. Unlike the ammonia solvents that have high solubility, the main disadvantage of Ca(OH)2 is its low solubility that limits the reuse of this solvent (Jaffar et al., 2016; Nowicka et al., 2019).

4.3.3. Redox reactions and Fenton reactions

Redox reactions (also known as oxidation/reduction reactions) refer to electron transfer from a reducing agent (electron donor) to an oxidizing agent (electron acceptor) (Lamb et al., 2019; Oxidation-Reduction Reactions). In any condition, the oxidation and reduction take place simultaneously, and it cannot occur independently (Maamir et al., 2017; Michalska et al., 2012). One of the chemical methods for lignocellulose pre-treatment based on the Redox processes is using Fenton-like reactions. During this process, a Fenton reagent (a solution of hydrogen peroxide, H2O2 reacts with iron sulfate (FeSO4) to generate Fe3+: Various ferrous ions (H2O2 and H+) and ferric ions (H2O2 and H+) are produced through oxidation of the ferric ions and H2O2. This cycle goes on until the H2O2 is depleted. The efficiency of this process depends on the concentration of the H2O2, the Fe2+/H2O2 ratio, the pH and the residence time (Lamb et al., 2019; Maamir et al., 2017).

4.3.4. Ionic liquid

Ionic liquid pre-treatment uses molten salts (like 1-ethyl-3-methylimidazolium acetate) and organic components such as N-methyl morpholine-N-oxide in moderate temperatures to cause the dissolution of the biomass components (Allison et al., 2016). Theses solvents can destroy the hydrogen bonds of cellulose and form new hydrogen bonds resulting in a reduction in cellulose crystallinity. Along with structural changes, the ionic liquids are capable of partial lignin removal (Kabir et al., 2014; Mancini et al., 2016b). Solvents in ionic liquid pre-treatments have a massive potential for recovery (more than 98%). The ionic liquid pre-treatment is more environmentally friendly, as by-products of the process have low toxicity, and ionic pre-treated biomass has a short digestion time through AD (Cheng et al., 2017; Mancini et al., 2016b, 2018).

Independent from the feed type, the acidic, alkaline and ionic liquid pre-treatment methods have shown better performance in biomethane yield improvement compared to the redox reaction methods. The chemical methods seem to be most effective when the substrate is agricultural-based rather than forestry by products and wastes (Table 5).

4.4. Biological and enzymatic pre-treatment

For an extended period, it was assumed that lignin is a resistant component in AD. In 1970, Barrie et al. were able to convert lignin to methane via anaerobic co-digestion (Barrie et al., 1970). It has been reported in several papers that the β-O-4 bond of lignin can be oxidised in the presence of sulfate-reducing bacteria (Kim et al., 1998). These bacteria compete with methanogens for hydrogen and acetate. The methanogens are capable of directly using lignin due to the complex structure of lignin. They degrade it through a co-metabolism by consuming easily degradable substrates. The radical components released during degradation of the cellulose can enhance the oxidation of lignin-derived aromatic materials in AD (Maso Cater et al., 2014). Kato et al. (2015) employed an enriched methanogenic microbial community in order to assess the degradation of the lignin-derived aromatic components (vanillate and syringate). The results from this study showed that the
Table 5
Common chemical pre-treatment methods for lignocellulosic material.

| Substrate                  | Pre-treatment condition | Methane yield (untreated) | Methane yield (treated) | Increased biomethane mL/g VS | Treatment condition | Ref.          |
|---------------------------|-------------------------|---------------------------|-------------------------|----------------------------|---------------------|--------------|
| Acidic                    |                         |                           |                         |                            |                     |              |
| Corn straw                | 3% \(+\)/H\(_2\)O\(_2\), 22 \(^\circ\)C, 7 days | 100.6 mL/g VS             | 216.7 mL/g VS           | 116.1                      | Lab-scale AD, (Z. Song et al., 2014) | (2014)       |
| Corn straw                | 2% \(+\)/HCl, 22 \(^\circ\)C, 7 days | 100.6 mL/g VS             | 163.4 mL/g VS           | 62.4                       | Lab-scale AD, (Z. Song et al., 2014) | (2014)       |
| Corn straw                | 2% \(+\)/H\(_2\)SO\(_4\), 22 \(^\circ\)C, 7 days | 100.6 mL/g VS             | 175.6 mL/g VS           | 75                         | Lab-scale AD, (Z. Song et al., 2014) | (2014)       |
| Cotton waste              | Citric acid 0.5 mmol/g VS | 95.4 mL/g VS              | 147.1 mL/g VS           | 54                         | Lab-scale AD, Pelleria and Gidarakos (2018) |              |
| Pulp and paper sludge     | H\(_2\)PO\(_4\), pH = 2  | 227 mL/g VS               | 359 mL/g VS             | 132                        | Lab-scale AD, Montelius (2014)         |              |
| Pulp and paper sludge     | H\(_2\)PO\(_4\), pH = 4  | 227 mL/g VS               | 303 mL/g VS             | 76                         | Lab-scale AD, Montelius (2014)         |              |
| Swine manure              | 7 mL HCl for 300 g manure | 206.7 mL/g VS             | 173 mL/g VS             | –33.7                      | Lab-scale AD, González-Fernández et al. (2008) | (2008)       |
| Salvinia molesta          | 6% \(+\)/H\(_2\)SO\(_4\) | 11.2 mL/g VS              | 17.8 mL/g VS            | 63                         | Lab-scale AD, Syachurrozi et al. (2019) | (2019)       |
| Alkaline                  |                         |                           |                         |                            |                     |              |
| Wheat straw               | 4% w/w NaOH, 37 \(^\circ\)C, 120 h | 78.4 mL/g VS              | 165.9 mL/g VS           | 87.6                       | Lab-scale AD, Chandra et al. (2012c) | (2012c)      |
| Wheat straw               | 6% KOH, 3 days, room temperature | 183 mL/g VS              | 258 mL/g VS             | 75                         | Lab-scale AD, Jaffar et al. (2016) | (2016)       |
| Giant reed                | 20% g NaOH/g TS, 24 h, room temperature | 107 mL/g TS              | 137 mL/g TS             | 30                         | Lab-scale AD, Jiang et al. (2017) | (2017)       |
| Giant reed                | 20% g Ca(OH)\(_2\)/g TS, 24 h, room temperature | 107 mL/g TS              | 131.8 mL/g TS           | 25                         | Lab-scale AD, Jiang et al. (2017) | (2017)       |
| Giant reed                | 20 g NaOH/l, 24 h       | 217 mL/g VS               | 353.7 mL/g VS           | 37                         | Lab-scale AD, Jiang et al. (2016) | (2016)       |
| Corn straw                | 8% \(+\)/Ca(OH)\(_2\), 22 \(^\circ\)C, 7 days | 100.6 mL/g VS             | 206.6 mL/g VS           | 106                        | Lab-scale AD, (Z. Song et al., 2014) | (2014)       |
| Corn straw                | Ammonia 10% \(+\)/       | 100.6 mL/g VS             | 168.3 mL/g VS           | 67.3                       | Lab-scale AD, (Z. Song et al., 2014) | (2014)       |
| Wheat straw               | 1.2% w/w NaOH, 30 \(^\circ\)C, 24 h | 274 mL/g VS              | 315 mL/g VS             | 41                         | Lab-scale AD, Pelleria and Gidarakos (2018) | (2018)       |
| Swine manure              | 7 mL NaOH to 300 g manure | 206.7 mL/g VS             | 154 mL/g VS             | –52                        | Lab-scale AD, González-Fernández et al. (2008) | (2008)       |
| Pig manure                | Ca(OH)\(_2\) at 70 \(^\circ\)C | 140 mL/g VS              | 240 mL/g VS             | 100                        | Lab-scale AD, Rafique et al. (2010) | (2010)       |
| Pulp and paper sludge     | 8 gNaOH/100 g TS        | 113 mL/g VS              | 320 mL/g VS             | 207                        | Lab-scale AD, Lin et al. (2009) |              |
| Pulp and paper sludge     | NaOH/pH = 9 at 70 \(^\circ\)C | 227 mL/g VS              | 314 mL/g VS             | 87                         | Lab-scale AD, Montelius (2014)         |              |
| Pulp and paper sludge     | NaOH/pH = 11 at 70 \(^\circ\)C | 227 mL/g VS              | 299 mL/g VS             | 72                         | Lab-scale AD, Montelius (2014)         |              |
| Pulp and paper sludge     | Ca(OH)\(_2\)/pH = 9 at 70 \(^\circ\)C | 227 mL/g VS              | 223 mL/g VS             | –4                         | Lab-scale AD, Montelius (2014)         |              |
| Pulp and paper sludge     | Ca(OH)\(_2\)/pH = 11 at 70 \(^\circ\)C | 227 mL/g VS              | 303 mL/g VS             | 76                         | Lab-scale AD, Montelius (2014)         |              |
| Redox reactions/           | Birch wood              | 0.001M FeCl\(_2\), 0.01M H\(_2\)O\(_2\), 2 h | 341.32 mL/g VS         | 357.9 mL/g VS             | Lab-scale AD, Lamb et al. (2019) | (2019)       |
| Fenton reactions          |                         |                           |                         |                            | Lab-scale AD, Michalska et al. (2012) | (2012)       |
| Ionic liquid              | Miscanthus               | [Fe\(^{+2}\)/H\(_2\)O\(_2\)] equals 1:2.5, 2 h | 7 Ndm\(^3\)/kg TS    | 12.5 Ndm\(^3\)/kg TS      | Lab-scale AD, Michalska et al. (2012) | (2012)       |
|                         | Sida                    | [Fe\(^{+2}\)/H\(_2\)O\(_2\)] equals 1:2.5, 2 h | 12 Ndm\(^3\)/kg TS    | 17 Ndm\(^3\)/kg TS      | Lab-scale AD, Michalska et al. (2012) | (2012)       |
|                         | Sorghum Moenschi        | [Fe\(^{+2}\)/H\(_2\)O\(_2\)] equals 1:2.5, 2 h | 20 Ndm\(^3\)/kg TS    | 21.5 Ndm\(^3\)/kg TS      | Lab-scale AD, Maanir et al. (2017) | (2017)       |
| Olive milled waste        |                         | [H\(_2\)O\(_2\)/[Fe\(^{+2}\)] = 1000, 2h, 22 \(^\circ\)C | 335 mL/g VS               | 225 mL/g VS             | Lab-scale AD, Kabir et al. (2014) | (2014)       |
| Barley straw              | 85% NMNO, 90 \(^\circ\)C, 7 h | 120 mL/g VS              | 220 mL/g VS             | 100                        | Lab-scale AD, Kabir et al. (2014) | (2014)       |
| Pine and spruce residues  | 85% NMNO, 90 \(^\circ\)C, 30 h | 80 mL/g VS              | 150 mL/g VS             | 70                         | Lab-scale AD, Kabir et al. (2014) | (2014)       |
| Tomato pomace             | 1-ethyl-3-methylimidazolium acetate, 130 \(^\circ\)C, 3 h | – | – | 12% increase | Lab-scale AD, Allison et al. (2016) | (2016)       |
| Rice straw                | NMNO, 120 \(^\circ\)C, 3 h | 206 mL/g VS              | 374 mL/g VS             | 168                        | Lab-scale AD, Mancini et al. (2016b) | (2016b)      |
| Cocoa shell               | NMNO, 120 \(^\circ\)C, 3 h | 199 mL/g VS              | 226 mL/g VS             | 27                         | Lab-scale AD, Mancini et al. (2016b) | (2016b)      |

Aromatic compounds first degraded to intermediate products (protocatechuate, catechol and gallate) via acetogens and ring-cleaving fermenters. Archaea methanogens consume the product from this step in a syntrophic manner (Kato et al., 2015). Lignin can be degraded either under aerobic or anaerobic conditions (Masa Cater et al., 2014). The aerobic degradation of lignin involves the secondary metabolism of the white- and brown-rot fungi, where different extracellular oxidases (including lignin
peroxidases, manganese peroxidases, hybrid peroxidases, laccases, alcohol oxidases and glyoxal oxidases) produce H₂O₂ (i.e., the presence of H₂O₂ can also degrade cellulose). Although fungi are capable of degrading lignin, lignin degradation by using extracellular enzymes in absence of an oxidizing agent (e.g., H₂O₂) is impossible as the oxidation of aromatic rings by extracellular enzymes requires oxygen (Dollhofer et al., 2015; Haider and Guggenberger, 2005). The white- and soft-rot fungi are also capable of degrading cellulose, and the brown-rot fungi can reduce the cellulose crystallinity. One method that can supply oxygen for lignin degradation and enhance the performance of the fungi is micro-aeration. Micro-aeration not only increases the production of the extracellular enzymes (Zhu et al., 2009), but can also enhance the solubilization of the lignocellulose (Zhang et al., 2007) through increased activity of the aerobic and facultative microorganisms (Tsapekos et al., 2017).

Biological methods are counted as efficient alternatives for energy-intensive pre-treatment methods, including thermal and mechanical methods. These processes not only reduce the chemical consumption required in other methods but also contain lower concentrations of inhibitors for AD microorganisms (Hernandez-Beltran et al., 2019). Despite this, the main weaknesses of biological pre-treatment methods is their low reaction rates and long residence times (Montgomery and Bochmann, 2014), which increase the cost and space requirements of the implementation of such processes (Aghor et al., 2011; Cho et al., 2013). Table 6 gives an overview of the biological pre-treatment methods commonly used.

4.4.1. Ensiling

Ensiling has been used as a storage technique for agricultural industries since the 1800s (Ambye-Jensen et al., 2013). It is a well-known biochemical process involving lactic acid bacteria (LAB) that produce organic acids and ethanol by consuming sugars from the feedstock. An increase in organic acid concentration can lead to a lower pH that inhibits the growth of undesirable organisms (e.g., fungi and yeast) (Feng et al., 2018; Huan Zhang et al., 2018). Despite this, some biomass does not have sufficient sugars for LAB. To compensate for the lack of lactic acid concentration and prevent the loss of dry materials several alternatives are available (Ambye-Jensen et al., 2013). These alternatives include adding organic acids instead of LABs, adding enzymes to release carbohydrates from lignocellulose or increasing sugar concentration to boost the LAB’s activities (Yang et al., 2006). Several factors influence ensiling pre-treatment efficiencies (e.g., particle size, biomass composition, dry matter content and storage time). Ensiling pre-treatment is a cost-effective method that requires significantly lower energy input compared to thermal and mechanical pre-treatment processes; however, its main problem is the long residence period for biomass (X. Yang et al., 2019; Zhao et al., 2018).

4.4.2. Fungi

Among white-, soft- and brown-rot fungi, white-rot fungi have shown better performance due to their unique ligninolytic systems and their oxidative activities. Lignin peroxidase (LiP), manganese peroxidase (MnP) and laccase are the main oxidative enzymes from white-rot fungi (Liu et al., 2014; Shirkavand et al., 2016). Recent studies have indicated that the white-rot fungi degrade lignin by involving several reactions such as oxidation, demethylation, side-chain oxidation and cleavage. Brown-rot fungi remove cellulose and hemicellulose through minor changes to the lignin structure, resulting in lignin being the main residue from pre-treatment by brown-rot fungi (Wan and Li, 2012; Zhao et al., 2014). Fungal pre-treatment has several advantages over thermal, chemical and physical pre-treatment methods such as low energy consumption, reduced inhibitors, low waste and reduced downstream process cost. White-rot fungi are advantageous over other organisms due to the lower loss of cellulose and higher lignin degradation potential (Mustafa et al., 2016). To prevent the growth of inappropriate microorganisms, sterilisation processes either using pressure and steam or chemicals may be required. This preliminary stage can significantly increase the investment cost (Akyol et al., 2019; Rouches et al., 2016b). The main disadvantage of the fungal pre-treatment is its long pre-treatment time.

4.4.3. Micro-aeration

Micro-aeration refers to the supply of tiny amounts of oxygen into the anaerobic culture to enhance both aerobic and anaerobic activities within a single- or multi-stage anaerobic process. It is reported that the activity of the synthesised hydrolytic enzymes is considerably increased. Furthermore, in the presence of oxygen, the facultative anaerobes enhance the growth rate of strict anaerobes resulting in a better hydrolysis process (Ngumah et al., 2017; Tsapekos et al., 2017). Some aerobic bacteria (e.g., Rhodococcus species) can produce ligninolytic enzymes that boost the enzymatic hydrolysis of the lignocellulose. The use of aerobic bacteria increases the value of the micro-aeration process as bacteria have a higher adaptability and faster propagation rate compared to fungus (Fu et al., 2015a; Zhu et al., 2009). The micro-aeration process is an economically and environmentally friendly process, yet the process is highly sensitive to the method of oxygen supply. Inappropriate dosage of oxygen may reduce the process efficiency or even inhibit the whole AD process. Since the hydrolysis process effectiveness depends on the presence of specific aerobic bacteria, it is essential to provide an inoculum including targeted bacteria for an enhanced micro-aeration step (Fu et al., 2015a, 2015b).

4.4.4. Microbial consortium

In the natural environment, complex structures of lignocellulosic biomass are degraded by various types of bacteria, fungi, cellulolytic and hemicellulolytic enzymes (Liang et al., 2018). In contrast with fungal or enzymatic pre-treatment that use single bacteria or enzymes, the microbial consortium pre-treatment method benefits from dual or complex microbial consortia. This method can also remove contaminants from the substrate (Ali et al., 2019; Liang et al., 2018; Mishra et al., 2018; Tantayotai et al., 2017). By developing a stable and efficient microbial consortium, this method could be an option for industrial applications; however, it is slow in culture development and screening process (i.e., can take up to 12 months) (Kanokratana et al., 2018; Liang et al., 2018; Zhang et al., 2011).

4.4.5. Enzymatic pre-treatment

Cellulases, endoglucanases, cellobiohydrolases (also known as endocellulases) and β - Glucosidases (or cellobiases) are enzymes that hydrolyse cellulose to glucose. Fungi are known as a potential source for cellulolytic enzymes. Xylanases are enzymes that can extract sugars from xylan through hemicellulose decomposition. Several hydrolytic enzymes such as endo-1,4-β-xylanase, β-xylanidase, α-arabinofuranosidases and esterases can convert xylan to sugar (Cannella et al., 2016; Eibinger et al., 2014). Lignin peroxidase and manganese peroxidase can sufficiently degrade lignin to produce cation radicals (Hasunuma et al., 2013; Schroyen et al., 2014). Laccase, as a copper-containing oxidising enzyme, can also be produced by bacteria and white-rot fungi (de Gonzalo et al., 2016). The most important application of these enzymes is to degrade lignin and other polymer deposits (e.g., Swollenin theralon is isolated from Trichoderma reesei), can enhance the cellulase activities without significantly affecting the hydrolysis process (Mosier et al., 2005b; Rouches et al., 2016a).
| Pre-treatment method | Substrate                  | Pre-treatment condition | Methane yield (Untreated) | Methane yield (Treated) | Increased biomethane mL/g VS | Treatment Condition | Ref.                      |
|----------------------|----------------------------|-------------------------|---------------------------|-------------------------|----------------------------|---------------------|-------------------------|
| Ensiling             | Wheat straw                | Lab-scale ensiling in plastic bag | 179 mL/g VS | 275 mL/g VS | 96 | Lab-scale batch AD, 38 °C | Gallegos et al. (2017) |
|                      | Tall fescue                | Pilot-scale ensiling for 3 months, 25 L barrel | 316 mL/g TS | 318 mL/g TS | 2 | Lab-scale batch AD, 34 °C | Feng et al. (2018)     |
| Fungi                | Corn stover                | *P. chrysosporium*, 28 °C, 7 days | 215.5 mL/g VS | 265 mL/g VS | 49.5 | Solid state batch AD, 37 °C | Liu et al. (2014)      |
|                      | Cow manure                 | *T. versicolor*, 7 days, 27 °C | 167 mL/g VS | 236 mL/g VS | 69 | Batch AD at 37 °C for 21 days | Tisma et al. (2018)     |
|                      | Yard trimmings             | Mycelium grown, 30 days | 20 mL/g VS | 40 mL/g VS | 20 | Solid state batch AD, 37 °C | Zhao et al. (2018)      |
|                      | Corn stover                | *Pleurotus ostreatus*, 75% moisture, 20 days | 316 mL/g VS | 318 mL/g VS | 59 | Lab-scale batch AD, 37 °C | Wyman et al. (2018)     |
|                      | Rice straw                 | *Pleurotus ostreatus*, 75% moisture, 20 days | 316 mL/g VS | 318 mL/g VS | 59 | Lab-scale batch AD, 37 °C | Wyman et al. (2018)     |
|                      | Willow sawdust             | *Leiotrametes menziesii*, 30 days | 316 mL/g VS | 318 mL/g VS | 59 | Lab-scale batch AD, 37 °C | Wyman et al. (2018)     |
|                      | Willow sawdust             | *Abortriporus biennis*, 30 days | 316 mL/g VS | 318 mL/g VS | 59 | Lab-scale batch AD, 37 °C | Wyman et al. (2018)     |
|                      | Pulp and paper sludge      | Active and inactive mushroom compost extracts (MCE)/250 A.U./g VS sludge | 98.2 mL/g VS | 230 mL/g VS | 131.8 | Lab-scale batch AD, 37 °C | Yunqin et al. (2010)    |
|                      | Micro-aeration             | Wheat straw              | -- | -- | 7.2% increase | -- | Lab-scale batch AD, 55 °C | Tsapekos et al. (2017)  |
|                      | Corn straw                 | 10 mL O₂/g VS            | 296.3 mL/g VS | 380.6 mL/g VS | 84 | Lab-scale two stage AD, mesophilic/thermophilic | Fu et al. (2015a)      |
|                      | Rice straw                 | 5 mL O₂/g VS             | 230.8 mL/g VS | 270.8 mL/g VS | 40 | Batch AD, 37 °C | Xue et al. (2018)       |
|                      | Rice straw                 | Originated from horse manure, 50 °C, 7 days | 26.05 mL/g VS | 109.6 mL/g VS | 84 | Batch AD, 37 °C | Tantayotai et al. (2017) |
|                      | Rice straw                 | Originated from decomposed wood, 50 °C, 7 days | 26.05 mL/g VS | 161.5 mL/g VS | 136 | Batch AD, 37 °C | Tantayotai et al. (2017) |
|                      | Cassava residues           | 12 h pre-treatment time | 132 mL/g VS | 259.5 mL/g VS | 128 | Lab-scale AD, 55 °C | Zhang et al. (2011)    |
|                      | Wheat straw                | TC-5, 12 days            | 229.8 mL/g VS | 314 mL/g VS | 84 | Lab-scale batch AD, 37 °C | Kong et al. (2018)      |
|                      | Saw dust                   | 10 days                  | 89.9 mL/g VS | 155.2 mL/g VS | 66 | Lab-scale batch AD, 30 °C | Ali et al. (2017)       |
|                      | Pulp and paper sludge      | Microbial consortium OEM1 | 179 mL/g VS | 429.19 mL/g VS | 250.19 | Lab-scale CSTR in mesophilic condition | Lin et al. (2017)       |
|                      | Enzymatic                  | Avicel cellulose         | H₂O₂, 85% Celluclast and 15% NcLPMO9C (Cell + 9C) blend | 230 mL/g VS | 225 mL/g VS | 5 | Batch AD | Costa et al. (2019) |
|                      |                           | Birch                    | H₂O₂, 85% Celluclast and 15% NcLPMO9C (Cell + 9C) blend | 120 mL/g VS | 49 mL/g VS | 71 | Batch AD | Costa et al. (2019) |
|                      |                           | Spruce                   | H₂O₂, 85% Celluclast and 15% NcLPMO9C (Cell + 9C) blend | 80 mL/g VS | 38 mL/g VS | 42 | Batch AD | Costa et al. (2019) |
|                      |                           | Lignin-rich residues     | H₂O₂, 85% Celluclast and 15% NcLPMO9C (Cell + 9C) blend | 90 mL/g VS | 58 mL/g VS | 32 | Batch AD | Costa et al. (2019) |
Lytic polysaccharide monooxygenases (LPMOs) are monooxygenase redox enzymes that were discovered in 2010 (Vaajekolstad et al., 2010). LPMOs catalyse the degradation of cellulose through hydroxylation of glycosidic linkages (i.e., C1 and/or C4 that connects glucose units in cellulose). This hydroxylation leads to the disruption of the crystalline structure of the cellulose and provides substrates with higher capability for hydrolysis than conventional cellulose. In order to catalyse the described reactions, LPMOs need two electrons for their reaction cycle. These electrons should be supplied from another source such as oxygen or H2O2 (LPMOs do not work in anaerobic conditions) (Müller et al., 2018; Villares et al., 2017).

The main advantages of enzymatic pre-treatment over fugal pre-treatment are the higher treatment rates, shorter residence times and possibilities to select and use appropriate enzymes for specific biomasses (Mosier et al., 2005b; Ngumah et al., 2017). A method for enzymatic degradation of the lignocellulose is the introduction of some enzymes extracted from genetically modified organisms (GMOs) (Hosseini Koupaei et al., 2019). This method has been studied for lignocellulose pre-treatment for biofuel production; however, its effects on biogas production enhancement have not yet been investigated. According to the previous studies regarding GMOs, the enzymes from GMOs not only tolerate extreme operational conditions in terms of temperature and pH, but also can digest cellulose and hemicellulose simultaneously to glucose and xylose (Hosseini Koupaei et al., 2019). It is reported that such enzymes can increase the yield and improve the availability of carbohydrate sources for further digestion steps (Ngumah et al., 2017). The enzymes from GMOs are quite expensive for large scale applications and the process for these types of enzymes is expensive due to strict rules and required processing (Mosier et al., 2005b; Ngumah et al., 2017). In general, the application of the enzymes can reduce the concentration of phenolic compounds and consequently lower the inhibitory effects of the substrate. Hydrolytic enzymes are commercially available, but some of the main problems associated with these enzymes are technical challenges regarding enzyme production and their high price, which can influence the operational cost at an industrial scale (Bonilla et al., 2018; Herrero Garcia et al., 2019).

### 4.5. Hybrid pre-treatment technologies

A single pre-treatment method always has weaknesses that prevent its application in full-scale industrial projects. In terms of biological pre-treatment, the main barriers for implementation of such methods at the industrial scale are the slow growth rate of the lignocellulose degrading bacteria and long retention time of materials in biological pre-treatment processes.

In the last decades, hybrid pre-treatment methods have attracted much attention (Zheng et al., 2014b). Wet oxidation (a thermophysical-chemical method) and ammonia fiber explosion (a thermal-physical-chemical method) not only degrade lignin but also reduce the cellulose crystallinity. It has been observed that some hybrid methods may reduce the amount of chemical utilisation while optimising the energy consumption of thermal pre-treatment methods (Chandra et al., 2012b; Wan et al., 2011). Hybrid pre-treatment methods may benefit from the advantages of each individual pre-treatment method, while minimising their negative impacts of economic cost, operational complexity and environmental impacts. Table 7 gives an overview of the achievements of the hybrid pre-treatment methods.
Table 7

Hybrid methods for pre-treatment of lignocellulosic material.

| Hybrid method          | Substrate                   | Pre-treatment process              | Operational condition | Increased biomethane yield mL/g VS | Ref.                  |
|------------------------|-----------------------------|------------------------------------|-----------------------|-----------------------------------|-----------------------|
| **Thermochemical**     |                             |                                    |                       |                                   |                       |
| Pulp and Paper sludge  | NaOH at 140 °C, pH 9        | Batch, mesophilic                  | 30 mL/g VS            | Montelius (2014)                  |                       |
| Pulp and Paper sludge  | Ca(OH)₂ at 140 °C, pH 9     | Batch, mesophilic                  | 213 mL/g VS           | Montelius (2014)                  |                       |
| Pulp and Paper sludge  | Ca(OH)₂ at 140 °C, pH 11    | Batch, mesophilic                  | 386 mL/g VS           | Montelius (2014)                  |                       |
| Pulp and Paper sludge  | H₃PO₄ at 140 °C, pH 12      | Batch, mesophilic                  | 99 mL/g VS            | Montelius (2014)                  |                       |
| Pulp and Paper sludge  | H₃PO₄ at 140 °C, pH 13      | Batch, mesophilic                  | 83 mL/g VS            | Montelius (2014)                  |                       |
| Wheat straw            | Blender and 1% NaOH for 1 h at 100 °C | Batch AD | 98 mL/g VS | Sambusiti et al. (2013) |                       |
| Ensiled Sorghum        | Cutter and NaOH 40 °C       | Batch AD                           | 45 mL/g VS            | Sambusiti et al. (2013)           |                       |
| Sunflower Stalks       | Cutter and NaOH at 55 °C    | Batch AD                           | 69 mL/g VS            | Monlau et al. (2013)              |                       |
| Grass silage           | Blender and 2.5% NaOH for 12 h at 100 °C | Batch AD | 75 mL/g VS | Xie et al. (2011)                 |                       |
| Switchgrass            | Blender and 5.5% NaOH for 6 h at 100 °C | Batch AD | 39 mL/g VS | Jin et al. (2014)                 |                       |
| Birch                  | Ball mill and NaOH at 100 °C | Batch AD                           | 210 mL/g VS           | Mirahmadi et al. (2010)           |                       |
| Rice straw             | 3% NaOH at 37 °C, hydrothermal at 200 °C for 10 min | Batch AD | 72 mL/g VS | Chandra et al. (2012b)           |                       |
| Rice straw and corn stalk | Chemicals pre-treatment for 7 days/thermal pre-treatment at 70–90 °C for 2, 6 and 10 h. | Batch AD, mesophilic | Increase biomethane yield by 62 and 66% | Pavotwary and Baruah (2018) |                       |
| Sugar cane bagasse     | Thermal pre-treatment at 160–180 °C for 20 min/1.7%–11.9% acid solution. | Batch AD, mesophilic | 108 mL/g VS | Mustafa et al. (2018)            |                       |
| Physicochemical         |                                 |                                    |                       |                                   |                       |
| Rice straw             | Extruder and 3% NaOH for 48 h at 35 °C | Batch AD | 101 mL/g VS | Zhang et al. (2015)               |                       |
| Rice straw             | Millier and 3% NaOH for 5 d at 37 °C | Batch AD | 14.3 mL/g VS | Chandra et al. (2012b)           |                       |
| Rice straw             | Hammer mill and 6% NaOH for 21 d at 20 °C | Batch AD | 160 mL/g VS | He et al. (2008)                  |                       |
| Wheat straw            | Millier and 4% NaOH for 5 d at 37 °C | Batch AD | 87.5 mL/g VS | Chandra et al. (2012c)           |                       |
| Corn stover            | Hammer miller and 2% NaOH for 3 d at 20 °C | Batch AD | 100.3 mL/g VS | Zheng et al. (2010)              |                       |
| Pin wood               | Millier NaOH for 48 h at 100 °C | Batch AD                           | 77 mL/g VS            | Salehian et al. (2013)            |                       |
| Rice straw             | Extruder/NaOH 3–120 h at 35 °C | Batch AD                           | 101 mL/g VS           | Zhang et al. (2015)               |                       |
| Rice straw             | Extruded(Ca(OH)₂) (ranging from 5% to 15%) at 25 °C for 72 h | Batch AD, mesophilic | 90 mL/g VS | Gu et al. (2015)                  |                       |
| Corn Stover            | Chemical pre-treatment at 30–50 °C for 6–12 h/ultrasound (150 W power and 40 KHz) | Batch AD, mesophilic | Up to 60% lignin degradation. | You et al. (2019a) |                       |
| Thermal-biological     | Populus tomentosus          | Boiling biomass in 140–200 °C for 30 min. | – | 92% hemicellulose degradation/2.25-fold more glucose yield. | Wang et al. (2012) |
| Seaweed                | Steam explosion at 190 °C for 5 min/ enzymatic pre-treatment at 50 °C for 72 h. | Up-flow anaerobic sludge bed (UASB), mesophilic | 57% increase in methane production. | Niemkia and Morto (2011) |                       |
| Birch wood             | Steam-explosion at 210 °C for 10 min/cellulolytic bacterium Caldicellulosiruptor becici | Batch AD, thermophilic (62 °C) | 120 mL/g VS | Mulat et al. (2018)              |                       |
| Physical-biological    | Corn cob, vine trimming shoots (VTS) | Ultrasonic (150–750 W with 20 KHz)/commercial enzyme was at 30 °C | Batch AD, mesophilic | Pérez-Rodríguez et al. (2016) |                       |
| Wheat straw            | Chopping/ enzymatic/ silage. | Batch AD, mesophilic | 65 mL/g VS | Gallegos et al. (2017)           |                       |
| Thermal-chemical-physical | Biofibres from degraded manure | Steam explosion with chemical catalysts like H₃PO₄ and NaOH in 160 °C for 15 min. | Batch AD, thermophilic | Bruni et al. (2010)              |                       |
| Wet Oxidation          | Winter rye straw            | 195 °C, 15 min, 2 g L⁻¹ Na₂CO₃ and 12 bar oxygen | Batch AD, 42 °C | 34% increase in methane yield | Petersson et al. (2007) |
|                        | Olisseed rape straw         | 195 °C, 15 min, 2 g L⁻¹ Na₂CO₃ and 12 bar oxygen | Batch AD, 42 °C | 8% increase in methane yield | Petersson et al. (2007) |
|                        | Faba bean straw             | 195 °C, 15 min, 2 g L⁻¹ Na₂CO₃ and 12 bar oxygen | Batch AD, 42 °C | No effect                       | Petersson et al. (2007) |
|                        | Miscanthus                   | –                                   | Full-scale AD         | 160 mL/g VS | Uellendahl et al. (2008)         |
|                        | willow                       | –                                   | Full-scale AD         | 160 mL/g VS | Uellendahl et al. (2008)         |
|                        | AFEX                        | 10% ammonia, 50% ethanol, 70 °C, 24 h | Lab-scale AD          | 194 mL/g VS | Sajad Hashemi et al. (2019)      |
Alexandropoulou et al. (2017) employed a chemical-biological pre-treatment process to degrade willow sawdust. They used A. biennis fungi together with NaOH as an alkaline source. It is reported that the combined pre-treatment method could improve the methane yield by 12.5% and 50.1% compared to the alkaline-only and fungi-only pre-treatment methods, respectively, and

### Table 7 (continued)

| Hybrid method | Substrate | Pre-treatment process | Operational condition | Increased biomethane yield mL/g VS | Ref. |
|---------------|-----------|-----------------------|-----------------------|------------------------------------|------|
| Wheat straw   | 7% ammonia, 55 °C | Lab-scale AD | 84 mL/g VS (D. Wang et al., 2019) |
| Wheat straw   | 7% ammonia, 105 °C | Lab-scale AD | 130 mL/g VS (D. Wang et al., 2019) |
| Physical-chemical-biological | Corn Cob | NaOH/extrusion/enzyme mixture at 30 °C. | Batch AD, mesophilic | 50 mL/g VS (Pérez-Rodríguez et al., 2017) |
| Wheat straw   | Ca(OH)₂/Milling/enzyme addition | Batch AD, mesophilic | 154 mL/g VS (Reilly et al., 2015) |
| Birch wood    | Steam explosion at 210 °C for 10 min/ultrasound (30 W and 24 KHz)/H₂O₂ with 2h residence period. | Batch AD, mesophilic | 16.7 mL/g VS (Lamb et al., 2019) |

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**Fig. 2.** Pre-treatment of lignocellulosic materials can change the structure of lignocellulose significantly. For example, steam explosion treatment of birchwood. Left: chips of around 30 mm prior to steam explosion; right: the dark and sticky birchwood with a less obvious fibre structure after steam explosion.

**Fig. 3.** The average biomethane production potential of different types of lignocellulosic materials before and after pre-treatment. The methane yield can significantly change by pre-treatment method, substrate type, digestion condition that is shown by error bars.
that the combined method could increase the methane yield by 115% compared to the untreated willow sawdust samples (Alexandropoulou et al., 2017).

4.5.1. Wet oxidation

Wet oxidation is conducted at an elevated temperature (i.e., 150–200 °C) under high-pressure conditions ranging from 10 to 20 bar for 10–15 min in the presence of oxygen or other oxidant reagents. At elevated temperatures (i.e., above than 170 °C) the process becomes an exothermic process that leads to a lower energy demand (Ahring et al., 1996; Olsson et al., 2004). The high pH wet oxidation process (also known as alkaline wet oxidation) can mitigate the formation of process inhibitors such as furfural and hydroxymethylfurfural. Wet oxidation is an effective pre-treatment technology to increase accessible surface area for enzymatic hydrolysis through solubilization of cellulose. It is an efficient method to solubilise the lignin and hemicellulose, and has been reported to significantly remove the lignin from the insoluble phase (up to 60–70%) in a stable condition (Olsson et al., 2004). During an optimum alkaline wet oxidation process of wheat straw, around 65% of cellulose and 70% of hemicellulose were converted to glucose, xylose and arabinose (Olsson et al., 2004; Schmidt and Thomsen, 1998).

4.5.2. Ammonia freeze explosion (AFEX)

AFEX is conducted similarly as the steam explosion pre-treatment. The dry substrates are smeared with a specific amount of liquid ammonia (1–2 kg ammonia per kg of biomass), and heated up to 50–100 °C under elevated pressure (10.1–20.2 bar) for a specified residence time. The pressure is then realised to atmospheric pressure resulting in recrystallisation of cellulose and disruption of the fibre structure. These variations in the structure lead to an increase in accessible surface area (Dupont, 2009; Holtzapple et al., 1991). The AFEX method is not capable of hydrolysing hemicellulose and does not remove the lignin (Olsson et al., 2004); however, this method can effectively pre-treat the low lignin content substrates such as herbaceous corps and grasses. The main advantages of the AFEX pre-treatment method are: i) low energy input compared to steam explosion (the maximum temperature for AFEX is 100 °C); ii) the efficiency of the method does not depend on the particle size; and, iii) lower inhibitor production (Olsson et al., 2004).

In some modified ammonia-based methods, other chemicals (e.g., ethanol) are employed in order to enhance the lignin degradation. Sajad Hashemi et al. (2019) reported the cleavage of the C–O–C bond of lignin during modified AFEX, resulting in a higher biogas yield. They reported 299.3 mL methane/g VS of pre-treated substrate, which was nearly three-fold of that for an untreated sample (105.6 mL/g VS) (Sajad Hashemi et al., 2019).

4.6. Suitable lignocellulosic feedstock for AD

Grasses and leaves, agricultural wastes and residues (i.e., wheat straws, corn stover and ensiled by products), oil seeds, fruit shells/wastes, sugarcane bagasse and hard woods have an average biogas potential of over 190 mL/gVS (Fig. 3) when they do not undergo pre-treatment. When pre-treatment is used, it can enhance the average BMP to over 250 mL/gVS for these types of the substrates. For some substrates with higher cellulose and hemicellulose content (e.g., grasses and leaves) the BMP can reach to over 400 mL/gVS. According to the information from Fig. 3, the pulp and papering has gained the most benefit from the pre-treatment. The pre-treatment could increase the average BMP of the pulp and papering by-products from 130 to over 200 mL/gVS. Flowers and local seeds, soft woods and sawdust from woody industry have the lowest BMP before and after pre-treatment.

4.7. Suitable pre-treatment method for different types of lignocellulosic materials

In this Section, the lignocellulosic feed stocks have been categorized in five main class as mentioned in Section 1. Fig. 4 gives a summary of these classes including error bars that contain the average BMP variations due to the type of the substrate and pre-treatment methods in each category.

4.7.1. Agricultural by-products and wastes

The hybrid pre-treatment methods (i.e., physicochemical and thermochemical methods) have the highest impact on average BMP enhancement (100 mL/g VS) of the agricultural by-products and
wastes. This indicates the importance of the size reduction and increase of the available surface area for enzymatic degradation.

4.7.2. Forestry by-products

Thermal pre-treatment methods can improve the average BMP of forestry residues and wastes (especially birch wood) by 200 mL/g VS, mainly due to disruption of the structure of lignocellulosic material that increases the available surface area and solubilizes the hemicellulose in higher temperature; however, as shown by error bars, it can cause the release of AD inhibitors in the system. The hybrid methods (i.e., thermal-physical and thermochemical) can moderate the operational costs and inhibitory effects while increasing the average BMP by over 100 mL/g VS. The biological techniques often have negative effects on BMP of the forestry by-products and waste.

4.7.3. Wood industry, pulp and papering

Among all pre-treatment methods, the thermal, physical and chemical methods are the most applied pre-treatment methods in woody industry and pre-treatment of pulp and paper sludge. The thermal pre-treatment can improve the average BMP by around 192 mL/g VS, while for the hybrid, chemical, biological and physical pre-treatment these values are 162, 92, 86 and 72 mL/g VS, respectively. Increased enzymatic hydrolysis, increased water-solubility, solubilization of the lignin and reduction of the crystallinity of the cellulose are the main sources for BMP enhancement of these types of substrates.

4.7.4. Livestock-based lignocellulose

The chemical pre-treatment seems to be the least effective technique for livestock by-products (mainly manure). The thermal and biological methods can enhance the BMP of the livestock by-products by 170 and 87 mL/g VS, respectively. Thermal pre-treatment of the manure increases the available surface area of the manure that enhances the hydrolysis step in AD and increases the concentration of the water-soluble substrates.

4.7.5. Grasses, leaves and local plants

These types of AD substrates contain low amounts of lignin and higher amounts of hemicellulose and cellulose (section 3.1). The thermal pre-treatment can solubilize the hemicellulose and disrupt the structure of cellulose resulting in an average BMP growth of 163 mL/g VS. The physical pre-treatment can reduce the crystallinity of the cellulose through size reduction and the average BMP will reach to 85 mL/g VS. The hybrid pre-treatment techniques including biological process can improve the enzymatic hydrolysis of the grasses and cause an average BMP improvement of 74 mL/g VS. The chemical pre-treatment methods seem to be ineffective techniques for pre-treatment of grasses and local plants.

4.8. Electrochemical approaches for lignocellulose degradation

4.8.1. Microbial fuel cell (MFC)

An approach for bio-degradation of lignocellulosic biomass is the use of low-temperature microbial fuel cells (Table 8). A microbial fuel cell (MFC) is a bio-electrochemical system that

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**Table 8**

| Method | Substrate | Electrodes | Highlights | Reference |
|--------|-----------|------------|------------|-----------|
| MFC    | Glucose from cellulose hydrolysis | Carbon felt (anode) and carbon cloth with Pt (cathode) | Anaerobic sludge used as culture, oxidizing agent was air and 0.00313 (mW cm⁻²) was the power density | (T. S. Song et al., 2014) |
|        | Glucose from cellulose hydrolysis | Carbon paper (anode) and carbon paper coated with Pt (cathode) | Bacteria of wastewater used as the main culture, oxidizing agent was air and 0.0262 (mW cm⁻²) was power density with proton exchange membrane (PEM). | Liu and Logan (2004) |
|        | Arabinose from hemicellulose hydrolysis | Carbon cloth (anode) and carbon cloth coated with Pt (cathode) | Mixed bacteria with air as oxidizing agent and 0.203 (mW cm⁻²) was power density (PEM). | Catal et al. (2008) |
|        | Gluconic acid from hemicellulose hydrolysis | Carbon cloth (anode) and carbon cloth coated with Pt (cathode) | Mixed bacteria with air as oxidizing agent and 0.203 (mW cm⁻²) was power density (PEM). | Catal et al. (2008) |
|        | Phenolic compounds | Carbon cloth (anode) and carbon cloth coated with Pt (cathode) | Anaerobic sludge, power density was 0.00165 (mW cm⁻²). | (T. S. Song et al., 2014) |
|        | Natural lignin from sugarcane bagasse | Modified carbon (cathode), Scedosporium dehoogii biofilm (bio anod). | Fungal microbes, the lignin was completely degraded with maximum power density of 16 16 mW/m² | Pontié et al. (2019) |
| MEC and Electrochemical cells | Rice straw | Both anode and cathode were made of polymethyl methacrylate | Microbial culture including cellulose hydrolysis enzymes, maximum hydrogen production of 2.46 mmol/L/D | Wang et al. (2017) |
|        | Pinewood flour and hazelnut leaves | Carbon clothes were used as electrode materials | Enriched culture from wastewater treatment and maximum output of the cell was 0.43 V | Catal et al. (2019) |
|        | Soluble lignin wastewater | Electro-microbial system (EMS) using different direct current (DC) | 2-fold increase in lignin degradation compared to control with a microbial cell including Pseudoxanthomonas and Mycobacterium | Zhang et al. (2019) |
|        | Natural lignin | Anion exchange membrane (AEM) lignin electrolysis cell | High hydrogen rate of 45.6 mL/h | Bateni et al. (2019) |
|        | Yard waste | Graphite electrode | 55.4% increase in biomethane production from pre-treated yard waste | Panigrahi and Dubey (2019) |
generates electricity from anaerobic oxidation of the biomass as a result of the catalytic activity of the microorganisms (Ucar et al., 2017). MFCs can be used for lignocellulose degradation by employing cellulose-degrading microorganisms and extracellular enzymes in the anode compartment to generate electricity. The complete degradation of the lignocellulosic components to digestible sugars can be achievable in the MFC by the diversity of microorganisms; however, the complex structure of the lignocellulosic materials and lack of catalysts for AD of aromatic rings of lignin can reduce the power output from the MFCs (X. Zhao et al., 2017). In the case of using the degraded residues of the electrochemical pre-treatment process as a substrate for AD, it may introduce some phenolic components that can inhibit the AD process.

Besides the electricity generation from an MFC, the degraded lignocellulose material can be further degraded through AD to
produce biogas; however, it depends on the digestibility of the final products, especially from the lignin degradation process. Pontié et al. (2019) developed a fungal microbial fuel cell (FMFC) for degrading natural lignin from sugarcane bagasse. They used a Scedosporium dehoogii biofilm at the anode to catalyse the lignin degradation. They reported complete oxidation of the lignin with a power density of 16 mW/m² (Pontié et al., 2019).

4.8.2. Microbial electrolysis cell (MEC)

Microbial electrolysis cells (MEC) are similar to microbial fuel cell, but hydrogen or methane is produced by applying an external electric current. Microorganisms in MECs are attached to the anode, and the material of anode can be the same as the material used in the MFC. An energy source such as acetic acid is used by microorganisms to release hydrogen ions. The electrical potential of this process is around 0.3 V. Unlike MFCs that use this electric potential, in MEC an extra voltage is delivered to the system to reduce protons and generate molecular hydrogen. Lignin oxidation through MEC is in an early stage and needs further research and development to enhance the hydrogen/methane production yield (Brooks et al., 2018).

Zhang et al. (2019) developed a MEC reactor, including Pseudoxanthomonas and Mycobacterium as lignin-degrading bacteria. The concentration of fatty acids increased and the lignin degradation from lignin wastewater was doubled when using a MEC compared to a non-bio-electrochemical degradation method.

5. Implementation of lignocellulosic pre-treatment methods

There is a need to extend a techno-economical investigation to assess the viability of pre-treatment, and for selecting the best financial and environmental option. Limited information regarding continuous scale reactors is available in the literature that could indicate the economic feasibility of different pre-treatment methods. Some articles conclude by considering the potential cost of pre-treatment and comparing it with the average methane yield increase as a result of the pre-treatment. Fig. 5 provides an overview of the potential expenses and profits for a biogas production plant, including a pre-treatment process for lignocellulosic biomass as a substrate (Uellendahl et al., 2008). The pre-treatment cost is expected to be 19–22% of the final price of the bio-products. The final price of the fermentable sugar from lignocellulosic biomass includes the overall costs of pre-treatment and may reflect the suitability of the different pre-treatment methods in terms of the total cost (Fig. 6). Even though the values in Fig. 6 are fixed values and have been collected from literature and experimental data, the process design options can affect the final price of fermentable sugars as shown by the error bars in Fig. 6 (Hernández-Beltrán et al., 2019).

Fig. 7 shows the biogas production via different pre-treatment methods versus the cost of the pre-treatment. Similar to enzymatic pre-treatment, the alkaline pre-treatment method with NaOH is an expensive pre-treatment mainly due to difficulty of the chemical recovery. The CaO pre-treatment method is the most cost-effective method among all presented pre-treatment methods shown in Fig. 7. Contrary to what one might imagine about the energy requirement for steam explosion process, this method can be economically viable mainly due to the possibility of energy recovery and process integration (Vochzoška et al., 2016).

In order to attain a reliable result in the techno-economic assessment from an experimental setup and developing these results into a real case, it is crucial to consider the possible cost reductions through process design (e.g., process integration and energy recovery). This section further discusses these possible solutions in order to reduce the final costs of the pre-treatment process (Uellendahl et al., 2008; You et al., 2019b).

5.1. Production vs cost

The operation cost correlates with the final enhancement of energy production and the possibility of process integration. The chemical cost in a chemical-based pre-treatment method is high, but it can be reasonable when considering the final biogas production rate and biomethane yield (Ringoet et al., 2012; Uellendahl et al., 2008). The investment costs can be reduced by increasing the pre-treatment rate since the investment cost is independent of biomass yield (Uellendahl et al., 2008). Physical pre-treatment methods have the highest substrate production rate (i.e.,
continuous flow with adjustable flow rate), while the biological pre-treatment methods have the longest residence time (up to a few months) and the lowest production rate among all the pre-treatment methods (Vasco-Correa and Shah, 2019). Uellendahl et al. (2008) have provided detailed information regarding the rational relation between production rate and cost of biogas production.

5.2. Direct integration into anaerobic digester

Direct integration into an AD reactor can result in more compact process and can reduce the investment costs. Chemical pre-treatments can introduce substrates with either extremely high or low pH. This may influence the pH of the AD and interrupt the biological processes if integrated directly into the AD reactor. Chemical recovery can be another issue for the integrated chemical pre-treatment process. Formic acid will rapidly be consumed inside the AD reactor by microorganisms before pre-treating the lignocellulosic material; however, when performing separate pre-treatment of lignocellulose by formic acid, the chemical can be recovered and be used again. Chemical pre-treatment processes cannot be straightforwardly integrated into an AD reactor, and substrates from these pre-treatment methods may need pH adjustment that can further increase the operation costs (Hesami et al., 2015; Wan et al., 2011). During the thermal pre-treatment, the substrate temperature can reach up to 200 °C, which will eliminate microbes if integrated into the AD process (Vivekanand et al., 2013). It is not possible to combine thermal pre-treatment processes with AD reactor. Most of the biological pre-treatment methods can be integrated directly into an AD reactor. The enzymes or bacterial consortia could directly be used inside the AD reactor to help the breakdown of lignocellulosic biomasses without interfering with the biogas production pathways (Yang et al., 2010). Paul and Dutta (2018) have provided information on the challenges and possibilities of direct integration of lignocellulosic-based substrates into AD.

5.3. Cost of pre-treatment

5.3.1. Implementation costs

Some of the pre-treatment methods (including mechanical, thermal and chemical methods), are not able to be integrated directly within the AD reactor (Mönch-Tegeder et al., 2014). This means that the biogas production plants need extra area to implement these types of pre-treatment technologies, resulting in higher costs (Fan et al., 2019). A chemical pre-treatment process requires a separate tank and transportation facilities made of specific material corresponding to the chemicals used in the process, which also will increase the cost (Paudel et al., 2017). In the case of a thermal pre-treatment technology, the process requires high pressure- and temperature-resistant materials. The biomass may need specific transportation facilities to avoid contamination and loss of biodegradable components. For a biological pre-treatment, the reactor size may need to be increased significantly due to the long residence time, leading to higher costs. A hybrid pre-treatment method may reduce the residence time of the substrate and result in a smaller reactor size (Amin et al., 2017; Dahunsi, 2019), but the requirements of the other treatment stages (e.g., mechanical, thermal and chemical) will remain similar to that of the non-hybrid pre-treatment methods, but potentially at a smaller scale (Gaworski et al., 2017).

5.3.2. Operational costs

For chemical pre-treatment, the operational cost can be the highest among all the pre-treatment methods. The regulations regarding safety in chemical handling and training for operational personnel should also be considered; however, by exploring new technologies and the possibility of chemical recovery, the cost of chemical pre-treatment can significantly be reduced (Baral and Shah, 2017). Wang et al. (2019) observed that it was possible to achieve recovery of more than 99% of the ammonia used for pre-treatment of the wheat straw in an AFEX process. The physical methods are energy-intensive and may have a high maintenance cost. Even though the thermal pre-treatment methods are energy-intensive, one of the options that thermal pre-treatment can provide is heat recovery either through the AD reactor for maintaining the mesophilic or thermophilic conditions or for district heating and the overall energy efficiency of the plant can also increase (Jiang et al., 2016). Uellendahl et al. (2008) and Van Fan et al. (2018) have shown the important factors affecting the calculation of the operational and implementation costs of a pre-treatment method for biogas production (Uellendahl et al., 2008; Van Fan et al., 2018).

5.4. Storage

Although using the storage type and period to enhance the quality of the biomass to be used in further steps of the pre-treatment process (e.g., drying or moisture reduction) (Li et al., 2011), it may be possible to integrate pre-treatment and raw material storage as one. The storage can be used to fast-track the time-consuming part of the process. Harvesting of biomass sources (e.g., energy crops) takes place just a few times per year. In order to have a continuous energy production process, the storage element is a substantial part of the whole process (Huan Zhang et al., 2018). Biological pre-treatment can be part of the storage process (Ambye-Jensen et al., 2013). Since some processes of biomass degradation have been conducted during the storage period, the biological process itself becomes faster in general. A straightforward example of this method is the ensiling, where the acidic conditions reduce the pH to around three and inhibit the growth of undesired organisms. The ensiled biomass has a higher potential for biogas production since the degradable organics are not degraded during the storage period. The required time for the AD can be shorter since the AD hydrolysis may be improved as the facultative anaerobes are restrained (Musyoka et al., 2018; Sibiya et al., 2014).

5.5. Process integration and energy recovery

Both mechanical and thermal energy can be recovered in varying degrees. Consideration of the energy requirement for a pre-treatment method individually cannot provide a full picture of the whole process due to the possibility of process integration and energy recovery. This means that the contribution of the technology to the overall process energy requirement can still be small even if the technology has a high energy requirement by itself (Kong et al., 2016). With thermal pre-treatment, it is possible to use a steam flow with high temperatures to conduct mechanical work. Even after this utilisation, most of the energy is still available at lower temperatures for further use. This is known as cascading, and often a large portion of the energy used is possible to recover by cascading the energy (Baral and Shah, 2017; Olof et al., 2009). Dahunsi (2019) claimed the possibility of thermal energy recovery of up 80% by a heat exchanger with a 90% efficiency (Dahunsi, 2019).

In the thermo-mechanical pulping process of the pulp and paper industry, after conducting the work, about 70–80% of the energy loaded to the machines (in the form of electricity in order to conduct work) can be transformed to steam that is normally used for drying in paper machines (Olof et al., 2009; Uprichard and Corson, 2006). The integration of downstream processing with
the steam explosion, wet oxidation, AFEX and, thermophysical pre-treatment methods can significantly affect cost and energy demand of the AD. The methanation process (i.e., converting CO₂ and H₂ to CH₄) through the Sabatier reaction (Kirchbacher et al., 2018) is an exothermic reaction that release heat. This waste heat can be used in several processes including thermophysical pre-treatment processes resulting in lower energy consumption of pre-treatment. Further information about energy balance, calculations and possible energy recovery from a pre-treatment process can be found in Olof et al. (2009), Baral and Shah (2017), and Dahunsi (2019) (Baral and Shah, 2017; Dahunsi, 2019; Olof et al., 2009).

5.6. Digestibility of pre-treated feedstocks

Mechanical pre-treatment provides substrates that can be either used directly as a substrate or as an initial feed for the other pre-treatment methods such as chemical, thermal and biological. Physical pre-treatment can significantly reduce the particle size to around 0.2 mm (Sharma et al., 1988); however, the end-products from the physical pre-treated substrates still have a low potential for biogas production (Kuster Mooro et al., 2017). A chemically pre-treated substrate (or a hybrid method including chemical pre-treatments such as AFEX) has the highest potential for biogas production (as shown in Tables 4 and 7). Depending on the material that is used as the lignocellulosic biomass source, the final products from thermally pre-treated lignocellulosic biomass (especially hardwoods) are rich in organics and can enhance both the biogas production and the methane yield in the AD process (Lamb et al., 2019). Although the treatment rates for the biological methods are slow, the end-products are quite suitable for biogas production with higher methane yields.

6. Future research area for lignocellulosic-based feedstocks

Lignocellulosic materials have shown a high potential for biomethane generation (i.e., from 100 mL/g VS up to 300 mL/g VS) and pre-treatment can increase this potential by 50–200 mL/g VS (Figs. 3 and 4). Considering the energy content of pure biomethane to be 37.8 kJ/L, the pre-treatment can provide up to 7.6 MJ/kg VS extra energy from the lignocellulosic materials; however, in some pre-treatment conditions the biomethane yield can also reduce (Fig. 4). Depending on the pre-treatment method, a specific portion of the extra energy gained from the pre-treatment will be consumed in form of clean energy (electricity) during the pre-treatment. Several factors play a crucial role in the future application of lignocellulosic materials as the main substrate for the AD. These factors include the type of lignocellulosic materials and availability of the feedstock, selecting a suitable pre-treatment method for that type of feedstock, energy recovery, and applying a combination of different pre-treatment methods to maximise the energy extraction while moderating the processes cost and energy requirements. Techno-economic investigation of the several available methods can lead to selecting a suitable pre-treatment method; however, a standard calculation method for techno-economic assessment of AD including a pre-treatment technique needs to be developed.

Beside the energy perspective of the lignocellulosic-based biomass, the environmental aspects also need to be considered. Even though recent research is directed toward lignin degradation in order to achieve the maximum improvement production from lignocellulosic materials, this issue is still unsolved. Lignin degradation and utilisation in AD may negatively affect the atmospheric carbon cycle through unbalancing the carbon transfer from the atmosphere into the soil. Lignin still has an unknown destiny within the AD process. Even though some pre-treatment methods such as electrochemical methods can degrade the lignin completely, the by-products from this process are not easily degradable in the AD process, which may suggest lignin is better used as a soil improvement agent. This can help the carbon cycle in order to transfer atmospheric carbon to the soil.

7. Conclusions

Among different substrates, the grasses, different types of straws (e.g., wheat straw) and livestock manure have the highest average biomethane production potential without pre-treatment ranging from 150 to 300 mL/g VS. Despite the method used for the pre-treatment, the pre-treatment has shown a significant impact on average methane yield enhancement when using pulp and paper residues, sugarcane bagasse, grasses and leaves, and hardwoods. Thermally pre-treated substrates have the highest methane yield improvement among all types of the pre-treatment methods and can be an effective pre-treatment method for different types of lignocellulosic materials. Process integration can play a significant role in reducing energy demand of the thermal pre-treatment methods. This is followed by promising pre-treatment techniques using hybrid, physical, chemical and biological methods. However, their performance can vary a lot due to the type of substrate used.

Although the pre-treatment methods have the potential to significantly increase the methane yields and digestion rates of lignocellulosic material, there can be some negative aspects involved (e.g., increased cost or slow treatment rate). Along with enzymatic pre-treatment (specially genetically modified enzymes), the chemical pre-treatments are the most expensive methods for pre-treatment of lignocellulosic materials. These types of pre-treatment have not yet been industrially applied in AD (specially NaOH and enzymatic pre-treatment), due to the high requirements for chemical recovery and downstream processing. The biological processes are inexpensive methods for increasing the methane yield. The main problem with these methods is their slow treatment rate, which can be addressed by integrating the pre-treatment process into the substrate storage process.

Pre-treatment of the lignocellulosic biomass imposes extra energy and cost requirements to the whole biogas production process. As shown in this review, the pre-treatment process is not always economically viable and may reduce the total profit of the biogas production plant. However, the process integration, energy recovery and chemical recovery can significantly reduce the pre-treatment costs. In some cases where lignocellulosic materials are already in use for biogas production, it may be economically unfavourable to implement further pre-treatment methods. In these cases, the benefits of the lignin-containing digestate being used as a soil fertiliser can be considered as a suitable option, as this may lead to restoring atmospheric carbon in the soil and increase soil quality.

Declaration of competing interest

I would like to submit the manuscript with the title of “A review of pre-treatment methods for lignocellulosic-based streams as a feedstock for anaerobic digestion” by Behnam Hashemi, Shiplu Sarker, Jacob J. Lamb and Kristian M. Lien as the authors to be considered for publication as a review paper in the Journal of Cleaner Production.

The submitted manuscript has reviewed the recently developed methods for pre-treatment of lignocellulosic materials to be used in anaerobic digestion. In this manuscript, the woody based biomass and livestock manure have been studied as lignocellulose sources. Different types of lignocellulose pre-treatment methods that contribute to enhancement of methane production have been
reviewed. Moreover, the economic and environmental effects of such processes have been investigated to provide tangible information for readers to distinguish effective and non-effective pretreatment methods.

This work contributes to providing scientific knowledge on how to select a cost-efficient pretreatment method with high efficiency and low cost.

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