



Review

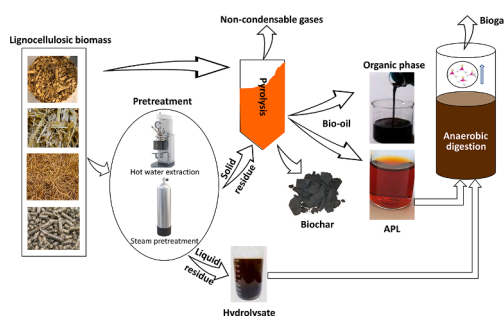
Liquefaction of lignocellulosic biomass for methane production: A review

Nirmal Ghimire^{a,*}, Rune Bakke^{a,1}, Wenche Hennie Bergland^a^a Department of Process, Energy and Environmental Technology, University of South-Eastern Norway, Kjølnes Ring 56, NO-3918 Porsgrunn, Norway

HIGHLIGHTS

- Liquefaction of lignocellulosic biomass by pretreatment for efficient AD is focused.
- Anaerobic digestion of hydrolysate and APL from pyrolysis is reported.
- Effects of inhibitors in hydrolysate and APL are discussed.
- Pretreatment tuning to increase methane yield is discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Lignocellulosic biomass
Liquefaction
Hydrothermal pretreatment
Pyrolysis
Liquid state anaerobic digestion

ABSTRACT

Hydrothermal pretreatment (HTP) (Hot water extraction (HWE) and steam pretreatment) and pyrolysis have the potential to liquefy lignocellulosic biomass. HTP produces hydrolysate, consisting mainly of solubilized hemicellulose, while pyrolysis produces aqueous pyrolysis liquid (APL). The liquid products, either as main products or by-product, can be used as anaerobic digestion (AD) feeds, overcoming shortcomings of solid-state AD (SS-AD). This paper reviews HWE, steam pretreatment, and pyrolysis pretreatment methods used to liquefy lignocellulosic biomass, AD of liquefied products, effects of inhibition from intermediate by-products such as furan and phenolic compounds, and pretreatment tuning to increase methane yield. HTP, focusing on methane production, produces less inhibitory compounds when carried out at moderate temperatures. APL is a challenging feed for AD due to its complexity, including various inhibitory substances. Pre-treatment of biomass before pyrolysis, adaptation of microorganism to inhibitors, and additives, such as biochar, may help the AD cultures cope with inhibitors in APL.

1. Introduction

Lignocellulosic biomass is recognized as the most abundant source of renewable energy globally, available in the forms of softwood, hardwood, energy crops, grasses, and agricultural residues (Nitsos et al., 2013). Bioethanol, biodiesel, and biogas are biofuel products from

lignocellulosic material with increasing demands. Large amount of cellulose and hemicellulose makes lignocellulosic biomass attractive for biogas production through anaerobic digestion (AD) (He et al., 2015). Biogas from AD is an environmentally friendly, widely accepted, and highly promising bioenergy alternative to fossil-derived energy (Sawatdeenarunat et al., 2015). Lignocellulosic biomass also has

* Corresponding author.

E-mail address: nirmal.ghimire@usn.no (N. Ghimire).¹ The author passed away.

competitive advantages over other AD feedstocks due to their abundance, low price, relatively high yield, and non-interference with food supply (Dahadha et al., 2017). It can however vary to what extent these feedstocks can be treated in sustainable ways by AD to produce biogas. A wide range of lignocellulosic biomass has been considered as feeds for AD.

Lignocellulosic biomass has historically been used for energy production by direct combustion or methane production by solid-state AD (SS-AD), after simple pretreatments such as milling, but is not limited to only energy production. With the invention of new technologies and methods, it has been considered for various new products. Recently, cascade utilization of lignocellulosic biomass is considered to obtain maximum utilization that would make biofuels more economically competitive with fossil fuels (Rasi et al., 2019). This approach brings forest-based lignocellulosic biomass into a domain of AD where it can be applied in conjunction with producing several energy carrier products, including biochar and bio-oils, and high value chemicals (Rasi et al., 2019). Similarly, lignocellulosic biomass is pretreated by hydrothermal methods to make it more favorable for subsequent use such as to improve mechanical strength of the solid biomass based material (Alvarez-Chavez et al., 2019). During these processes of thermal pretreatment, hemicellulosic sugar-rich liquid with some dissolved lignin, commonly called hydrolysate, is released during hydrothermal pretreatment (HTP) and aqueous pyrolysis liquid (APL) during pyrolysis as by-products (Liu, 2015). It is important to utilize these organic rich liquid streams. Hydrolysate is pentose rich and not considered suitable for bioethanol production due to requirement of genetically modified microorganisms thriving on pentose (Kaparaju et al., 2009) and high sensitivity to inhibitors like furfural and hydroxyl methyl furfural (HMF) present in the hydrolysate (Torry-Smith et al., 2003). It has also been previously considered for production of hydrogen through dark fermentation, production of health food additive, acetic acid, ethanol, butanol, lactic acid, and polyhydroxyalkanoates (PHA), but the results are not promising (Liu, 2015). Similarly, APL is a challenging substrate with various toxic compounds that can be handled only with robust consortia of microorganisms. Therefore, AD could be a good choice to exploit and handle the organic rich liquid by-product stream to produce methane.

AD is a biological process where a mixed community of microorganisms act together to break down organic compounds to produce biogas (about 50–75% methane (CH₄) and 25–50% carbon dioxide (CO₂)) in the absence of free oxygen. An advantage of such consortia of microorganisms is their ability to synergistically break down various complex, recalcitrant and inhibiting compounds (at low concentrations) to methane after some adaptation time (Benjamin et al., 1984).

Reported AD of pretreated lignocellulosic biomass is mostly SS-AD that is operated at a total solid (TS) content of 15% or higher, contrary to liquid-state AD (L-AD) that operates at TS content of less than 15% (Guendouz et al., 2010). SS-AD has several advantages but also several inherent problems. Some of the well noted problems are low methane yield, slow mass transfer between AD microorganisms and feedstocks, potential instability, acidification, ammonia inhibition, nutrient imbalance, temperature disturbance, and obstacles in using end products (Yang et al., 2015). Several methods have been proposed to overcome these issues (Xu et al., 2019). Liquefaction of lignocellulosic biomass is the most disruptive approach as it changes the inlet mode of lignocellulosic biomass from solid to liquid so that a wider range of AD reactors, including high-rate sludge bed, can be applied. Review of L-AD of liquefied lignocellulosic biomass, however, is still scarce although a notable number of research papers on such solutions are published.

This review aims to encapsulate research related to L-AD of thermally pretreated lignocellulosic biomass, without addition of chemicals, where AD can both be a method to treat by-products from utilization of lignocellulosic biomass for other purposes or being the main process. The constraints and challenges of AD of lignocellulosic biomass is first presented, followed by elucidating different thermal pretreatment

methods that overcome recalcitrance by liquefying the lignocellulosic biomass. Both the favorable and unfavorable products formed during the pretreatments are discussed followed by their effects on AD. Optimization of pretreatments to increase AD yield and challenges and perspectives are discussed before conclusions.

2. Constraints and challenges for AD of lignocellulosic biomass

Lignocellulosic biomass can be treated anaerobically to produce biogas. However, hydrolysis, the rate-limiting step for lignocellulosic material that breaks down the complex organic polymer components during AD, is a very slow process for lignocellulosic materials and is sensitive to the type and composition of the substrate (Dahadha et al., 2017).

Other constraints to the AD process is the heterogeneity and low density of lignocellulosic substances that hampers AD by forming a floating layer on the surface of AD reactors (Tian et al., 2015). This leads to poor substrate accessibility for the microorganisms, worsening mass and heat transfer and reducing the methane yield (Wang et al., 2018). High carbon to nitrogen (C/N) ratio can also limit AD of lignocellulosic biomass (Sawatdeenarunat et al., 2015) but it can be adjusted by adding nitrogen sources (at added cost) or co-digesting with substrate with higher nitrogen content. These extra costs can be offset by increased biogas production and make lignocellulosic biomass a lucrative AD feed for methane production.

3. Pretreatment methods

Pretreatments can be categorized into different groups such as mechanical or physical, thermal, hydrothermal, chemical, and biological. Each pretreatment method works differently, resulting in different yields and products. A single pretreatment cannot necessarily be recommended for each feedstock, as their compositions vary considerably, and pretreatment at the same operational conditions would therefore behave differently for the same feedstock (Ahmad et al., 2018). Pretreatments can be applied alone, or combined, and should be chosen based on feedstock and the desired final products (Pelaez-Samaniego et al., 2013). Readers are referred elsewhere to a comprehensive review for an in-depth understanding of aforementioned pretreatments (Zheng et al., 2014).

Pretreatment typically accounts for 30% of the total cost of a biofuel (Alonso et al., 2013) and it has to be cost-effective to be applied at a large scale (Di Girolamo et al., 2013). Pretreatment involving chemicals tends to be costly, both due to added costs of chemicals and due to added cost of handling chemical waste streams and are therefore not included here. Only the liquefying pretreatments hydrothermal (example; steam pretreatment and hot water extraction) and pyrolysis are covered in this paper.

3.1. Hydrothermal

HTP is the most common pretreatment to convert lignocellulosic biomass into biofuel or other valuable products (Di Girolamo et al., 2013). Hydrothermal is commonly defined as “a reaction occurring under the conditions of high temperature and pressure in aqueous solutions in a closed system” (Rabemanolontsoa & Saka, 2016). Hydrothermal temperature and pressure are maintained under the critical point (374 °C and 22.1 MPa) for water (He et al., 2015). The hydrothermal process does not need washing, chemical recovery, or detoxification steps (Sun et al., 2014), and additional advantages like no catalyst requirement, low reactor cost, and direct utilization of wet or fresh lignocellulosic materials make HTP very attractive (Batista et al., 2019; Sun et al., 2016). The process can also have limitations that must be considered before industrial implementation such as difficult tasks of separation and extraction of different streams at industrial scale (Ahmad et al., 2018). Only two primary hydrothermal treatments, viz. hot water

extraction and steam pretreatment, with or without explosion, for biogas production are found and discussed in this paper.

Several review articles are available on hydrothermal treatment of lignocellulosic biomass (Elliott et al., 2015). However, as per our knowledge, only two review articles are available on HTP of lignocellulosic biomass especially for AD (Ahmad et al., 2018; He et al., 2015). The review by Ahmad et al. (2018) delivers deep insights into effects on structural components and techno-economic analysis coupled with life cycle assessment (LCA). The review by He et al. (2015) covers operating conditions of hydrothermal treatment for subsequent biogas production.

3.1.1. Hot water extraction

Hot water extraction (HWE) (also called liquid hot water (LHW) or hydrothermolysis) is a mild HTP carried out in the temperature range 120–230 °C and at various pressure conditions at which water is kept in subcritical conditions (Nitsos et al., 2013). Its objective is to efficiently extract sugars, acids, or other chemicals from lignocellulosic biomass without considering any structural changes in the extracted wood (Pelaez-Samaniego et al., 2013). Sometimes, the term HWE is used for milder condition while LHW pretreatment is used for harsh condition (in terms of temperature and pressure). They are not differentiated as such in this review.

3.1.2. Steam pretreatment/steam explosion

Steam pretreatment can be performed in two different ways; (i) without addition of other chemicals as catalysts, also called ‘autohydrolysis’ and (ii) with additional of other chemicals like acid, alkali, or supercritical catalysts to reduce process severity, called ‘catalyzed steam-pretreatment’. During autohydrolysis, which is discussed here, acetyl residues from xylan hemicellulose are liberated as acetic acid and catalyze the reaction (Rabemanolontsoa & Saka, 2016). To prevent acetic acid loss by evaporation, low pH and high temperature should be avoided (Bruni et al., 2010).

Steam pretreatment and steam explosion pretreatment involves high temperature heating where the difference between the two methods is that at the end of steam explosion, water in the biomass explode due to the rapid depressurization and cooling down of the biomass to disrupt the biomass fibers (Hendriks & Zeeman, 2009). Typical ranges for temperature, pressure, and time are 160–260 °C, 0.69–4.83 MPa and several seconds to a few minutes, respectively (Sun & Cheng, 2002). Steam explosion is one of the most efficient hydrothermal physical or physio-chemical pre-treatment methods for recalcitrance disruption of lignocellulosic biomass (Wyman et al., 2005). It has been found that steam explosion saves almost 70% energy compared to conventional mechanical processes to attain the same particle size (Holtzapple et al., 1989). Its earliest patent is dated to 1924 although it is known since the 1800s (Rabemanolontsoa & Saka, 2016). Nowadays, it is commonly used for pretreatment of woody biomass (Vivekanand et al., 2013) and agricultural residues (Zhao et al., 2018). These pretreatments are claimed to have good environmental influence, low hazardous chemicals yields, and high-energy efficiency (Bhutto et al., 2017; Yan et al., 2016) while disadvantages for steam pretreatment/steam explosion may include high water demand and expensive equipment (Sun et al., 2016; Zheng et al., 2014).

In this article, the terms steam pretreatment and steam explosion pretreatment are used interchangeably since they have the same objective of producing sugar rich feed for the AD process. However, they should be treated independently if change in structure of biomass is to be studied.

3.2. Pyrolysis

Pyrolysis breaks down chemical bonds to form new compounds in the absence of oxygen and has a high flexibility in processing raw biomass materials for derived end products (Rasi et al., 2019). It converts biomass thermo-chemically into liquid (bio-oil also called pyrolysis

oil, pyrolysis liquid, bio-crude, wood liquid, wood oil, or wood distillate), charcoal (biochar), and non-condensable gases (syngas) by heating to about 480 °C or more (Pecchi & Baratieri, 2019). Bio-oil consists of molecules derived from the degradation of cellulose, hemicellulose, and lignin (Alvarez-Chavez et al., 2019). Higher cellulose content leads to higher liquid products, high hemicellulose content leads to higher gas production, and higher lignin content leads to more solid residues (Kumar et al., 2020). Due to the presence of high concentration of water in the feedstocks, the bio-oil is separated into aqueous phase (APL) and organic phase. The organic phase (or biocrude) is a complex mixture of oxygenated hydrocarbons and nitrogenated compounds such as aromatics, short chain carboxylic acids, ketones, phenolics, sugars, and derivatives of furan depending upon the type of biomass (Hassan et al., 2009). Its complex nature together with high oxygen levels makes it difficult to utilize this organic phase directly in AD, and it can enter the market as a renewable alternative to heavy fuel oil (Oasmaa et al., 2015). APL, on the other hand, has a high chemical oxygen demand (COD) concentration along with various potentially toxic organic compounds and can be environmentally harmful if not managed properly (Seyedi et al., 2019).

Process parameter adjustments varies the proportion of produced bio-oil, biochar, and syngas. Lower process temperature and longer vapor residence time favors char production. High temperature and longer residence time increases syngas formation, while moderate temperature and short vapor residence time produces optimum bio-oil (Bridgwater, 2012). Pyrolysis is differentiated into four main categories based on residence time, slow (or conventional), moderate (or intermediate), fast, and flash. In fast pyrolysis, liquid with only a single phase is obtained (Oasmaa et al., 2015) while intermediate pyrolysis produces two phase liquid (organic phase and aqueous phase (APL)) (Fabbri & Torri, 2016). Details of these processes can be found elsewhere (Kan et al., 2016).

4. Achievements during pretreatment

Pretreatment can efficiently deal with the slow hydrolysis of lignocellulosic materials by disrupting the lignin barrier, solubilizing the hemicellulose, reducing the cellulose crystallinity, increasing the surface for enzymatic attack, and homogenizing the lignocellulosic biomass to improve biodegradability (Bhatia et al., 2020; Di Girolamo et al., 2013; Sawatdeenarunat et al., 2015). However, pretreatment is not limited to improve biodegradability but can also be carried out for conditioning woody biomass to optimize production of other products such as biochar, bio-oil, and valuable products (Alvarez-Chavez et al., 2019; Pelaez-Samaniego et al., 2013; Rasi et al., 2019). According to these studies such processes may generate biproducts that can be handled by AD, but in-depth evaluations of such solutions are lacking. The products from hydrothermal treatment and pyrolysis are results of different temperatures, pressures, and water contents, forming a vast variety of components, from easily degradable to inhibiting.

4.1. Valuable pretreatment products and effects related to AD

4.1.1. Hydrothermal

During HTP, water or steam (or both) penetrates under high pressure (with or without catalysts) to liberate most of the hemicellulose and partial lignin, while making biomass more accessible to hydrolytic enzymes (Taherzadeh & Karimi, 2008). At pretreatment temperature of 100 °C, hemicellulose remains in the solid fraction but at temperature above 150 °C, hemicellulose hydrolyzes and dissolves into the liquid fraction (or hydrolysate) (Fernandez-Cegri et al., 2012; Hendriks & Zeeman, 2009). At temperature 150–180 °C, solubilization of firstly hemicellulose and shortly after lignin starts (Hendriks & Zeeman, 2009). Cellulose begins decomposing at 200 °C with a reaction rate faster at higher temperatures (>240 °C) and the reaction completing at around 280 °C (Minowa et al., 1997).

Aqueous hemicellulose (or the extract) consists mainly of oligomeric and monomeric products like xylose, acetyl, glucose, mannose, rhamnose, arabinose, and galactose (Mosier et al., 2005b). In the case of AD, HTP should liberate hemicellulosic organic compounds utilized by microorganism such as pentose (xylose and arabinose), hexose (mannose, galactose, glucose), volatile fatty acids (VFA), proteins, and lipids (Bruni et al., 2010). The composition of aqueous hemicellulose depends on the sources of lignocellulosic biomass and the extraction time. The major carbohydrate in the hydrolysate of e.g. sugar maple (hardwood) woodchips is xylose, with minor other sugars (Liu, 2015), but at short extraction time (around 60 min only) glucose and mannose concentrations are higher than xylose (Liu, 2013). Unlike hardwood, southern pine (softwood) has mannose as the dominant sugar species followed by other sugars in the hydrolysate (Liu, 2015). Part of the hemicellulose is hydrolyzed and form acids during hydrothermal processing. Acetic acid is the most abundant VFA produced while other VFAs are found to be negligible (Di Girolamo et al., 2013). The produced acetic acid acts as a catalyst during the process of degrading the polymers and thereby contributes in increasing the sugar yield (Mosier et al., 2005b).

In recent years, there is a significant increase of research using HTP for biogas production. Agricultural residues, which are increasingly becoming an issue of waste handling, are subjected to HTP to make them AD favorable for efficient utilization. HTP can also treat lignocellulose previously considered unsuitable for AD, such as wood to remove hemicellulose and lignin (to some extent), alter the crystallinity index of cellulose, or reduce the degree of polymerization of cellulose and lignin (Pelaez-Samaniego et al., 2013). HTP also acts as pretreatment to lignocellulosic biomass to make a suitable feedstock for processes such as pyrolysis to produce biochar, a product with multiple uses such as natural fertilizer or solid fuel (Feng & Lin, 2017). It has also been useful as an additive to AD for enhanced methane production (Torri & Fabbri, 2014).

4.1.1.1. Hot water extraction. During hot water extraction, part of the hemicellulose and some lignin are dissolved in the extraction water liquor (Hendriks & Zeeman, 2009). Cellulose cannot be dissolved during this process since concentrated acid or higher temperature is required (Monlau et al., 2013). This leads to relative increase in cellulose and lignin contents in the woody biomass as hemicellulose is removed. This has positive effects on the quality of the solid biomass products like composites and various board products made, such as reduced water absorption, improved mechanical properties, and improved resistance to decay (Pelaez-Samaniego et al., 2013). In case of using solid residues after hot water extraction for ethanol and biogas production, HTP enhances the yield as glucose (from cellulose) is better converted without the presence of mixed sugars (Liu, 2015) and cellulose mostly remains in the solid residue in a loose form for easier hydrolysis. Similarly, HTP is also in use to make cellulose better accessible for enzymatic fermentation in subsequent bioethanol production (Mosier et al., 2005b). HWE before pyrolysis also gives better bio-oil yield due to increased cellulose content while reducing ketones, acids, and water content in the bio-oil leading to higher heating value and significantly improved levoglucosan content (Chang et al., 2013). HWE also lowers the activation energy for thermal degradation during pyrolysis compared to untreated biomass (Kumar et al., 2020).

HWE has been successfully used in pre-treating agricultural residues to make them AD suitable (Baeta et al., 2016; Luo et al., 2019). However, reported HWE of woody biomass is limited mostly to making woody biomass rich in cellulose and lignin by removing hemicellulose (Pelaez-Samaniego et al., 2013), not considering AD for methane production.

4.1.1.2. Steam pretreatment. The objective of both steam pretreatment and steam explosion pretreatment is to obtain solubilized hemicellulose

(Bruni et al., 2010; Teghammar et al., 2010), but also some lignin will be removed from the lignocellulosic materials during both pretreatments (Pan et al., 2005). During steam explosion, pressure is reduced rapidly to atmospheric condition to disintegrate the biomass partly or completely, decreasing the particle size, depending upon the type of biomass (Rabemanolontsoa & Saka, 2016). This also increases the cellulose fiber reactivity of the residues, as the cellulose is made easily accessible for the enzymes (Laser et al., 2002). It can be beneficial if residues are also considered for bioprocesses, such as biogas or ethanol production, but at the expense of biochar yield.

Steam pretreatment is also applied to modify woody biomass to increase the strength of its products by removing hemicellulose, ash, and alkali metal contents (Biswas et al., 2011). Steam pretreatment also improves calorific value by enhancing carbon content and decreasing oxygen content, pellet density, impact resistance, and abrasive resistance of the pellets of biomass feedstock (Kan et al., 2016). Steam pretreatment is also used as HWE in making cellulose more accessible to enzymes by removing hemicellulose and lignin for further conversion to fermentable simple sugars (Simangunsong et al., 2018). In these processes a high yield of hemicellulosic sugars are recovered in the liquid phase consisting of monomers, oligomers, and polymers that have the possibility to be anaerobically digested (Simangunsong et al., 2018).

4.1.2. Pyrolysis

Bio-oil from pyrolysis is a dark brown, free flowing liquor with pungent smell that consists of a complex mixture of up to 400 organic compounds such as acids, sugars, alkenes, esters, ethers, and different oxygenates (Kan et al., 2017; Rezaei et al., 2014). Bio-oil can be upgraded to fuel due to the presence of phenolic monomers and dimers (Mortensen et al., 2011), its ideal carbon numbers (C₆-C₂₀), and relatively lower oxygen content compared to carbohydrate (Zhou et al., 2019). Similarly, engineered microorganisms (e.g. *Escherichia coli*) can utilize the pyrolytic sugars such as levoglucosan to produce fuels and chemicals (Layton et al., 2011). However, high water content of bio-oil poses several challenges such as low heating value and chemical and thermal instability (Zhou et al., 2019). To overcome such problems, bio-oil can be further divided into organic or oily phase (heavy fraction) and aqueous pyrolysis liquid (APL) (lighter fraction). The organic or oily phase is considered as an energy source and for chemical production (Rasi et al., 2019), and it has also been considered used for bio-based pesticides (Hagner et al., 2018) and for manure acidification (Keskinen et al., 2017).

The lighter fraction of the bio-oil, APL, has a high water content and contains C₂-C₆ sugars, furan derivatives, hydroxyacids, oligomers, water soluble phenols, and other water soluble organics formed during pyrolysis (Shanmugam et al., 2017). APL contains high concentration of acetic acid, ranging from 25 to 166 g/L, making it a suitable substrate for AD as acetic acid is directly converted to methane (Seyedi et al., 2020b; Wen et al., 2020). A fraction of the biochar produced can be used as effective additives for AD, improving the AD reactor conditions (Torri & Fabbri, 2014).

The combined process of HTP and pyrolysis is of interest as it improves the bio-oil quality, for upgrading to fuel, during the subsequent use of hydrothermally pretreated feedstock in pyrolysis (Alvarez-Chavez et al., 2019). It also improves pyrolysis and gasification efficiencies by removing alkali metal responsible for slagging, corrosion, and fluidized bed agglomeration while increasing energy content of the residues (Liu, 2015).

4.2. Unfavorable pretreatment products related to AD

4.2.1. Hydrothermal

The objective of HTP is to achieve sufficient solubilization of the hemicellulose while limiting the formation of inhibitory compounds for increased biogas yields (Bruni et al., 2010; Teghammar et al., 2010), however, moderate formation of inhibitory products will occur (Sun

et al., 2016; Zheng et al., 2014). Hydrothermal temperatures are maintained in a wide range of 160 to 240 °C to avoid degradation of cellulose which occurs at temperature above 240 °C (Cao et al., 2014). An increase in pretreatment temperature leads to formation of AD inhibitors like furans from sugars degradation (Mosier et al., 2005a; Simangunsong et al., 2018) and soluble phenolic compounds from degradation of lignin polymer and/or lignin oligomers (Monlau et al., 2014). In addition, partial lignin degradation leads to inhibitory compounds such as vanillin and syringaldehyde (Barakat et al., 2012). Humic acids, formed from the phenolic compounds (Bolyard et al., 2019; Zhang et al., 2019), can also be inhibitory. These degradation products are inhibitory to AD process and can lower the methane yield (Palmqvist et al., 1999).

Aqueous hemicellulose (or the extract), which consists mainly of oligomeric and monomeric sugars, have a relatively low inhibitor content in the treated samples (Mosier et al., 2005b). The furan compound 2-furaldehyde, referred to as furfural, forms due to degradation of pentose while 5-hydroxymethyl-2-furaldehyde, referred to as HMF, forms because of hexose degradation (Jonsson & Martin, 2016). Less HMF is formed compared to furfural due to limited hexose degradation (Chandel et al., 2011).

As part of the lignin can be dissolved along with the hemicellulose (Mosier et al., 2005b) it can inhibit different steps of AD (Koyama et al., 2017). Soluble lignin itself is either inert (Liu et al., 2017) or has a very low biodegradability under anaerobic condition (Benner et al., 1984), but hemicellulosic sugars, which are readily biodegradable, appear to be less biodegradable or even completely refractory when in combination with lignin (Li et al., 2018).

4.2.2. Pyrolysis

APL from pyrolysis consists of known inhibitory organic compounds such as cresol, hydroxyacetaldehyde, acetol, furans, phenols, and N-containing compounds such as pyrazine and pyridine, together with several compound with unknown effect (Kan et al., 2017). APL also contains inorganic constituents such as $\text{NH}_3\text{-N}$, H^+ or OH^- that can reduce methanogenic activity (Seyedi et al., 2020b).

5. Effect of thermal pretreatment on AD

HTP overcomes recalcitrance of lignocellulosic biomass by producing an organic rich hydrolysate. Although hydrolysates of agricultural residues and energy crops have been applied extensively in AD, an alternative use of hydrolysate from woody biomass as feed for AD is not explored much so far. The hydrolysate produced by hot water extraction and steam pretreatment of mainly agricultural residues and energy crops have been found effective in increasing the AD yield. Similarly, from pyrolysis the lighter fraction of the bio-oil (APL) has a high water content and is rich in components that can be converted to methane by AD (Cordella et al., 2012), but with significant inhibitors present. APL from pyrolysis of lignocellulosic biomass has shown promising results as feed for AD. Combining pyrolysis and AD has the potential to increase the overall product yields from organic feedstock by overcoming defects in each individual process, and several combinations of pyrolysis and AD are therefore considered.

5.1. Hot water extraction (HWE)

HWE can be considered a mild extraction method where the concentrations of inhibitors produced are low, typically limited to furfural and HMF, and remains within 1.5% of the organics (Phaiboonsilpa, 2010). The relatively high input of water during HWE implies that the solubilized lignin concentration is relatively low in the extracted liquid and precipitation of lignin compounds in AD is thus avoided (Hendriks & Zeeman, 2009). Some claim, however, that HWE based feed demands more energy for down-stream processing (AD) because of the large volume of water involved, making equipment cost high (Bhutto et al.,

2017; Sun et al., 2016), but this may not be so for an optimized process.

Although L-AD study on wood (Norway spruce) as feedstock was examined recently (Ghimire et al., 2021, 2020), L-AD of woody biomass is still rare. However, L-AD of different agricultural residues (Table 1) is studied and gives an enhanced methane production due to HWE pretreatment, compared to untreated, from 20% for wheat straw (Chandra et al., 2012b) to 222% for rice straw (Chandra et al., 2012a).

5.2. Steam pretreatment

Steam pretreatment has also been considered to enhance methane production, primarily from agricultural residues (Table 2). Increased methane yields (20–130%) are observed at different pretreatment temperatures (120–190 °C) and residence times (10–60 min). L-AD of hydrolysate of woody biomass after steam pretreatment is still lacking, and only SS-AD of birch, a woody biomass, after steam pretreatment has been examined (Vivekanand et al., 2013).

5.3. Pyrolysis

Pyrolysis is integrated with AD in order to improve the overall carbon and energy utilization efficiency (Corton et al., 2016). The integration is divided into three main types, anaerobic digestion-pyrolysis (AD-Py), pyrolysis-anaerobic digestion (Py-AD) and anaerobic digestion-pyrolysis-anaerobic digestion (AD-Py-AD). Out of these, Py-AD and AD-Py-AD are of main interest to convert lignocellulosic biomass into liquefied bio-oil (APL) for AD, while AD-Py may increase the net energy gain (Monlau et al., 2016). AD-Py integration is not relevant in this review as the end process is not AD, and readers interested in such integration are referred to the review by Feng and Lin (2017).

The combined process Py-AD utilizes the pyrolysis product APL as feedstock for AD (Torri et al., 2020). The other pyrolysis products like non-condensable gases and biochar can also be utilized as AD feeds. Non-condensable gases can be fermented and/or converted to methane in AD (Pecchi & Baratieri, 2019). Some of the biochar can be used as an additive in AD to help stabilize the process by adsorption of inhibitors, enhance buffering, binding and acclimatization of microbial cells (Masebinu et al., 2019), resulting in increased methane yield (Torri & Fabbri, 2014). Application of biochar and anaerobic fermentation of non-condensable gases in AD is beyond the scope of this paper and the reader is referred to the review by Masebinu et al. (2019) for a survey of these possibilities.

Pyrolysis in conjunction with AD of APL (Py-AD) is gaining interest as a low-cost environmentally friendly option with some investigations already started (Cordella et al., 2012; Hubner & Mumme, 2015). Life cycle analysis assessment performed on the coupling of AD has shown significant achievable reduction of greenhouse emission (Righi et al., 2016). AD of APL has been tested both through co-digestion and as a sole substrate (Table 3). Inhibition is targeted in batch tests, with observed efficient anaerobic degradation of APL up to 1 g L⁻¹ and complete inhibition at 20 g L⁻¹ initial APL content (Scherer & Meier, 2004) suggesting dilution through co-digestion as a reasonable solution. Co-digestion of up to 6.5% (v/v) pyrolytic acids (similar to APL), from pyrolysis of wood residue, mixed with swine manure is reported for a biofilm based AD (Andreoni, 1990). APL has been used as an additive during AD of swine manure and it is observed improved methanogenic capacity because of trace elements in APL and enhanced resistance of microorganisms to high ammonia nitrogen (TAN) concentration and its accumulation (Yu et al., 2020).

Recently, APL from woody biomass has been subjected to AD for methane production. APL from Douglas Fir wood has been examined in AD and increased methane production was observed in acetic acid (10%) washed biomass compared to untreated, due to increased concentration of levoglucosan and reduced concentration of hydroxyacetaldehyde (Liaw et al., 2020). Continuous AD of APL from pine

Table 1
Methane production from hot water extracted hemicellulose of different lignocellulosic biomass.

Lignocellulosic biomass	Reactor type, mode and volume	Applied pretreatment	Digestion period	Methane yield	Loading	Removal (%)	Reference
Sugarcane bagasse	UASB, continuous, 2.3 L, 20–30 °C	178.6 °C, 43.6 min	168 days	270 L CH ₄ /kg COD	OLR: 1.4 to 4.8 g COD/L/d HRT: 18.4 h	COD: 86	Ribeiro et al. (2017)
Wheat straw	Batch, 1130 mL (1000 mL working volume), 37 °C	200 °C, 10 min	60 days	0.206 m ³ CH ₄ /kg VS	S/I: 1	NA	Chandra et al. (2012b)
Rice straw	Batch, 1130 mL (1000 mL working volume), 37 °C	200 °C, 10 min	60 days	0.133 m ³ CH ₄ /kg VS	S/I: 1	NA	Chandra et al. (2012a)
Norway spruce (<i>Picea abies</i>)	Batch, 100 mL syringes, 55 °C	140 °C for 300 min 170 °C for 90 min	38 days	290 NmL CH ₄ /g COD 195 NmL CH ₄ /g COD	OL: 6 g COD/L	COD: 83 COD: 56	Ghimire et al. (2020)
Norway spruce (<i>Picea abies</i>)	Batch 100 mL syringes, 35 °C	140 °C for 300 min 170 °C for 90 min	103 days	266 NmL CH ₄ /g COD 276 NmL CH ₄ /g COD	OL: 6 g COD/L	COD: 76 COD: 79	Ghimire et al. (2021)

NA: Not Available; OL: Organic Loading; OLR: Organic Loading Rate; S/I: Substrate/Inoculum; HRT: Hydraulic Retention Time

Table 2
Methane production from hemicellulose from steam pretreatment of different lignocellulosic biomass.

Lignocellulosic biomass	Reactor type, mode and volume	Applied pretreatment	Digestion period	Methane yield	Loading rate	Removal (%)	Reference
Coffee husk	Batch, 160 mL (80 mL working volume), 35 ± 0.5 °C	Steam explosion a. 120 °C, 60 min b. 180 °C, 15 min	25 days	0.145 NmL CH ₄ /g COD 0.128 NmL CH ₄ /g COD	F/M: 0.7 g COD/g VS _{inoculum}	COD: 41 COD: 36	Baeta et al. (2017)
Rice straw	Batch, 37.5 °C, 118 mL	Steam explosion, 160–205 °C, 15 min	60 days	486 NmL/g VS	I/S: 2 g VS/g VS	VS: 97	Aski et al. (2018)
Wheat straw	Batch, 0.5 L (0.36 L working volume), 37 °C.	Steam explosion, 150 °C, 40 mins	12.5 days	195 ± 1 mL CH ₄ /g COD	I/S: 2 g VS/g VS	COD: 50 COD: 100	Buitrón et al. (2019)
Corn straw				369 ± 22 mL CH ₄ /g COD		COD: 50 COD: 66	
Sugarcane bagasse				178 ± 11 mL CH ₄ /g COD			
Agave bagasse				230 ± 8 mL CH ₄ /g COD			
Agave bagasse	Batch, 125 mL, 36 °C	Steam explosion, 0.38 MPa	30 days	317 mL CH ₄ /g COD	I/S: 2 g VS/g VS	COD: 89	Weber et al. (2019)

VS: Volatile solid; F/M: Food/Microorganism; I/S: Inoculum/Substrate

Table 3
Methane production utilizing APL from various lignocellulosic biomass.

Lignocellulosic biomass	Reactor type, mode and volume	Applied pretreatment	Digestion period	Methane yield	Loading	COD removal (%)	References
Pine wood	Batch, 700 mL, 37 °C	Fluidized bed flash pyrolysis at 460 °C for 1 sec	28 d	480 NmL CH ₄ /g substrate	1 g APL / 700 mL	95	Scherer and Meier (2004)
Corn stalk	Batch, 100 mL syringe (30 mL effective volume), 40 °C	Fixed bed intermediate pyrolysis at 400 °C for 10 min	225 d	126 mL CH ₄ /g bio-oil	OL: 35 g COD/L F/M: 0.6	34 ± 6	Torri and Fabbri (2014)
Digestate of cow manure and maize (4:3)	Batch, 100 mL syringe (20 mL effective volume), 40.5 ± 1 °C	Pyrolysis at 330 °C, 430 °C and 530 °C for 45 ± 15 min	49 d	199.1 ± 18.5 mL/g COD	OL: 0.129 to 49.1 g COD/L	56.9, 55.4 and 36.9	Hubner and Mumme (2015)
Pine wood (softwood)	Continuous (UASB) reactor, 80 mL, 40 °C	Pyrolysis at 400 °C for 30 min	79 d	34% of fed COD	OLR: 1.25 g COD/L/d HRT: 80 days	NA	Torri et al. (2020)

NA: Not Available; OL: Organic Load; OLR: Organic Loading Rate; F/M: Food/Microorganism; HRT: Hydraulic Retention Time

wood in up-flow anaerobic sludge bed (UASB) reactor showed that 52% of APL (COD based) was potentially biodegradable at organic loading rate of 1.5 gCOD L⁻¹ day⁻¹ (Torri et al., 2020). This should trigger more research on adaptation to this challenging substrate in continuous flow AD to make it feasible for industrial scale. Optimized integration of pre- and post-treatments together with adapted mixed AD cultures may be the key for full-scale AD of APL (Fabbri & Torri, 2016).

The AD-Py-AD combined process is applied to handle sludge from wastewater treatment, where AD stabilizes the sludge, makes it easier to dewater, and reduces the amounts by converting a significant fraction to biogas (Tchobanoglus et al., 2003). Using pyrolysis to handle AD digestate rich in lignocellulosic substances can be a sustainable solution to further reduce sludge volumes and convert more sludge to biogas. Currently, digestate is mainly used as soil amendment, dumped in

landfills or burnt at the cost of energy, which are not sustainable due to a range of negative environmental aspects (Fabbri & Torri, 2016).

In the AD-Py-AD process about half of the volatile matter in sludge digestate can be converted to bio-oil that can reach energy content values comparable to diesel (Cao & Pawłowski, 2012). Utilizing AD-Py-AD, this energy, or parts of it, can be converted to biogas by AD (Seyedi et al., 2020a).

Manure is also targeted by AD-Py-AD with promising results. AD of APL from pyrolysis of AD digestate of cow manure and maize (4:3 ratio) gave a COD removal of 63% and methane yield of 220 mL/g COD without any additives at a COD load of 12 gCOD/L, while permanent inhibition was observed at a COD load of 30 g/L (Hubner & Mumme, 2015).

6. Pretreatment inhibitors during AD

The most prominent AD inhibitors produced during HTP are furfural and HMF together with soluble lignin and its derivatives. A range of measures has been suggested to counteract inhibition problems (Jonsson & Martin, 2016; Kim, 2018). Readers interested in details regarding detoxification of hydrolysates are referred to the review articles by Bhatia et al. (2020) and Kumar et al. (2019).

The pyrolysis process also produces several toxic compounds at concentrations inhibitory to microorganisms, but several studies have shown that AD inoculum adapt to these compounds (Barakat et al., 2012; Benjamin et al., 1984). The ratio of inhibiting compounds to inoculum influences the adaptation process (Park et al., 2012). Powdered activated carbon (PAC) and biochar have also been found useful in mitigating inhibitory effects by inhibitor adsorption, enhancing buffer capacity of AD, and forming biofilm (Liu et al., 2017; Torri & Fabbri, 2014). Although biochar cannot be degraded to produce methane (Mumme et al., 2014), it can be added during AD to help in detoxification of APL while also supporting biofilm, favoring bio-methanation, or enhancing electron transfer thereby enhancing the biogas production (Masebinu et al., 2019). Developing a robust microbial consortia tolerant to toxicity of APL through metabolic evolution of organism has also been found effective for successful AD (Zhou et al., 2019).

6.1. Sugars derivatives

Sugar can degrade to furanic compounds that at high concentrations hamper microorganisms by inhibiting cell growth, inducing deoxyribonucleic acid (DNA) damage, and inhibits several enzymes of the glycolysis pathway (Palmqvist & Hahn-Haagerdal, 2000). The concentrations observed for partly or complete inhibition on methanogenic activity from HMF and furfural is in the range 2–4 g/L for furfural and 2–10 g/L for HMF depending on substrate compositions and inoculum in batch (Ghasimi et al., 2016). Furfural and HMF may have additive inhibitory effects when both are present (Taherzadeh et al., 1999), while furfural is found to be more inhibitory compared to HMF due to its lower molecular weight that eases its uptake by microbial cells (Quéméneur et al., 2012).

Furfural and HMF concentrations of 1 g/L each, tested separately, have been found to give no inhibition effect during mesophilic AD of xylose (1 g/L) and these compounds could be used as sole carbon sources (at 2 g/L) to produce methane (Barakat et al., 2012). During AD both furfural and HMF can be converted to less inhibitory compounds such as furfuryl and HMF alcohols by facultative anaerobes in AD, while furfural also can be converted to furoic acid and acetate, before being converted to methane and carbon dioxide (Monlau et al., 2014). For detailed mechanism of inhibitory products formation during HTP, readers are referred to Nitsos et al. (2013).

6.2. Soluble lignin

Soluble lignin, dissolved along with the hemicellulose, hinders efficient AD of hydrolysate by inhibiting the growth of methanogens (Baeta et al., 2016; Barakat et al., 2012), with negative linear correlation between lignin content and methane yield during AD of cellulose, hemicellulose, manure wastes, and acetate-rich wastewater (Li et al., 2018). A reduced anaerobic digestion rate for methanogenesis, acidogenesis and hydrolysis by 15%, 10% and 35% respectively at soluble lignin concentration higher than 5 g/L is observed (Koyama et al., 2017).

Negligible amounts of lignin is broken down during AD with only 2–7% of methane produced from lignin during co-digestion of natural lignin (organosolv, kraft, and lignosulfonates) with xylose (Barakat et al., 2012), and only 1.4% biodegradation of hardwood lignin compared to 16.9% of grass lignin (Benner et al., 1984). However, elevated AD temperature was found to enhance conversion rate of lignin and lignified substances to methane or lower molecular-weight aromatic compounds during AD (Benner & Hodson, 1985).

6.3. Lignin derivatives

Lignin derivatives, such as soluble phenolic compounds, are formed at pretreatment conditions above 160 °C (Hendriks & Zeeman, 2009). The produced phenolic compounds have in many cases inhibitory and toxic effects on bacteria and methanogens/archaea (Campos et al., 2009) as they can damage cell membranes, causing leakage of intracellular components and lead to inactivation of essential enzymatic systems (Heipieper et al., 1994). Inhibition by lignin derived phenolic compounds is directly related to molecular weight; low molecular weight are more toxic than high molecular weight phenolic compounds (Clark & Mackie, 1984).

Microorganisms are however capable of adapting to soluble phenolic compounds (Hendriks & Zeeman, 2009) with effective phenol degradation during AD (Fang et al., 2004) and Benzoate as a key intermediate (Fang et al., 2004). AD degradation efficiency of different phenols depends on temperature with higher degradation efficiency at mesophilic than at thermophilic conditions (Leven et al., 2012). Some degradation can also occur during the pretreatment with formation of AD inhibiting phenolic degradation products such as syringaldehyde and vanillin (Barakat et al., 2012).

6.4. Inhibitory and toxic compounds from pyrolysis

APL contains several toxic compounds, and AD containing mixed anaerobic consortia, possible of adaptation to a wide range of chemical substances (Appels et al., 2011), can be exploited for its capacity to degrade and convert such to methane (Torri & Fabbri, 2014; Wen et al., 2020).

Si et al. (2018) observed complete conversion of furfural and HMF to methane, while some phenolic compounds, such as 4-ethyl-phenol and 3-hydroxypyridine, degraded with some inhibition in acetogenesis during continuous AD.

Pyridine and pyridine derivatives can also be converted by AD at low biodegradation rates (Li et al., 2001). Sun et al. (2011) observed a synergistic effect of the inhibitors found in APL, in which phenol > 400 mg/L inhibited pyridine degradation. However, inhibition caused by phenol on pyridine degradation was less in immobilized compared to suspended cultures (Kim et al., 2006) implying that microbial aggregates (e.g. biofilm and granules) may handle APL toxins better than reported batch tests.

7. Pretreatment tuning to increase overall and AD yield

Pretreatment conditions should be chosen based on primary objective while also considering the utilization of by-product streams for enhanced resource recovery. The whole process should be optimized

according to the total set of products, including methane production by AD of the liquid. In this perspective, efficient hydrothermal pretreatment must extract hemicellulose while minimizing carbohydrates loss and limiting inhibitors formation in the total process (Benjamin et al., 1984) so that the hydrothermal extraction can produce value-added products, such as biogas, from compounds that are otherwise wasted in other pretreatment schemes (Liu, 2015).

7.1. Hydrothermal- effect of temperature

Biomethane potential of hydrolysate cannot be predicted on the basis of hydrothermal treatment alone due to factors such as difference in hemicellulose content between different lignocellulosic biomass, generation of inhibitors, hydrothermal reactor configuration, liquid and solid ratio, operation mode i.e. batch or continuous, and possible utilization of catalytic agent (Ahmad et al., 2018).

The biomethane potential is however clearly influenced by HTP temperature with some optimal combination of time and temperature determining the amount of sugar transferred to the liquid hydrolysate and the amounts of inhibitory compounds included. The choice of pretreatment severity (based on temperature and residence time) depends on the feedstock (Liu, 2015). Low severity pretreatment conditions form products such as oligosaccharides (xylooligosaccharides) of higher potential value due to their prospective use in medicinal, food, cosmetic, and health products (Qing et al., 2013). Higher severity leads to better extraction of hemicellulose from the biomass but forms inhibitors from degradation of monosaccharides extracted, with possible appearance of metal ions from reactor vessel in the extracted hydrolysate (Carvalho et al., 2016).

Recent studies suggest that operating temperatures between 100 and 230 °C is best to obtain hydrolysate for biogas production (He et al., 2015) and HTP temperatures above 250 °C is not recommended to avoid unwanted pyrolysis reactions (Dahadha et al., 2017). If biochar is the main product of the process, temperature should be chosen (dependent on the biomass type) to extract hemicellulose as much as possible while avoiding lignin and cellulose solubilization. Review by He et al. (2015) covers specific operational parameters crucial for lignocellulosic biomass for biogas production. These aspects are beyond the scope of this review.

7.1.1. Hot water extraction

The hydrolysate composition after hot water extraction vary depending upon the origin of lignocellulosic biomass and process conditions such as reaction temperature, solid to liquid ratio, type of reaction vessel, and mode of operation, i.e. batch or continuous (Ahmad et al., 2018).

Temperature affects the extraction mass removal (Lu et al., 2012), where an optimal extraction severity can be observed. E.g. HWE of *sorghum sudanense* treated at 100 °C for 1 h produced the highest yield (0.282 m³ CH₄/kg VS) of the conditions tested and treatment at lower and higher temperatures led to lower AD methane yield (Sambusiti et al., 2013).

A higher extraction pressure maintains the liquid hot water as solvent to solubilize mainly the hemicellulose, which makes the cellulose better accessible and reduces the formation of inhibitors (Hendriks & Zeeman, 2009; Liu, 2015). pH can also influence the formation of inhibitors and should be maintained between 4 and 7 (Mosier et al., 2005a). This optimized pH also maximizes the solubilization of the hemicellulose fraction and reduces the formation of monomeric sugars, and therefore also the formation of inhibitory degradation products (Mosier et al., 2005a).

7.1.2. Steam pretreatment

Optimal steam pretreatment/steam explosion treatment depending on the characteristics desired for the product can be achieved by manipulating parameters like temperature, residence time, catalyst

dosage, time of pre-soaking, particle size, and moisture content of the substrate (Talebnia et al., 2010). However, clear correlation between different parameters are not yet found (Simangunsong et al., 2018). As in HWE, higher temperature and retention time leads to higher extraction of hemicellulosic sugars, but also increased inhibitor concentration due to degradation of sugars.

Although the effect of particle size of the biomass in pretreatment is not much discussed, reducing the particle size before pretreatment is crucial for the optimization of sugar conversion, as particle size has a major influence on the kinetics of the hydrolytic process (Ballesteros et al., 2000). Small particles leads to easy and high extraction of hemicellulosic sugars, whereas the largest particles may lead to lower extraction (Simangunsong et al., 2018). However, concentration of inhibitors (furfural and HMF) is higher during the steam pretreatment of smaller particles (Cullis et al., 2004). Maximum hemicellulose extraction with low concentration of inhibitors and soluble lignin should be in focus when the hydrolysate is meant for AD. Lignin and cellulose is preferred in the solid residue used in pyrolysis for biochar and bio-oil production.

7.2. Pyrolysis

Pyrolysis parameters should be tuned for higher APL yield if the side stream is to be treated by AD, producing bio-oil. This will increase easily degradable ketones and acids and decrease the concentration of recalcitrant or toxic carbon compounds such as hydroxyacetaldehyde, acetol, furans, N-heterocyclic compounds, and phenols in APL, for enhanced methane yield (Alvarez et al., 2014; Rezaei et al., 2014). Parameter tuning should be chosen accordingly if biochar or syngas production is also considered, where low process temperature and long vapor residence time favors char production and high temperature and long residence time increases syngas formation (Bridgwater, 2012).

Physical, thermal, chemical, and biological pretreatments on biomass before pyrolysis can also help in avoiding inhibitors and increasing the sugar concentration in APL, to favor AD methane production. HWE before pyrolysis removes hemicellulose and alkali metals (Na and K) leading to increased sugar concentration, mainly levoglucosan, while reducing possible AD inhibitors such as acetic acid, carboxylic acids, ketones, and phenols in the bio-oil (Chang et al., 2013; Kan et al., 2016). Similarly, steam explosion pretreatment also reduces acids, furfural, and HMF concentration in the bio-oil, while increasing the concentration of levoglucosan and other anhydrosugars increasing the methane production (Liaw et al., 2020; Wang et al., 2011). Comprehensive reviews on details of such pretreatments are published by Alvarez-Chavez et al. (2019) and Kumar et al. (2020).

8. Challenges and perspectives

AD of lignocellulosic biomass is limited to mostly agricultural residues as suggested by limited publications on AD of woody biomass. The main reason can be attributed to higher pretreatment cost, as woody biomass consumes more energy during pretreatment compared to agricultural residues because of more complex structure, that cannot be offset by methane production. However, the search for different renewable bio-based material, such as pretreated wood products or biochar by pyrolysis, as the main product, has increased the use of woody biomass, resulting in by-product streams that need to be handled before disposal. Pyrolysis is also gaining interest for reducing volume of different wastes, including agricultural and forest residues.

Therefore, more research is needed to improve AD of such by-product streams as they contain several inhibitors and recalcitrant compounds. Hemicellulose extract from hydrothermal pretreatment of agro-industrial wastes and grasses have been extensively used for AD, but mostly in laboratory scale. On the other hand, extract from woody biomass as feed for biomethane production is still limited. The hemicellulosic extract can also be utilized for extraction of value-added

products, such as lignin and furfural, before AD to improve the methane yield. Many ideas have been investigated with limited success.

Pyrolysis in combination with AD is gaining attention over time with AD-Py-AD handling digestate that is rich in lignocellulose. Organic rich, but complex, APL produced during pyrolysis needs to be handled well before disposing, as it contains several challenging substances. However, this field is still in its infancy with limited relevant data hindering a detailed evaluation of such integrated system in terms of efficiency and synergies. Limited, but positive, results regarding use of APL as AD feed for methane production imply that this should be given further attention, focusing on a) Microbial adaptation to challenging substrates utilizing continuous flow AD processes to overcome toxicity and inhibition issues. b) Observed positive effects of biochar as additives in AD for the same purpose should be studied to understand the mechanisms involved and establish appropriate dosages. c) Co-digestion with easily degradable substrates can also contribute to efficient utilization of challenging APLs, where sugars extracted in pre-treatment processes discussed here can be especially relevant. Pretreatment of APL, to remove different toxic compounds before AD, should also be focused on to improve the methane yield.

Proper lignocellulosic waste management and production of renewable bio-based products will produce huge amount of hydrolysate and APL in the future. So far, AD seems to be a promising solution for handling these streams, largely due to consortia of various microorganism that can act upon different substances, even toxic and inhibitory with adaptation. Continuous AD can improve the biodegradability to enhance the overall energy recovery from the lignocellulosic biomass, which should be focused on more.

9. Conclusions

Hydrolysate from hot water extraction and steam pretreatment is a suitable AD feed due to high organic carbon content and low concentration of inhibitors. However, it is favorable that this pretreatment is at moderate temperatures before using the hydrolysate as AD feed. APL produced from pyrolysis is a challenging feed for AD due to the presence of various known and unknown complex inhibitors, but evidence for its feasibility is found in the literature. Pre-treatment of biomass before pyrolysis, adaptation of microorganism to inhibitors, and additives, such as biochar, can help the AD cultures cope with inhibitors in APL.

CRedit authorship contribution statement

Nirmal Ghimire: Conceptualization, Visualization, Investigation, Writing - original draft, Writing - review & editing. **Rune Bakke:** Funding acquisition, Supervision, Writing - review & editing. **Wenche Hennie Bergland:** Conceptualization, Visualization, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This research is done as a part of Norske Skog innovation project Pyrogas, co-funded by The Norwegian Research Council (EnergyX programme; Project number: 269322).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2021.125068>.

References

- Ahmad, F., Silva, E.L., Varesche, M.B.A., 2018. Hydrothermal processing of biomass for anaerobic digestion – A review. *Renew. Sustain. Energy Rev.* 98, 108–124.
- Alonso, D.M., Wettstein, S.G., Mellmer, M.A., Gurbuz, E.I., Dumesic, J.A., 2013. Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass. *Energy Environ. Sci.* 6 (1), 76–80.
- Alvarez-Chavez, B.J., Godbout, S., Palacios-Rios, J.H., Le Roux, É., Raghavan, V., 2019. Physical, chemical, thermal and biological pre-treatment technologies in fast pyrolysis to maximize bio-oil quality: A critical review. *Biomass Bioenergy* 128.
- Alvarez, J., Lopez, G., Amutio, M., Bilbao, J., Olazar, M., 2014. Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor. *Fuel* 128, 162–169.
- Andreoni, V., 1990. Anaerobic digestion of wastes containing pyrolytic acids. *Biological waste*(34), 203–214.
- Appels, L., Lauwers, J., Degreve, J., Helsen, L., Lievens, B., Willems, K., Van Impe, J., Dewil, R., 2011. Anaerobic digestion in global bio-energy production: Potential and research challenges. *Renew. Sustain. Energy Rev.* 15 (9), 4295–4301.
- Aski, A.L., Borghai, A., Zenouzi, A., Ashrafi, N., Taherzadeh, M.J., 2018. Effect of steam explosion on the structural modification of rice straw for enhanced biodegradation and biogas production. *Bio. Resources* 14 (1), 464–485.
- Baeta, B.E., Lima, D.R., Adarme, O.F., Gurgel, L.V., Aquino, S.F., 2016. Optimization of sugarcane bagasse autohydrolysis for methane production from hemicellulose hydrolysates in a biorefinery concept. *Bioreour. Technol.* 200, 137–146.
- Baeta, B.E.L., Cordeiro, P.H.d.M., Passos, F., Gurgel, L.V.A., de Aquino, S.F., Fdz-Polanco, F., 2017. Steam explosion pretreatment improved the biomethanization of coffee husks. *Bioreour. Technol.*, 245, 66–72.
- Ballesteros, I., Oliva, J.M., Navarro, A.A., González, A., Carrasco, J., Ballesteros, M., 2000. Effect of chip size on steam explosion pretreatment of softwood. *Appl. Biochem. Biotechnol.* 84 (1), 97–110.
- Barakat, A., Monlau, F., Steyer, J.P., Carrere, H., 2012. Effect of lignin-derived and furan compounds found in lignocellulosic hydrolysates on biomethane production. *Bioreour. Technol.* 104, 90–99.
- Batista, G., Souza, R.B.A., Pratto, B., Dos Santos-Rocha, M.S.R., Cruz, A.J.G., 2019. Effect of severity factor on the hydrothermal pretreatment of sugarcane straw. *Bioreour. Technol.* 275, 321–327.
- Benjamin, M.M., Woods, S.L., Ferguson, J.F., 1984. Anaerobic toxicity and biodegradability of pulp mill waste constituents. *Water Res.* 18 (5), 601–607.
- Benner, R., Hodson, R.E., 1985. Thermophilic anaerobic biodegradation of [C]lignin, [C] cellulose, and [C]lignocellulose preparations. *Appl. Environ. Microbiol.* 50 (4), 971–976.
- Benner, R., Maccubbin, A., Hodson, R.E., 1984. Anaerobic biodegradation of the lignin and polysaccharide components of lignocellulose and synthetic lignin by sediment microflora. *Appl. Environ. Microbiol.* 47 (5), 998–1004.
- Bhatia, S.K., Jagtap, S.S., Bedekar, A.A., Bhatia, R.K., Patel, A.K., Pant, D., Rajesh Banu, J., Rao, C.V., Kim, Y.-G., Yang, Y.-H., 2020. Recent Developments in Pretreatment Technologies on Lignocellulosic Biomass: Effect of Key Parameters, Technological Improvements, and Challenges. *Bioreour. Technol.*, p. 122724
- Bhutto, A.W., Qureshi, K., Harijan, K., Abro, R., Abbas, T., Bazmi, A.A., Karim, S., Yu, G., 2017. Insight into progress in pre-treatment of lignocellulosic biomass. *Energy* 122, 724–745.
- Biswas, A.K., Yang, W., Blasiak, W., 2011. Steam pretreatment of Salix to upgrade biomass fuel for wood pellet production. *Fuel Process. Technol.* 92 (9), 1711–1717.
- Bolyard, S.C., Reinhart, D.R., Richardson, D., 2019. Conventional and fourier transform infrared characterization of waste and leachate during municipal solid waste stabilization. *Chemosphere* 227, 34–42.
- Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 38, 68–94.
- Bruni, E., Jensen, A.P., Angelidaki, I., 2010. Steam treatment of digested biofibers for increasing biogas production. *Bioreour. Technol.* 101 (19), 7668–7671.
- Buitrón, G., Hernández-Juárez, A., Hernández-Ramírez, M.D., Sánchez, A., 2019. Biochemical methane potential from lignocellulosic wastes hydrothermally pretreated. *Ind. Crops Prod.* 139.
- Campos, F.M., Couto, J.A., Figueiredo, A.R., Toth, I.V., Rangel, A.O., Hogg, T.A., 2009. Cell membrane damage induced by phenolic acids on wine lactic acid bacteria. *Int. J. Food Microbiol.* 135 (2), 144–151.
- Cao, X., Peng, X., Sun, S., Zhong, L., Sun, R., 2014. Hydrothermal conversion of bamboo: identification and distribution of the components in solid residue, water-soluble and acetone-soluble fractions. *J. Agric. Food Chem.* 62 (51), 12360–12365.
- Cao, Y., Pawlowski, A., 2012. Sewage sludge-to-energy approaches based on anaerobic digestion and pyrolysis: Brief overview and energy efficiency assessment. *Renew. Sustain. Energy Rev.* 16 (3), 1657–1665.
- Carvalho, F., Duarte, L.C., Gírio, F., Moniz, P., 2016. Hydrothermal/Liquid Hot Water Pretreatment (Autohydrolysis): A Multipurpose Process for Biomass Upgrading. in: *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery*, (Ed.) S.I. Mussatto, Elsevier. Amsterdam, 315–347.
- Chandel, A.K., Silva, S.S.d., Singh, O.V., 2011. Detoxification of Lignocellulosic Hydrolysates for Improved Bioethanol Production. in: *Biofuel Production-Recent Developments and Prospects*, (Ed.) M.A.d. Santos, Intech Open.
- Chandra, R., Takeuchi, H., Hasegawa, T., 2012a. Hydrothermal pretreatment of rice straw biomass: A potential and promising method for enhanced methane production. *Appl. Energy* 94, 129–140.
- Chandra, R., Takeuchi, H., Hasegawa, T., Kumar, R., 2012b. Improving biodegradability and biogas production of wheat straw substrates using sodium hydroxide and hydrothermal pretreatments. *Energy* 43 (1), 273–282.

- Chang, S., Zhao, Z., Zheng, A., Li, X., Wang, X., Huang, Z., He, F., Li, H., 2013. Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor. *Bioresour. Technol.* 138, 321–328.
- Clark, T.A., Mackie, K.L., 1984. Fermentation inhibitors in wood hydrolysates derived from the softwood *Pinus radiata*. *J. Chem. Technol. Biotechnol.* 34 (2), 101–110.
- Cordella, M., Torri, C., Adamiano, A., Fabbri, D., Barontini, F., Cozzani, V., 2012. Bio-oils from biomass slow pyrolysis: a chemical and toxicological screening. *J. Hazard. Mater.* 231–232, 26–35.
- Corton, J., Donnison, I.S., Patel, M., Buhle, L., Hodgson, E., Wachendorf, M., Bridgwater, A., Allison, G., Fraser, M.D., 2016. Expanding the biomass resource: sustainable oil production via fast pyrolysis of low input high diversity biomass and the potential integration of thermochemical and biological conversion routes. *Appl. Energy* 177, 852–862.
- Cullis, I.F., Saddler, J.N., Mansfield, S.D., 2004. Effect of initial moisture content and chip size on the bioconversion efficiency of softwood lignocelluloses. *Biotechnol. Bioeng.* 85 (4), 413–421.
- Dahadha, S., Amin, Z., Bazary Lakeh, A.A., Elbeshbishy, E., 2017. Evaluation of different pretreatment processes of lignocellulosic biomass for enhanced biomethane production. *Energy Fuels* 31 (10), 10335–10347.
- Di Girolamo, G., Grigatti, M., Barbanti, L., Angelidaki, I., 2013. Effects of hydrothermal pre-treatments on Giant reed (*Arundo donax*) methane yield. *Bioresour. Technol.* 147, 152–159.
- Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J., Jones, S.B., 2015. Hydrothermal liquefaction of biomass: developments from batch to continuous process. *Bioresour. Technol.* 178, 147–156.
- Fabbri, D., Torri, C., 2016. Linking pyrolysis and anaerobic digestion (Py-AD) for the conversion of lignocellulosic biomass. *Curr. Opin. Biotechnol.* 38, 167–173.
- Fang, H.H., Liu, Y., Ke, S.Z., Zhang, T., 2004. Anaerobic degradation of phenol in wastewater at ambient temperature. *Water Sci. Technol.* 49 (1), 95–102.
- Feng, Q., Lin, Y., 2017. Integrated processes of anaerobic digestion and pyrolysis for higher bioenergy recovery from lignocellulosic biomass: A brief review. *Renew. Sustain. Energy Rev.* 77, 1272–1287.
- Fernandez-Cegri, V., Angeles De la Rubia, M., Raposo, F., Borja, R., 2012. Effect of hydrothermal pretreatment of sunflower oil cake on biomethane potential focusing on fibre composition. *Bioresour. Technol.* 123, 424–429.
- Ghasimi, D.S.M., Aboudi, K., de Kreuk, M., Zandvoort, M.H., van Lier, J.B., 2016. Impact of lignocellulosic-waste intermediates on hydrolysis and methanogenesis under thermophilic and mesophilic conditions. *Chem. Eng. J.* 295, 181–191.
- Ghimire, N., Bakke, R., Bergland, W.H., 2021. Mesophilic anaerobic digestion of hydrothermally pretreated lignocellulosic biomass (Norway Spruce (*Picea abies*)). *Processes* 9 (2).
- Ghimire, N., Bakke, R., Bergland, W.H., 2020. Thermophilic methane production from hydrothermally pretreated Norway spruce (*Picea abies*). *Appl. Sci.* 10 (14).
- Guendouz, J., Buffiere, P., Cacho, J., Carrere, M., Delgenes, J.P., 2010. Dry anaerobic digestion in batch mode: design and operation of a laboratory-scale, completely mixed reactor. *Waste Manag* 30 (10), 1768–1771.
- Hagner, M., Tiilikkala, K., Lindqvist, I., Niemelä, K., Wikberg, H., Källi, A., Rasa, K., 2018. Performance of liquids from slow pyrolysis and hydrothermal carbonization in plant protection. *Waste Biomass Valorization* 11 (3), 1005–1016.
- Hassan el, B.M., Steele, P.H., Ingram, L., 2009. Characterization of fast pyrolysis bio-oils produced from pretreated pine wood. *Appl. Biochem. Biotechnol.* 154 (1–3), 3–13.
- He, L., Huang, H., Zhang, Z., Lei, Z., 2015. A review of hydrothermal pretreatment of lignocellulosic biomass for enhanced biogas production. *Curr. Org. Chem.* 19, 437–446.
- Heipieper, H.J., Weber, F.J., Sikkema, J., Keweloh, H., de Bont, J.A.M., 1994. Mechanisms of resistance of whole cells to toxic organic solvents. *Trends Biotechnol.* 12 (10), 409–415.
- Hendriks, A.T., Zeeman, G., 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour. Technol.* 100 (1), 10–18.
- Holtzapple, M.T., Humphrey, A.E., Taylor, J.D., 1989. Energy requirements for the size reduction of poplar and aspen wood. *Biotechnol. Bioeng.* 33 (2), 207–210.
- Hubner, T., Mumme, J., 2015. Integration of pyrolysis and anaerobic digestion—use of aqueous liquor from digestate pyrolysis for biogas production. *Bioresour. Technol.* 183, 86–92.
- Jonsson, L.J., Martin, C., 2016. Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects. *Bioresour. Technol.* 199, 103–112.
- Kan, T., Strezov, V., Evans, T.J., 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* 57, 1126–1140.
- Kan, X., Yao, Z., Zhang, J., Tong, Y.W., Yang, W., Dai, Y., Wang, C.H., 2017. Energy performance of an integrated bio-and-thermal hybrid system for lignocellulosic biomass waste treatment. *Bioresour. Technol.* 228, 77–88.
- Kaparu, P., Serrano, M., Thomsen, A.B., Kongjan, P., Angelidaki, I., 2009. Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. *Bioresour. Technol.* 100 (9), 2562–2568.
- Keskinen, R., Hyvälouma, J., Wikberg, H., Källi, A., Salo, T., Rasa, K., 2017. Possibilities of using liquids from slow pyrolysis and hydrothermal carbonization in acidification of animal slurry. *Waste Biomass Valorization* 9 (8), 1429–1433.
- Kim, D., 2018. Physico-chemical conversion of lignocellulose: Inhibitor effects and detoxification strategies: A mini review. *Molecules* 23 (2).
- Kim, M.K., Singleton, I., Yin, C.R., Quan, Z.X., Lee, M., Lee, S.T., 2006. Influence of phenol on the biodegradation of pyridine by freely suspended and immobilized *Pseudomonas putida* MK1. *Lett. Appl. Microbiol.* 42 (5), 495–500.
- Koyama, M., Yamamoto, S., Ishikawa, K., Ban, S., Toda, T., 2017. Inhibition of anaerobic digestion by dissolved lignin derived from alkaline pre-treatment of an aquatic macrophyte. *Chem. Eng. J.* 311, 55–62.
- Kumar, R., Strezov, V., Weldekidan, H., He, J., Singh, S., Kan, T., Dastjerdi, B., 2020. Lignocellulosic biomass pyrolysis for bio-oil production: A review of biomass pretreatment methods for production of drop-in fuels. *Renew. Sustain. Energy Rev.* 123.
- Kumar, V., Yadav, S.K., Kumar, J., Ahluwalia, V., 2019. A Critical Review on Current Strategies and Trends Employed for Removal of Inhibitors and Toxic Materials Generated During Biomass Pretreatment. *Bioresour. Technol.*, p. 122633.
- Laser, M., Schulman, D., Allen, S.G., Lichwa, J., Jr., M.J.A., Lynd, L.R., 2002. A comparison of liquid hot water and steam pretreatments of sugar cane bagasse for bioconversion to ethanol. *Bioresour. Technol.* 81, 33–44.
- Layton, D.S., Ajarapu, A., Choi, D.W., Jarboe, L.R., 2011. Engineering ethanologenic *Escherichia coli* for levoglucosan utilization. *Bioresour. Technol.* 102 (17), 8318–8322.
- Leven, L., Nyberg, K., Schnurer, A., 2012. Conversion of phenols during anaerobic digestion of organic solid waste—a review of important microorganisms and impact of temperature. *J. Environ. Manage.* 95 (Suppl), S99–S103.
- Li, W., Khalid, H., Zhu, Z., Zhang, R., Liu, G., Chen, C., Thorin, E., 2018. Methane production through anaerobic digestion: Participation and digestion characteristics of cellulose, hemicellulose and lignin. *Appl. Energy* 226, 1219–1228.
- Li, Y., Gu, G., Zhao, J., Yu, H., 2001. Anoxic degradation of nitrogenous heterocyclic compounds by acclimated activated sludge. *Process Biochem.* 37, 81–86.
- Liaw, S.-S., Perez, V.H., Westerhof, R.J.M., David, G.F., Frear, C., Garcia-Perez, M., 2020. Biomethane production from pyrolytic aqueous phase: Biomass acid washing and condensation temperature effect on the bio-oil and aqueous phase composition. *BioEnergy Research*.
- Liu, B., Ngo, V.A., Terashima, M., Yasui, H., 2017. Anaerobic treatment of hydrothermally solubilised sugarcane bagasse and its kinetic modelling. *Bioresour. Technol.* 234, 253–263.
- Liu, S., 2013. Chemical reactions on surfaces during woody biomass hydrolysis. *J. Bioprocess Eng. Biorefinery* 2 (2), 125–142.
- Liu, S., 2015. A synergetic pretreatment technology for woody biomass conversion. *Appl. Energy* 144, 114–128.
- Lu, H., Hu, R., Ward, A., Amidon, T.E., Liang, B., Liu, S., 2012. Hot-water extraction and its effect on soda pulping of aspen woodchips. *Biomass Bioenergy* 39, 5–13.
- Luo, T., Huang, H., Mei, Z., Shen, F., Ge, Y., Hu, G., Meng, X., 2019. Hydrothermal pretreatment of rice straw at relatively lower temperature to improve biogas production via anaerobic digestion. *Chin. Chem. Lett.* 30 (6), 1219–1223.
- Masebinu, S.O., Akinlabi, E.T., Muzenda, E., Aboyade, A.O., 2019. A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. *Renew. Sustain. Energy Rev.* 103, 291–307.
- Minowa, T., Zhen, F., Ogi, T., Varhegyi, G., 1997. Liquefaction of cellulose in hot compressed water using sodium carbonate Products distribution at different reaction temperatures. *J. Chem. Eng. Jpn.* 30, 186–190.
- Monlau, F., Barakat, A., Trably, E., Dumas, C., Steyer, J.-P., Carrère, H., 2013. Lignocellulosic materials into biohydrogen and biomethane: Impact of structural features and pretreatment. *Crit. Rev. Environ. Sci. Technol.* 43 (3), 260–322.
- Monlau, F., Francavilla, M., Sambusiti, C., Antoniou, N., Solhy, A., Libutti, A., Zabanitout, A., Barakat, A., Monteleone, M., 2016. Toward a functional integration of anaerobic digestion and pyrolysis for a sustainable resource management. Comparison between solid-digestate and its derived pyrochar as soil amendment. *Appl. Energy* 169, 652–662.
- Monlau, F., Sambusiti, C., Barakat, A., Quemeneur, M., Trably, E., Steyer, J.P., Carrere, H., 2014. Do furanic and phenolic compounds of lignocellulosic and algae biomass hydrolyzate inhibit anaerobic mixed cultures? A comprehensive review. *Biotechnol. Adv.* 32 (5), 934–951.
- Mortensen, P.M., Grunwaldt, J.D., Jensen, P.A., Knudsen, K.G., Jensen, A.D., 2011. A review of catalytic upgrading of bio-oil to engine fuels. *Appl. Catal. A* 407 (1–2), 1–19.
- Mosier, N., Hendrickson, R., Ho, N., Sedlak, M., Ladisch, M.R., 2005a. Optimization of pH controlled liquid hot water pretreatment of corn stover. *Bioresour. Technol.* 96 (18), 1986–1993.
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M., 2005b. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* 96 (6), 673–686.
- Mumme, J., Srocke, F., Heeg, K., Werner, M., 2014. Use of biochars in anaerobic digestion. *Bioresour. Technol.* 164, 189–197.
- Nitsos, C.K., Matis, K.A., Triantafyllidis, K.S., 2013. Optimization of hydrothermal pretreatment of lignocellulosic biomass in the bioethanol production process. *ChemSusChem* 6 (1), 110–122.
- Oasmaa, A., van de Beld, B., Saari, P., Elliott, D.C., Solantausta, Y., 2015. Norms, standards, and legislation for fast pyrolysis bio-oils from lignocellulosic biomass. *Energy Fuels* 29 (4), 2471–2484.
- Palmqvist, E., Grage, H., Meinander, N.Q., Hahn-Hagerdal, B., 1999. Main and interaction effects of acetic acid, furfural, and p-hydroxybenzoic acid on growth and ethanol productivity of yeasts. *Biotechnol. Bioeng.* 63 (1), 46–55.
- Palmqvist, E., Hahn-Hagerdal, B., 2000. Fermentation of lignocellulosic hydrolysates II inhibitors and mechanisms of inhibition. *Bioresour. Technol.* 74, 25–33.
- Pan, X., Xie, D., Gilkes, N., Gregg, D.J., Saddler, J.N., 2005. Strategies to Enhance the Enzymatic Hydrolysis of Pretreated Softwood with High Residual Lignin Content. In: Davison, B.H., Evans, B.R., Finkelstein, M., McMillan, J.D. (Eds.), *Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals*. Humana Press, Totowa, NJ, pp. 1069–1079.
- Park, J.H., Yoon, J.J., Park, H.D., Lim, D.J., Kim, S.H., 2012. Anaerobic digestibility of algal bioethanol residue. *Bioresour. Technol.* 113, 78–82.

- Pecchi, M., Baratieri, M., 2019. Coupling anaerobic digestion with gasification, pyrolysis or hydrothermal carbonization: A review. *Renew. Sustain. Energy Rev.* 105, 462–475.
- Pelaez-Samaniego, M.R., Yadama, V., Lowell, E., Espinoza-Herrera, R., 2013. A review of wood thermal pretreatments to improve wood composite properties. *Wood Sci. Technol.* 47 (6), 1285–1319.
- Phaiboonsilpa, N., 2010. Chemical conversion of lignocellulosics as treated by two-step semi-flow hot-compressed water. in: Graduate School of Energy Science, Vol. PhD, Kyoto University, Kyoto, Japan.
- Qing, S., Li, H., Kumar, R., Wyman, C.E., 2013. Xylooligosaccharides Production, Quantification, and Characterization in Context of Lignocellulosic Biomass Pretreatment. in: *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, (Eds.) C.V.Stevens, C.E.Wyman.
- Quéméneur, M., Hamelin, J., Barakat, A., Steyer, J.-P., Carrère, H., Trably, E., 2012. Inhibition of fermentative hydrogen production by lignocellulose-derived compounds in mixed cultures. *Int. J. Hydrogen Energy* 37 (4), 3150–3159.
- Rabemanolontsoa, H., Saka, S., 2016. Various pretreatments of lignocellulosics. *Bioresour. Technol.* 199, 83–91.
- Rasi, S., Kilpeläinen, P., Rasa, K., Korpinen, R., Raitanen, J.-E., Vainio, M., Kitunen, V., Pulkkinen, H., Jyske, T., 2019. Cascade processing of softwood bark with hot water extraction, pyrolysis and anaerobic digestion. *Bioresour. Technol.*, p. 292.
- Rezaei, P.S., Shafaghath, H., Daud, W.M.A.W., 2014. Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: A review. *Appl. Catal. A* 469, 490–511.
- Ribeiro, F.R., Passos, F., Gurgel, L.V.A., Baeta, B.E.L., de Aquino, S.F., 2017. Anaerobic digestion of hemicellulose hydrolysate produced after hydrothermal pretreatment of sugarcane bagasse in UASB reactor. *Sci. Total Environ.* 584–585, 1108–1113.
- Righi, S., Bandini, V., Marazza, D., Baioli, F., Torri, C., Contin, A., 2016. Life Cycle Assessment of high ligno-cellulosic biomass pyrolysis coupled with anaerobic digestion. *Bioresour. Technol.* 212, 245–253.
- Sambusiti, C., Monlau, F., Ficara, E., Carrère, H., Malpei, F., 2013. A comparison of different pre-treatments to increase methane production from two agricultural substrates. *Appl. Energy* 104, 62–70.
- Sawatdeenarunat, C., Surendra, K.C., Takara, D., Oechsner, H., Khanal, S.K., 2015. Anaerobic digestion of lignocellulosic biomass: challenges and opportunities. *Bioresour. Technol.* 178, 178–186.
- Scherer, P.A., Meier, D., 2004. Anaerobic digestion of wood after conversion by ablative flash pyrolysis. *Proceedings of the 10th World Congress on Anaerobic Digestion, Montreal*. IWA Publishing, Colchester. pp. 2141–2146.
- Seyedi, S., Venkiteshwaran, K., Benn, N., Zitomer, D., 2020a. Inhibition during Anaerobic Co-Digestion of Aqueous Pyrolysis Liquid from Wastewater Solids and Synthetic Primary Sludge. *Sustainability* 12 (8).
- Seyedi, S., Venkiteshwaran, K., Zitomer, D., 2020b. Current status of biomethane production using aqueous liquid from pyrolysis and hydrothermal liquefaction of sewage sludge and similar biomass. *Rev. Environ. Sci. Bio/Technology*.
- Seyedi, S., Venkiteshwaran, K., Zitomer, D., 2019. Toxicity of various pyrolysis liquids from biosolids on methane production yield. *Front. Energy Res.* 7.
- Shanmugam, S.R., Adhikari, S., Wang, Z., Shakya, R., 2017. Treatment of aqueous phase of bio-oil by granular activated carbon and evaluation of biogas production. *Bioresour. Technol.* 223, 115–120.
- Si, B., Li, J., Zhu, Z., Shen, M., Lu, J., Duan, N., Zhang, Y., Liao, Q., Huang, Y., Liu, Z., 2018. Inhibitors degradation and microbial response during continuous anaerobic conversion of hydrothermal liquefaction wastewater. *Sci. Total Environ.* 630, 1124–1132.
- Simangunsong, E., Ziegler-Devin, I., Chrusciel, L., Girods, P., Wistara, N.J., Brosse, N., 2018. Steam explosion of beech wood: Effect of the particle size on the Xylans recovery. *Waste Biomass Valorization* 11 (2), 625–633.
- Sun, J.-Q., Xu, L., Tang, Y.-Q., Chen, F.-M., Liu, W.-Q., Wu, X.-L., 2011. Degradation of pyridine by one rhodococcus strain in the presence of chromium (VI) or phenol. *J. Hazard. Mater.* 191 (1–3), 62–68.
- Sun, S., Cao, X., Sun, S., Xu, F., Song, X., Sun, R.-C., Jones, G.L., 2014. Improving the enzymatic hydrolysis of thermo-mechanical fiber from *Eucalyptus urophylla* by a combination of hydrothermal pretreatment and alkali fractionation. *Biotechnol. Biofuels* 7 (116).
- Sun, S., Sun, S., Cao, X., Sun, R., 2016. The role of pretreatment in improving the enzymatic hydrolysis of lignocellulosic materials. *Bioresour. Technol.* 199, 49–58.
- Sun, Y., Cheng, J., 2002. Hydrolysis of lignocellulosic materials for ethanol production A review. *Bioresour. Technol.* 83, 1–11.
- Tahezadeh, M.J., Gustafsson, L., Niklasson, C., Lidén, G., 1999. Conversion of furfural in aerobic and anaerobic batch fermentation of glucose by *Saccharomyces cerevisiae*. *J. Biosci. Bioeng.* 87 (2), 169–174.
- Tahezadeh, M.J., Karimi, K., 2008. Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. *Int. J. Mol. Sci.* 9 (9), 1621–1651.
- Talebniya, F., Karakashev, D., Angelidaki, I., 2010. Production of bioethanol from wheat straw: An overview on pretreatment, hydrolysis and fermentation. *Bioresour. Technol.* 101 (13), 4744–4753.
- Tchobanoglu, G., Burton, F., Stensel, H.D., 2003. Wastewater engineering: Treatment and reuse. *Am. Water Works Assoc. J.* 95 (5), 201.
- Teghammar, A., Yngvesson, J., Lundin, M., Tahezadeh, M.J., Horváth, I.S., 2010. Pretreatment of paper tube residuals for improved biogas production. *Bioresour. Technol.* 101 (4), 1206–1212.
- Tian, L., Zou, D., Yuan, H., Wang, L., Zhang, X., Li, X., 2015. Identifying proper agitation interval to prevent floating layers formation of corn stover and improve biogas production in anaerobic digestion. *Bioresour. Technol.* 186, 1–7.
- Torri, C., Fabbri, D., 2014. Biochar enables anaerobic digestion of aqueous phase from intermediate pyrolysis of biomass. *Bioresour. Technol.* 172, 335–341.
- Torri, C., Pambieri, G., Gualandi, C., Piraccini, M., Rombolà, A.G., Fabbri, D., 2020. Evaluation of the potential performance of hyphenated pyrolysis-anaerobic digestion (Py-AD) process for carbon negative fuels from woody biomass. *Renewable Energy* 148, 1190–1199.
- Torry-Smith, M., Sommer, P., Ahring, B.K., 2003. Purification of bioethanol effluent in an UASB reactor system with simultaneous biogas formation. *Biotechnol. Bioeng.* 84 (1), 7–12.
- Vivekanand, V., Olsen, E.F., Eijsink, V.G., Horn, S.J., 2013. Effect of different steam explosion conditions on methane potential and enzymatic saccharification of birch. *Bioresour. Technol.* 127, 343–349.
- Wang, D., Shen, F., Yang, G., Zhang, Y., Deng, S., Zhang, J., Zeng, Y., Luo, T., Mei, Z., 2018. Can hydrothermal pretreatment improve anaerobic digestion for biogas from lignocellulosic biomass? *Bioresour. Technol.* 249, 117–124.
- Wang, H., Srinivasan, R., Yu, F., Steele, P., Li, Q., Mitchell, B., 2011. Effect of acid, alkali, and steam explosion pretreatments on characteristics of bio-oil produced from pinewood. *Energy Fuels* 25 (8), 3758–3764.
- Weber, B., Estrada-Maya, A., Sandoval-Moctezuma, A.C., Martínez-Cienfuegos, I.G., 2019. Anaerobic digestion of extracts from steam exploded Agave tequilana bagasse. *J. Environ. Manage.* 245, 489–495.
- Wen, C., Moreira, C.M., Rehmann, L., Berruti, F., 2020. Feasibility of anaerobic digestion as a treatment for the aqueous pyrolysis condensate (APC) of birch bark. *Bioresour. Technol.* 307, 123199.
- Wyman, C.E., Dale, B.E., Elander, R.T., Holtzapfle, M., Ladisch, M.R., Lee, Y.Y., 2005. Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover. *Bioresour. Technol.* 96 (18), 2026–2032.
- Xu, N., Liu, S., Xin, F., Zhou, J., Jia, H., Xu, J., Jiang, M., Dong, W., 2019. Biomethane production from lignocellulose: Biomass recalcitrance and its impacts on anaerobic digestion. *Front Bioeng Biotechnol.* 7, 191.
- Yan, L., Ma, R., Li, L., Fu, J., 2016. Hot water pretreatment of lignocellulosic biomass: An effective and environmentally friendly approach to enhance biofuel production. *Chem. Eng. Technol.* 39 (10), 1759–1770.
- Yang, L., Xu, F., Ge, X., Li, Y., 2015. Challenges and strategies for solid-state anaerobic digestion of lignocellulosic biomass. *Renew. Sustain. Energy Rev.* 44, 824–834.
- Yu, X., Zhang, C., Qiu, L., Yao, Y., Sun, G., Guo, X., 2020. Anaerobic digestion of swine manure using aqueous pyrolysis liquid as an additive. *Renewable Energy* 147, 2484–2493.
- Zhang, Y., Xu, S., Cui, M., Wong, J.W.C., 2019. Effects of different thermal pretreatments on the biodegradability and bioaccessibility of sewage sludge. *Waste Manage.* 94, 68–76.
- Zhao, S., Li, G., Zheng, N., Wang, J., Yu, Z., 2018. Steam explosion enhances digestibility and fermentation of corn stover by facilitating ruminal microbial colonization. *Bioresour. Technol.* 253, 244–251.
- Zheng, Y., Zhao, J., Xu, F., Li, Y., 2014. Pretreatment of lignocellulosic biomass for enhanced biogas production. *Prog. Energy Combust. Sci.* 42, 35–53.
- Zhou, H., Brown, R.C., Wen, Z., 2019. Anaerobic digestion of aqueous phase from pyrolysis of biomass: Reducing toxicity and improving microbial tolerance. *Bioresour. Technol.* 292, 121976.