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Review Article

Subcritical Water Pretreatment for Anaerobic Digestion Enhancement: A Review

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ABSTRACT

This work reviews hydrothermal subcritical water pretreatment to enhance biogas production through anaerobic digestion. The complexity of the lignocellulosic structure has been the main limitation contributing to unsatisfactory biogas production throughout the anaerobic digestion. The high resistance of the structure to biological hydrolysis has increased the interest in applying pretreatment prior to anaerobic digestion to facilitate hydrolysis. Hydrothermal subcritical water technology, an environmentally friendly pretreatment that uses water as the main medium, is gaining prominence in biogas enhancement. However, the subcritical water pretreatment influence on structural properties, biogas production, and the production of anaerobic process inhibitors signifies a knowledge gap and needs an evaluation. This review presents the need for pretreatment reaction and properties in the subcritical water region, biogas production from subcritical water pre-treated waste, production of inhibitors, and its challenges

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are discussed. This pretreatment could be a promising option and further enhance biogas production throughout the anaerobic digestion process.

Keywords: Anaerobic digestion, biogas, hydrothermal, lignocellulosic pretreatment, subcritical water

INTRODUCTION

In recent years, researchers have focused on using agricultural and food waste to value goods on the ground of the waste-to-wealth idea to lower the downsides of inappropriate waste management practices (Hamzah et al., 2016; Rico et al., 2020). The derivation of energy from agricultural and food waste can be seen as a sustainable approach in line with the 12th Malaysia Plan 2021–2025 (RMK12) and Sustainable Development Goals (SDG) (RMK12, 2021). By focusing on implementing a circular economy and accelerating the adoption of integrated resources management, this plan encourages the public and private sectors to implement and integrate the SDGs values in their decision-making in pursuing sustainability. Apart from ensuring supply safety, the circular economy will reduce dependency on non-renewable energy, waste production, pollution, and greenhouse gas emissions. Replacement of non-renewable energy sources through bioenergies such as biofuels and biogas could be one possible way toward sustainability plans (Lemaire & Limbourg, 2019). Biogas is produced through anaerobic digestion by degrading substrates assisted by microbes throughout some biochemical phases (Aili et al., 2021).

The anaerobic digestion process has four major phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The process is carried out by several mixed-culture microbial communities working through syntropy (Morales-Polo et al., 2018). The hydrolysis phase is the rate-determining step, while methanogenesis restricts the digestion rate of more easily degradable substrates (Paudel et al., 2017). Improving the hydrolysis and biogas production during anaerobic digestion generates improvement opportunities and challenges for anaerobic digestion since the lignocellulosic substrates have different characteristics, indicating different kinds and levels of boundaries to accomplish the ideal anaerobic digestion process (Carlsson et al., 2012). Therefore, pretreatment for biodegradability improvement is a prerequisite for the amendment of lignocellulosic biomass for anaerobic digestion. The primary purpose of the pretreatment for lignocellulose feedstock is to disrupt lignin structure; consequently, cellulose and hemicellulose become accessible for microbial attack. In addition, the crystallinity of cellulose decreased, and the porosity of the substrate increased with pretreatment. (Brodeur et al., 2011; Carrere et al., 2016). Therefore, the problem mentioned above can be eliminated by pretreatment. Over the years, pretreatment has been commonly practiced before anaerobic digestion, and various pretreatment technologies have been conducted, including thermal, chemical, biological, and combined pretreatment or its combination (Chen et al., 2020; Dahunsi, 2019; Pečar et al., 2020; Sun et al., 2016).

Biogas production using the acai pre-treated by subcritical water (SCW) pretreatment presented a noteworthy performance compared to the untreated acai processing waste, resulting in 30% more methane in the biogas and 100 times higher yield (Maciel-Silva et al., 2019). According to Edwiges et al. (2019), when compared to untreated garden waste, alkaline pretreatment followed by solid/liquid phase separation at 5% NaOH concentration at 20°C for 12 hours produced the best results, increasing methane yield by 70%. However, despite high methane yield, the final effluent with high soluble chemical oxygen demand (COD) was produced from the digestion. Dilute acid pretreatment by 0.2M acetic acid yielded the highest sugar recovery of 95% and improved the crystallinity index to 56% after disrupting complex lignocellulosic during pretreatment (Saha et al., 2018). In addition, substrate hydrolysis of agricultural waste was improved through intermediate ozonation (Almomani et al., 2017). As a result, utilization of the substrates by the microbes is quicker, and the ozonation reduces the hydrolysis period while increasing the microbial activity in the digester.

Combined biological and chemical pretreatment of maize straw using 1% NaOH and enzyme transformed cellulose and hemicellulose into reducing sugars and monomers, making them ready to use by microbes in the anaerobic digestion process, improving 20.24% of the biogas (Zhao et al., 2018). Chen et al. (2020) reported using acid and alkali pretreatments for wheat straws. The study reported that biogas production increased by 7% with the addition of 0.01 mol/L NaOH pre-treated wheat straw. In contrast, 0.1 mol/L NaOH negatively affected biogas yield due to the inhibition of propionic acid into acetic acid in the systems (Chen et al., 2020). All these studies concluded that the available pretreatment technology of lignocellulosic wastes is vital, especially for complex substrates feedstocks, to improve biogas and methane yield, better hydrolysis, and higher lignin, cellulose, and hemicellulose removal, as well as a few more parameters. Thus, before anaerobic digestion, pretreatment application should fully utilize the substrate potential.

Hydrothermal pretreatment at SCW temperature has been broadly accepted as an eco-friendly green technology due to its excellent performance for bioenergy generation from lignocellulosic wastes. The pretreatment promotes structure-breaking and substrate availability after pretreatment (Wang et al., 2018a). Hydrothermal pretreatment is also commonly identified as SCW pretreatment, autohydrolysis, liquid hot water, hydrothermal carbonization, aquasolv, hydro thermolysis, or hot-compressed water pretreatment (Ahmad et al., 2018; Saha et al., 2013; Shitu et al., 2015; Toor et al., 2011). SCW pretreatment promotes structure-breaking and substrate availability after pretreatment (Wang et al., 2018a). SCW pretreatment technology is gaining prominence in biogas production enhancement. SCW pretreatment involves using very sustainable and environmentally friendly water since it does not require acid recycling and is non-corrosive, non-toxic, and inflammable (Antwi et al., 2019; Saha et al., 2013). Water penetrates the lignocellulosic structure to hydrate cellulose, solubilize hemicellulose and partially remove lignin (Ahmad et al., 2018). The practicality of the SCW depends on the process parameters such as temperature, reaction time, and water-to-solid ratio. These parameters are the aspects of dominant importance concerning pretreatment efficiency and anaerobic digestion.

This review aims to present basic knowledge, and recent states of hydrothermal SCW pretreatment applied to the anaerobic of various lignocellulosic wastes. This review also discussed the major recalcitrance components in lignocellulosic wastes that hinder the anaerobic digestion of lignocellulosic waste. Recent studies discuss fundamental information on the reaction and properties of the pretreatment at the subcritical region. The recent study on the enhancement of biogas production from hydrothermal SCW pretreatment as the effective pretreatment method is reviewed. The inhibitory potential of this pretreatment as the main challenge of pretreatment during the process was also provided.

Pretreatment

The addition of pretreatment can enhance the performance of anaerobic digestion. Owing to the irregularity of lignocellulosic compounds, an ideal pretreatment process and conditions rely on its compositions (Zheng et al., 2014). The structure and compositions of lignocellulosic wastes were found to have influences on lignocellulosic biodegradability. The purpose of pretreatment is to modify the lignocellulosic structure, especially lignin, to improve and assist the enzymes and microbial attack (Ahmad et al., 2018; Carrere et al., 2016). Through pretreatment strong structure of the lignocellulose parts becomes easily disintegrated, lignin and hemicellulose are degraded, and the hydrolysis of cellulose occurs more efficiently, thus converting them to the soluble fraction. The expected outcome of pretreatment on lignocellulosic wastes is shown schematically in Figure 1. Several pretreatment approaches have been developed to improve the utilization of carbohydrates as the primary source of biogas. Pretreatment enhances microbial hydrolysis, evades the degradation of sugars, minimizes the formation of inhibitors, recovers lignin, and is cost-effective by operating in an anaerobic digester by reducing heat and power requirements (Brodeur et al., 2011).

The optimal pretreatment method and conditions depend on the types of lignocellulose present (Neshat et al., 2017). It is essential to analyze its characteristics since different lignocellulosic waste is divergent according to their types. It is also vital to ensure the microbial stability and balance of the nutrient for an effective process. Lignin supports the cell structure, covering cellulose and hemicellulose and resisting hydrolysis for microbial attack (Atelge et al., 2020). The structure's resistance to hydrolysis is correlated with crystalline cellulose, recalcitrant lignin, and its linkage (Paudel et al., 2017). Figure 2 shows the close association of cellulose, hemicellulose, and lignin. Pretreatment has commonly been subjected before being applied to anaerobic digestion to eliminate the problem associated with the lignocellulosic compound, as mentioned above.

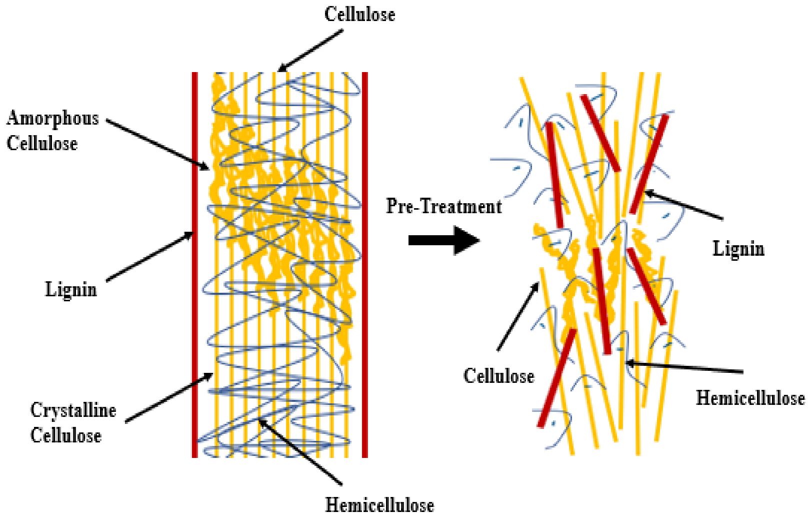

Figure 1. The schematic effect of pretreatment on the lignocellulosic waste (adapted and modified from Ahmed et al. (2019))

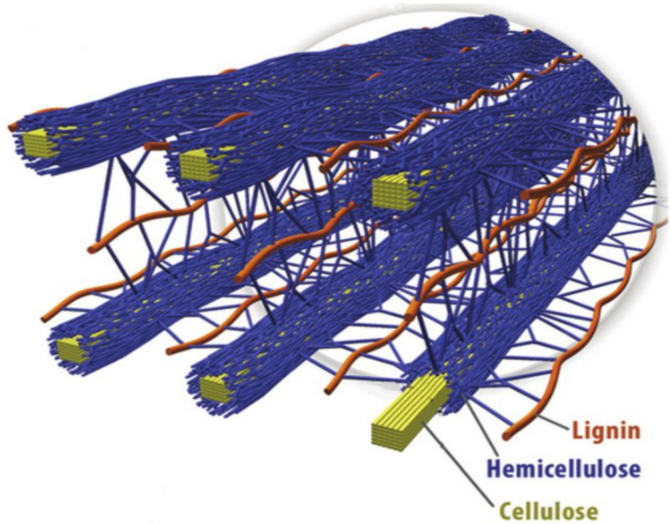

Figure 2. Cellulose strands surrounded by hemicellulose and lignin (Brandt et al., 2013)

Composition of Lignocellulosic Waste

The main difficulty hindering the efficiency of biogas generation from lignocellulosic waste feedstocks is overcoming the slow hydrolysis due to the recalcitrance of these wastes towards microbial degradation. Lignocellulose wastes have complex structures that restrict microbial attack due to combinations of interactions between lignocellulosic fractions (Atelge et al., 2020). Lignocellulosic wastes are mainly make-ups of a skeleton surrounded by three types of polymers: cellulose (30–70%), hemicellulose (15–30%), and lignin (10–25%), with extractives, and a number of inorganic materials (Ahmad et al., 2018; Brodeur et al., 2011). Table 1 shows the composition of some lignocellulosic waste reported by researchers. After hydrolysis, carbohydrates release fermentable sugar, making it an appropriate source for biogas production. Though, very complex structures make it resistant to hydrolysis by microorganisms (Zheng et al., 2014).

Table 1

Composition of lignocellulosic waste

Lignocellulosic waste	Lignin (%)	Cellulose (%)	Hemicellulose (%)	References
Rice straw	23–24	29–32	16–17	Wang et al. (2018a); Xiang et al. (2021)
Wheat straw	11.9	38.7	23	Tian et al. (2020)
Cocoa pods	21.29	26.10	4.82	Antwi et al. (2019)
Napier grass	4–23	36–42	20–27	Jomnonkhaow et al. (2022); Suaisom et al. (2019)
Paper tube	23	NS	NS	Teghammar et al. (2010)
Acai	24.56	43.81	25.89	Maciel-Silva et al. (2019)
OFMSW	48.93	85.28	54.81	Dasgupta and Chandel (2019)

Note. NS: Not Stated, OFMSW: organic fraction of municipal solid waste

Cellulose

Cellulose is the key component of lignocellulose cell walls and the most abundant linear polysaccharide of cellobiose, making a molecular chain between 100 and 14,000 units (Paudel et al., 2017; Zheng et al., 2014). Cellulose is strongly linked by β,1–4 glycosidic linkages (Ahmad et al., 2018; Paudel et al., 2017). The cellulose units contain organized crystalline structures with poorly organized amorphous structures and form the so-called cellulose fibrils or cellulose bundles (Carrere et al., 2016). Cellulose chains are intertwined by hydrogen bonds and van der Waals forces (Zheng et al., 2014). The intramolecular hydrogen bonds made microfibrils with high tensile strength and hydrophilic, but they are not highly soluble in water due to their large size. The bonds support cellulose by creating a crystalline and amorphous structure (Paudel et al., 2017). Cellulose chains have numerous angles of amorphous regions intertwined with crystalline cellulose, which determine their crystallinity level (Ahmad et al., 2018). The bond of hydrogens between glucan units influences its crystallinity, characterized by the crystallinity index. They consist of two regions: amorphous (low crystallinity) and crystalline (high crystallinity) regions (Zheng et al., 2014). At a high crystallinity index, the degradation of cellulose turns out to be more complex. The cellulose chains also are packed into microfibrils and stabilized by hydrogen bonds. Hemicelluloses connect these fibrils, amorphous polymers, and other polymers, such as pectin, and are protected by lignin (Brodeur et al., 2011). It makes cellulose complicated and resistant to biological and chemical attacks. While the chain length is contrarywise relative to hydrolysis effectiveness, they are insoluble in water and are most prone to microbial degradation (Ahmad et al., 2018).

Hemicellulose

Hemicelluloses are more amorphous than cellulose and are made of linear, highly-branched heteropolymers of pentoses, hexoses, and acids (Ahmad et al., 2018). Hemicellulose is not attached to the cellulose by a covalent bond and builds an amorphous region in the lignocellulosic structure (Brandt et al., 2013). Hemicellulose has amorphous structures and is more readily hydrolyzed than cellulose (Carrere et al., 2016). They are also firm due to the short and branched chains that assist in forming a structure with cellulose fibrils and interact with lignin. Due to these properties, hemicelluloses are highly susceptible to hydrolysis (Zheng et al., 2014). Cellulose has a higher molecular weight than hemicellulose, a low polymerization degree (70 to 200ºC), and less crystal with arbitrary amorphous composition, making hemicellulose more sensitive to hydrolysis (Ahmad et al., 2018; Brodeur et al., 2011). Hemicellulose is not as robust, and mostly amongst others, it performs a weighty part in firming the lignocellulosic complex in covering cellulose fibrils (Paudel et al., 2017).

Lignin

Lignin is the second most abundant natural polymer after cellulose and is a combination of aromatic complexes and consists of aquaphobic heteropolymers alcohols linked through ether bonds. Also include hydroxyl, methoxyl, and carbonyl functional groups, the C-C bonds, or a linkage of C-C and ether (Ahmad et al., 2018; Carrere et al., 2016; Zhao et al., 2018). Coniferyl alcohol is the main monomer in softwood lignin and is the foundation for lignin, especially hardwood. Other than that, aromatic monomers are also integrated into the lignin structure that protects the cellulose and hemicellulose as a hydrophobic layer (Ahmad et al., 2018). Lignin is an amorphous polymer cross-linked between the hemicellulose and cellulose to a rigid three-dimensional structure of the lignocellulosic matrix. The fibrils present in the lignocellulosic structure are often associated with packs or macro fibrils cellulose (Brodeur et al., 2011). The fibrils are mainly crystalline, hindering microbial attack, and are the primary physical block between polymers (Brodeur et al., 2011; Paudel et al., 2017). Moreover, lignin commonly forms a covalent bond, mainly with hemicellulose. The rigidity of lignin makes them resistant to biological degradation (Carrere et al., 2016). Lignin is also hydrophobic and optically inert and only dissolve at high temperature (> 180°C). Therefore, lignin is the main obstacle to biodegradation; the higher the percentage of lignin, the resistance to microbial degradation are greater, and softwood lignin is the most recalcitrant to pretreatment and bioconversion (Talaiekhozani & Rezania, 2020; Zheng et al., 2014).

Subcritical Water (SCW) Technology

The SCW, known as hydrothermal pretreatment has been broadly accepted due to its excellent performance in improving bioenergy generation (Lee et al., 2019; Shitu et al., 2015; Toor et al., 2011). This pretreatment destroys the crystallographic structure of cellulose and promotes lignocellulosic structure-breaking and substrate availability after pretreatment (Wang et al., 2018a). The SCW pretreatment occurs when substrates are subjected to water at a higher temperature (100 to 374°C) in a liquid state at a selected reaction time and pressure (Dasgupta & Chandel, 2019). The water in the subcritical region is still in a liquid state (Figure 3), and in these environments, water has a range of exotic properties (Möller et al., 2011; Shitu et al., 2015). Match up to conventional pretreatments such as acid and alkali; after SCW pretreatment, the solid filtrate contains high cellulose and lignin. At the same time, most hemicellulose solubilizes in the liquid portion (Figure 4), thus showing the possibility of improving lignocellulosic hydrolysis and biogas yield and promoting changes in lignocellulosic structure.

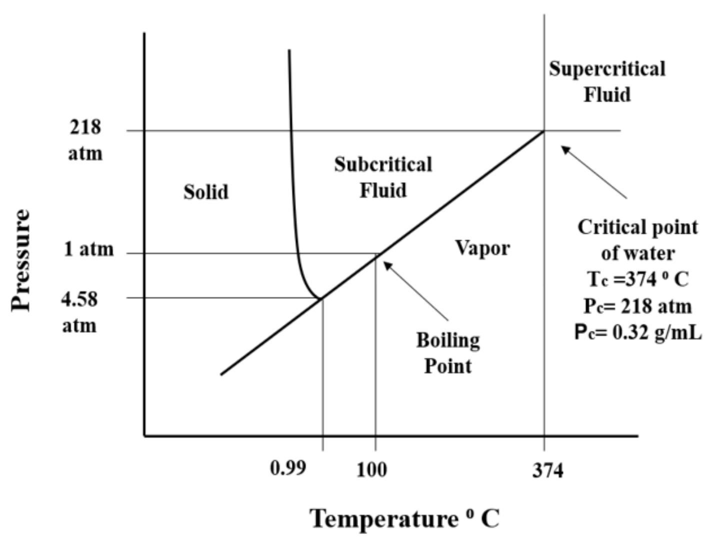

Figure 3. Water phase diagram as a function of pressure and temperature (Shitu et al., 2015)

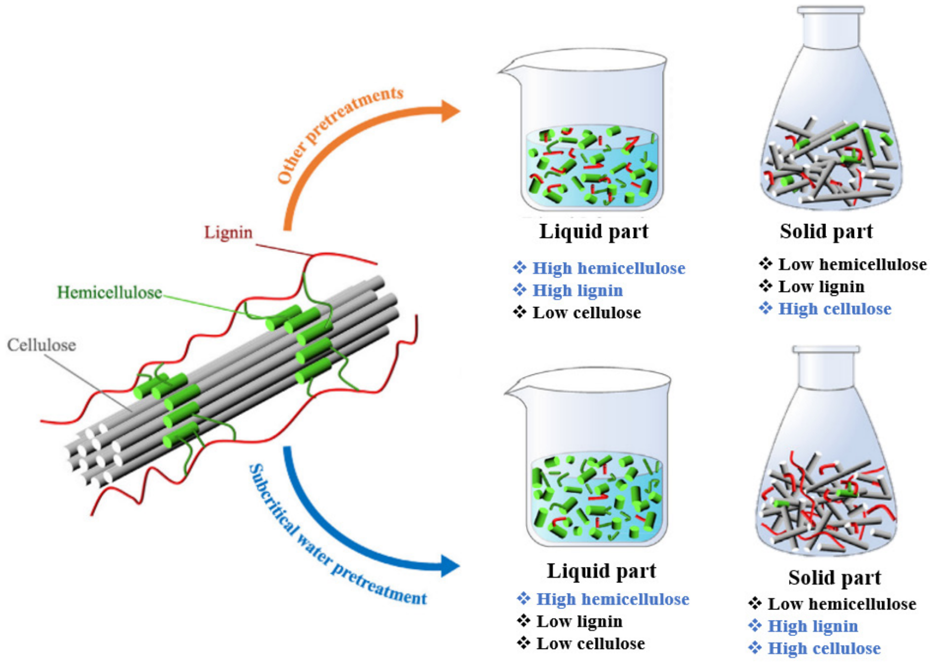

Figure 4. Changes in lignocellulosic content between SCW pretreatment and other pretreatments (adapted and modified from Chen et al., 2021)

Reaction and Properties at Subcritical Water Condition

During SCW pretreatment, lignocellulosic waste undertakes high temperatures in water at high pressure at a specific reaction time and solid-to-water ratio (Lachos-Perez et al., 2017; Lee et al., 2019). SCW promotes structural modification to the lignocellulosic waste by enlarging the available surface area of cellulose, improving cellulose degradation, and generating low inhibitors concentration in pre-hydrolysates, compared with low pH pretreatment methods (Chen et al., 2021; Maciel-Silva et al., 2019; Suaisom et al., 2019). Water in SCW regions possesses some unique characteristics, it stays in liquid states and does not require any chemical as a medium, and is considered an environmentally friendly technique for lignocellulosic pretreatment. SCW has a low dielectric constant and high ionic product, indicating water polarity and solubility. Water behaves as an acid catalyst due to autoionization at high temperatures.

The water autoionization release acid hydronium ion (H_3O^+) that catalyze the polysaccharides (mainly hemicellulose) hydrolysis to form sugars (pentoses and hexoses) (Jomnonkhaow et al., 2022). The increase in reaction temperature increased the ionic constant of water and created a low pH medium for subsequent hydrolysis. The affinity of water performing as reaction media indicates the dielectric constant. Water in the SCW region has the same polarity as an organic solvent because the dielectric constant is reduced and contributes to the organic compound's solubilization. Reduction of the dielectric constant reduced the polarity of water while increasing hydrocarbon solubility. Water reduced the quantity of organic solvent required during hydrolysis since the increase in temperature increases the mid-polar compound solubilization.

High kinetic energy at high temperatures increases the polymerization reactions rate for the rupture of cell wall structure while enhancing diffusivity and decreasing viscosity are beneficial to enhance the mass transfer and pretreatment effectiveness. (Abdelmoez et al., 2014; Ahmad et al., 2018; Chen et al., 2021; Lachos-Perez et al., 2017; Maciel-Silva et al., 2019; Shitu et al., 2015). Thus, in general, SCW penetrates the structure to hydrate cellulose, solubilize a substantial part of hemicellulose and partially remove lignin. Increases in the polymerization rate help breakdown down the cell wall and cellulose swelling. It increases cellulose accessibility by expanding the surface area following enzymatic reaction. Also, subcritical water assists in acetyl and uronic acid groups' cleavage yielding acetic acid and other organic acids and boosting the solubilization of oligosaccharides (Ahmad et al., 2018). Thus, the subcritical water allows the depolymerization of the lignocellulosic biomass by cleavage, dehydration, swelling, and recombination of reactive fragments (Toor et al., 2011).

Subcritical Water Pretreatment Process Parameters

The SCW pretreatment parameters, temperature, reaction time, and solid-to-water ratio are the aspects of dominant importance concerning pretreatment efficiency and, subsequently, anaerobic digestion (Ahmad et al., 2018; Toor et al., 2011). Therefore, the effect of those parameters is discussed further in the following subsection.

Temperature. The extent of the SCW pretreatment at the SCW temperature region's effect on the lignocellulosic composition modification is influenced mainly by the reaction temperature. The pretreatment disrupts the cellulose microfibrils bundles, improving surface porosity, fractures, and drains on the deformed surface, increasing the surface area depending on pretreatment severity (Ahmad et al., 2018; Maciel-Silva et al., 2019). The sugar production increased with temperature, and the highest sugar produced from SCW pre-treated spent Java citronella was obtained at 160°C (Timung & Goud, 2018). Higher pretreatment temperatures over 200°C caused the formation of furfural and 5-hydroxymethylfurfural (HMF), one of the methanogenesis inhibitors (Phuttaro et al., 2019). Tian et al. (2020) observed a reduction in methane yield after pre-treated wheat straw at 175°C. At 90°C and 180°C, Wang et al. (2018a) reported that biogas produced from pre-treated rice straw improved compared to untreated rice straw. Temperature 210°C presented a 30% reduction with a more extended lag period. Antwi et al. (2019) observed that optimum biogas yield was obtained at 150°C with low severity of 2.65. The SCW on cocoa pod waste observed that temperature influences the lignin solubilization compared to reaction time (Antwi et al., 2019). Higher SCW temperature has resulted in more significant degradation, and soluble sugars produced from hemicellulose solubilization have been stated at 160 and 200°C (Dasgupta & Chandel, 2019).

The cellulose microfibrils are linked by hemicellulose and amorphous polymers and protected by lignin (Brodeur et al., 2011). Cellulose is crystalline and has a high level of polymerization (Ahmad et al., 2018; Toor et al., 2011), and disruption of the structure through the SCW pretreatment can modify the bond between cellulose and make cellulose more accessible to microbial attack. According to Ahmed et al. (2019), the decomposition of cellulose begins at a temperature of 230°C. The cellulose hydrolysis rate and conversion increase from temperature 240 to 270°C (Ahmed et al., 2019; Lachos-Perez et al., 2017; Toor et al., 2011). Hemicelluloses are amorphous and easily hydrolyzed compared to cellulose, and solubilization occurs above 150°C and 180°C (Ahmed et al., 2019; Carrere et al., 2016). Lignin is also hydrophobic and optically inert and only dissolve at high temperature (> 180°C). Lignin is a major barrier to microbial attack; the higher the percentage of lignin, the higher the resistance to microbial degradation, and it is the most recalcitrant to pretreatment and bioconversion (Zheng et al., 2014). Furans (furfural and HMF) are inhibitory compounds formed through the degradation of hemicellulose to its monomeric sugars and depending upon pretreatment conditions, they might inhibit the anaerobic digestion process (Dasgupta & Chandel, 2019).

Reaction Time. Reaction time is also a parameter that affects the SCW pretreatment performance. Though, the temperature has a better impact on the digestibleness of cellulose than reaction time (Ahmad et al., 2018; Carrere et al., 2016). Previous studies stated that a longer reaction time is not an ideal approach since it contributes to excessive cellulose breakdown, formation of solid residue, and severity of the pretreatment (González et al., 2014; Toor et al., 2011). However, lignin in the solid fraction increases as time increases due to reordering between lignin and holocellulose (Ahmad et al., 2018). Furthermore, Chandra et al. (2012b) stated that energy could be saved by less reaction time than by higher reaction time. Besides, higher residency time causes pyrolysis, causing charring together with greater energy requirements. According to Dasgupta and Chandel (2019), at the SCW temperature region, the VS of municipal solid wastes increases as the reaction time increases to 120 minutes. Increasing the reaction time decreased the TS and VS by 6.4% and 11%, respectively.

The SCW on cocoa pod waste observed that reaction time does not influence the lignin solubilization compared to temperature (Antwi et al., 2019). However, maximum biogas production is produced at a shorter reaction time, and the optimal reaction time observed by the authors is 15 minutes. Therefore, lower severity of SCW pretreatment contributes to better biogas production. At high temperatures (>175°C), a shorter reaction time should be considered since high temperatures and longer reaction times risk the furans to aldehydes degradation and organic acids that will increase the accumulation of volatile fatty acid (VFA) inside the digester (González et al., 2014). Therefore, a longer reaction time seems beneficial for temperatures lower than 150°C. The pretreatment reaction time of 15 minutes was applied to rice straw (Wang et al., 2018a), empty fruit bunch (O-Thong et al., 2012), Napier grass (Phuttaro et al., 2019), and cocoa pods (Antwi et al., 2019). At the same time, a reaction time of 10 minutes was used to pre-treat rice straw (Chandra et al., 2012b) and wheat straw (Chandra et al., 2012b). A longer pretreatment reaction time of 30 minutes was conducted on municipal solid waste (Dasgupta & Chandel, 2019) and waste-activated sludge (Kim et al., 2015).

Solid to Water Ratio. The ratio of solid to water during the SCW pretreatment is one more significant parameter that influences the SCW pretreatment process and is generally expressed as the ratio of the solid (g) weight to the volume of water (mL). Water remains an alternate solvent in the sub-critical state to dissolve substrates due to its low viscosity, and high diffusivity allows the water to permeate the complex structure (Chen et al., 2021; Timung & Goud, 2018). According to the mass transfer theory, a high concentration gradient increases the diffusion rate due to a high solid-solvent ratio. It thereby facilitates the extraction by the solvent of solids (Shitu et al., 2015). Previously, optimization of SCW hydrothermal pretreatment of Napier grass for biogas production reported that the optimal Napier grass-to-water ratio of 1:6 gives optimal conditions for methane production. Similarly, Manorach et al. (2015) observed a significant effect of bagasse to water ratio for the sugarcane bagasse hydrolysis. The hydrolysis of sugarcane bagasse increased after applying SCW pretreatment at a 1:1.69 solid-to-water ratio. About 87.52% cellulose conversion rate was obtained by SCW pretreatment of wheat straw at a 1 to 5 solid-to-water ratio (5%).

Anaerobic Digestion

Biogas is produced through anaerobic digestion by degrading substrates facilitated by a group of microbes through several biochemical reactions (Hamzah et al., 2022). The anaerobic digestion process has four major phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The anaerobic digestion process is carried out by several mixed-culture microbial communities working through syntropy (Morales-Polo et al., 2018). The microbes work synergistically to decompose recalcitrant waste structures into their simplest form (Sawatdeenarunat et al., 2015). The hydrolysis process turns organic macromolecules into smaller compounds that acidogenic bacteria can use. While acidogenesis is the fastest reaction in which acidogens convert soluble molecules from the previous phase to acetic acid and other longer VFAs, alcohols, and carbon dioxide (Caruso et al., 2019). Then the

VFAs are then converted into acetate, carbon dioxide, and hydrogen via acetogenesis. At the last phase of anaerobic digestion, methane and carbon dioxide are produced by two groups of methanogens; acetoclastic and hydrogen-utilizing methanogens (Hagos et al., 2017).

Methane-rich biogas is produced from various feedstocks, consisting of primarily 50–75% methane, 19–34% carbon dioxide, and less than 1% hydrogen through the anaerobic digestion process (Hamzah et al., 2020; Elhenawy et al., 2021). Anaerobic digestion is a very complex method to produce biogas from different types of waste. The important process parameters should be learned to achieve the maximum potential of the anaerobic digestion process. Temperature, pH, carbon-to-nitrogen ratio, organic loading, mixing, and concentration of VFAs and ammonia nitrogen are among the most important parameters that affect the performance of an anaerobic digestion system. Mono digestion often observes lower biogas yield, and even with anaerobic co-digestion, the biogas yield is not satisfying due to the complexity of the structure. High resistance of lignocellulose to biological hydrolysis is associated with the presence of refractory lignin, its linkage to the strong bond between cellulose and hemicelluloses, and the presence of crystalline cellulose (Paudel et al., 2017). The primary purpose of the pretreatment for lignocellulose feedstock is to disrupt lignin structure; consequently, cellulose and hemicellulose become accessible for microbial attack. SCW pretreatment promotes structure-breaking and substrate availability after pretreatment (Wang et al., 2018a).

Biogas Production Using SCW Pretreatment

SCW pretreatment for biogas production has been broadly conducted to enhance methane yield from lignocellulosic wastes, including Napier grass (Phuttaro et al., 2019), acai residue (Maciel-Silva et al., 2019), rice straw (Wang et al., 2018a), cocoa pods waste (Antwi et al., 2019), and wheat straw (Chandra et al., 2012a). Table 2 shows some studies on SCW pretreatment using lignocellulosic waste to improve methane yield. According to Chen et al. (2021), SCW pretreatment of wheat straw destroyed the microstructure of the straw and increased the cellulose crystallinity. The SCW also reduced the hemicellulose by 18.37%, while most of the cellulose preserved in the solid part of lignin and cellulose increased by 8.81% and 25.92%, respectively. SCW pretreatment for spent citronella biomass increases the fermentable sugar production during the hydrolysis and increases the crystallinity index to 52.68% (Timung & Goud, 2018). Likewise, this pretreatment also boosts the pre-hydrolysis of straw, and the lag phase throughout the fermentation is correspondingly reduced (Tian et al., 2020). Enhancement of methane production from sewage sludge was reported at optimal pretreatment conditions of 186°C using response surface methodology (Park et al., 2021).

It is also reported that the hydrothermal SCW pretreatment was useful in enhancing the hydrolysis of the lignocellulosic complex and subsequently improving methane production (Dasgupta & Chandel, 2019). Earlier, hydrothermal SCW pretreatment sped up the pre-hydrolysis of rice straw resulting in biogas and methane enhancement in anaerobic digestion. The pre-treated rice straw improved by 225.6% and 222% of biogas and methane, respectively (Chandra et al., 2012b). Similar pretreatment applied to wheat straw reported that pre-treated wheat straw had an increase of 9.2% in their production of biogas, while methane production increased by 20.0% (Chandra et al., 2012a). Hydrothermal SCW pretreatment for empty fruit bunch and palm oil mill effluent by co-digestion at 230°C for 15 minutes improved the biodegradability to 64% (O-Thong et al., 2012).

However, adding NaOH in the pretreatment improved the biodegradability to 91%. Pretreatment of Napier grass at 190°C improves methane production (Jomnonkhaow et al., 2022). However, during the breakdown of the lignin, the two-step reaction occurs, which leads to a reduction in methane yield due to the two-step reaction. During the pretreatment, solubilization of lignin and subsequent lignin depolymerization occurs, causing insoluble condensation. Table 3 shows lignin, cellulose, and hemicellulose changes after SCW pretreatment. Pre-treated common reed at 120°C for 2 hours increased the methane yield by 28.8% and improved the volatile solid content by 15% (Vakalis et al., 2022). Also, the performance of biogas yield in a two-stage anaerobic digester improved with the application of pretreatment at 140°C for 2 minutes (Wei et al., 2022). The pretreatment at 140°C enriched Acetolactic methanogens during the methanogenic bacteria responsible for enhancing methane content.

Table 2
The SCW pretreatment using lignocellulosic waste to improve methane yield

Substrates	Temperature (°C)	Time (min)	Solid-to-water ratio	Improvement	Yield	References
Municipal solid waste	140	30	NS	Increase by 32% in biogas production	200 mL/gVS	Dasgupta and Chandel (2019)
Napier grass	175	15	1:10	Increase by 35% in biogas production	248.2 NmL/gVS	Phuttaro et al. (2019)
Wheat straw	175	60	1:20	Increase by 52% in biogas production	225.7 mL/gVS	Tian et al. (2020)
Acai residue	200	20	1:80	Increase of 30% in methane production	791.81 L/KgTVS	Maciel-Silva et al. (2019)

Table 2 *(Continue)*

Substrates	Temperature (°C)	Time (min)	Solid-to-water ratio	Improvement	Yield	References
Rice straw	180	15	1:10	Increase of 3% in methane yield	306.6 mL/g TS	Wang et al. (2018a)
Cocoa pods	150	15	1:5	Increase 1.70% methane yield	357 LN/gVS	Antwi et al. (2019)
Waste activated sludge	180	30	1:1	Increase methane content to 63.4% and VS removal to 60%	130.2 mL/gVS	Kim et al. (2015)

Notes. NS-not stated

Rice straw pre-treated at 110 to 120°C helps methane production rather than 180°C (Xiang et al., 2021). The release of the soluble portion from pretreatment helps the methanogenesis that is responsible for biogas enhancement. Antwi et al. (2019) reported optimal biogas production of pre-treated cocoa pods at 150°C for 15 min. The authors suggested that pretreatment at low severity enhances the biogas production, and a severity of more than three resulted in low biogas yield. Wang et al. (2018a) reported that pre-treated rice straw at 180°C improved the biogas yield by 3%, and increasing the SCW temperature to 210°C lowered the biogas production by 30%. López González et al. (2014) stated that the pretreatment increases 63% the methane yield of pre-treated sugar cane press mud at 150°C for 20 minutes. As the temperature increases over >200°C, methane production decrease with temperature due to the formation of a recalcitrant product (furfural) responsible for methanogenesis inhibition.

The effectiveness of SCW pretreatment is different for various types of lignocellulosic wastes, according to the chemical and structural characteristics and the ideal pretreatment conditions. Thus, it is essential to find the optimal set of pretreatment parameters to ensure the highest substrate utilization can be achieved. The most recent studies evaluating the performance of SCW pretreatment for biogas production observed that pre-treated common reed at 120°C increased the methane potential by 28.8%, while temperature over 200°C had an adverse effect on methane production (Vakalis et al., 2022). Similarly, pre-treated wheat straw at 120°C obtained the highest methane yield, which was 32% higher than that of unpretreated wheat straw (He et al., 2022). While highest methane production, with an increase of 19% compared to untreated wheat straw, was observed at 160°C for 45 minutes (Zerback et al., 2022). According to the authors, increasing the pretreatment intensity reduces the methane conversion potential.

Table 3

Changes in lignin, cellulose, and hemicellulose after hydrothermal SCW pretreatment

Lignocellulosic Waste	Lignin (%)	Cellulose (%)	Hemicellulose (%)	References
Rice straw	12	12	-16	Wang et al. (2018a)
Rice straw	29.4	46.4	NS	Xiang et al. (2021)
Wheat straw	7	10	14	Tian et al. (2020)
Cocoa pods	8	10	-0.38	Antwi et al. (2019)
OFMSW	17.9	NS	-43.5	Dasgupta and Chandel (2019)

Note. NS: Not Stated, OFMSW: organic fraction of municipal solid waste: reduction in the content, Changes extracted based on the optimal parameter set that gives the highest biogas production.

Potential Inhibitors

Depending upon SCW pretreatment conditions, the inhibitory compound may be formed from the hydrolysis of lignocellulosic biomass during the pretreatment. The formation of refractory inhibitors could inhibit methanogenesis and contribute to low biogas production. In addition, pretreatment could change the properties of the substrates through esterification, caramelization, or Maillard reaction, which causes nutrient loss and formation of toxic melanoidins and inhibitors, thus affecting the substrate's biodegradability and anaerobic digestion process (Carrere et al., 2016; Meegoda et al., 2018; Wenjing et al., 2019). Via Maillard reaction, sugars and amino acids are concurrently generated through hydrolysis and produce compounds such as pyrroles, pyridines, and other compounds containing nitrogen cyclic organic components. These compounds also act as free radical chain reaction inhibitors and scavengers often associated with biogas production at SCW (Toor et al., 2011).

It was also reported that at the higher reaction temperature, the Maillard reaction occurs with the generation of Maillard products, and the SCW pre-treated biomass changed from dark brown to black coloration due to this reaction (Dasgupta and Chandel, 2019; Tampio, 2016; González et al., 2014). Park et al. (2017) reported that the brown color of the pre-treated samples proved the presence of anaerobic digestion inhibitory compounds such as Amadori and melanoidins at temperatures of 200°C and 220°C. Furans (furfural and HMF) are refractory inhibitors during anaerobic digestion formed during the degradation of hemicellulose to monosaccharides, oligosaccharides, and monomers (Dasgupta & Chandel, 2019). Depending on the availability and concentration levels throughout the anaerobic digestion process, compounds such as phenols, organic acids, and furans can potentially be process inhibitors (Prado et al., 2014; Wang et al., 2018a).

Table 4 shows the concentration of inhibitory compounds from hydrothermal SCW pretreatment from various substrates. The inhibitory levels of HMF and phenolic acid were reported to be at 3 g/L and 10 g/L, respectively, according to López González et al. (2014). Furfural is more lethal than 5-HMF due to its low molecular weight, which assists in easy access to the microbial cell membrane (Ahmad et al., 2018). In an anaerobic environment, HMF and furfural are mostly transformed to furan dimethanol, and furfuryl alcohol, respectively, while respiratory metabolism produced furonic acid from furfural. The concentration of furfural and 5-HMF in SCW pre-treated slurry increased with temperature (Tian et al., 2020). The inhibition of both compounds is often significant at a temperature higher than 160°C (Timung & Goud, 2018). Phuttaro et al. (2019) reported the formation of 5-HMF and furfural when pre-treated the substrates at 200°C, significantly inhibiting methanogenesis.

Table 4
The inhibitory compound from hydrothermal SCW pretreatment from various substrates

Substrates	Pretreatment Temperature (°C)	Furfural (g/L)	5-HMF (g/L)	Maillard Reaction	References
Wheat straw	175	4.1	2.9	NS	Tian et al. (2020)
Rice Straw	210	ND	2.3	NS	Wang et al. (2018a)
Press Mud	210	2.3	0.3	Yes	González et al. (2014)
Sugarcane bagasse	290	10	1.37	NS	Prado et al. (2014)
Sugarcane bagasse	213	2.84	0.47	NS	Prado et al. (2014)
Rice Straw	180	0.13	0.04	NS	Xiang et al. (2021)

Note. NS: Not Stated

Challenges

The SCW pretreatment for lignocellulosic biomass appears with challenges. The production and generation of methanogenic inhibitors such as furfurals and HMFs are the most common challenges related to SCW pretreatment. Various studies reported HMF and furfural inhibition when dealing with elevated temperatures. Common inhibitors such as furan aldehydes, weak acids, and phenolic compounds are the most common fermentation and enzyme inhibitors (Ahmed et al., 2019). The reduction of the concentration and detoxification of these compounds is crucial before being subjected to anaerobic digestion.

Numerous physical, chemical, and biological methods, combined with those pretreatments, have been suggested to eliminate the inhibitors. The removal and detoxification approaches including extracting, evaporating, over-liming, pH adjustment, adsorption, and ion exchange of those compounds are some of the approaches conducted by former studies to remove these inhibitors (Malav et al., 2017; Wang et al., 2018b).

Removal of inhibitory compounds and giving a higher yield of available convertible sugar can be achieved by various chemical detoxification processes, however, these methods may contribute to high industrial costs, waste production, and wastage of fermentable sugars (Ahmed et al., 2019). Over 90% of the inhibitors, including weak acid, HMF, and furfural, were removed using ozonation (Rosen et al., 2022). Removal of inhibitors using nanofiber hybrid hydrogel beads provides an effective and practical method for removing inhibitors from lignocellulosic hydrolysates (Sun et al., 2022). According to the authors, this detoxification strategy removes the inhibitors and can also retain glucose and xylose. The loss of monosaccharides often occurs when dealing with inhibitory compound removals. Thus, this strategy might be useful to be extended since, according to the study, only 6.3% and 8.2% of glucose and xylose loss during the process, respectively. A comparison between nanofiltration and reverse osmosis for removing the inhibitory compound revealed that reverse osmosis membranes are better than nanofiltration membranes, especially for retaining monosaccharides (Wang et al., 2018b). Thus, extensive research should be conducted to remove the inhibitory compound formed during the SCW pretreatment process. The removal and detoxification method should be carefully selected to avoid wasting fermentable sugars and monosaccharides from the lignocellulosic biomass.

CONCLUSION

Based on a review regarding SCW pretreatment for agricultural wastes for anaerobic digestion, the SCW pretreatment efficiency is reliant on the characteristic of feedstocks—predominantly its composition, including lignin, cellulose, and also hemicellulose. SCW pretreatment is considered environmentally friendly on account of water usage as a pretreatment solvent. They promote structural breaking to help facilitate hydrolysis and can apply to a broad range of lignocellulosic waste. However, high lignocellulosic content needs a severer pretreatment, and these methods can give an impact on anaerobic digestion if not properly implemented. Thus, more extensive research should be conducted to test the efficacy of this SCW on a wide range of lignocellulosic waste for biogas enhancement.

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