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MICROWAVE-ASSISTED PRETREATMENT OF LIGNOCELLULOSIC BIOMASS: A REVIEW

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Abstract

Lignocellulosic biomass is an abundant biopolymer in nature as a by-product of agricultural industry which offers a cheap source of sugar and bio-alcohol. The production of bio-alcohol from lignocellulosic wastes requires pretreatment, hydrolysis and fermentation steps. Pretreatment technologies are aimed to break down the recalcitrant structure of lignocellulosic biomass and release the fermentable sugar in the extraction of sugar process for bio-alcohol production. Microwave-based pretreatment has been considered as one of the promising methods of pretreatment, utilising thermal and non-thermal effects that drive physical, chemical or biological reactions. The advantages of microwave-assisted process such as in waste treatment and food drying by reducing the plant footprint, higher throughput, higher reaction rates, higher yield and purity have increased more interest of late. This paper reviews the recent application of microwave-assisted pretreatment of lignocellulosic material via the combination of microwave pretreatment with other physical and chemical pretreatment methods. The synergistic effect of microwave-assisted pretreatment with other pretreatment methods could enhance the fermentable sugar yield from various feedstocks. Different operating parameters that govern the reducing sugar yields such as biomass loading, microwave intensity, and irradiation time are presented. Formation of inhibitor compounds during microwaved-assisted pretreatment are also discussed.

Keyword: Lignocellulosic biomass, Pretreatment, Microwave, Sugar, Operating parameters.

1. Introduction

For the past three decades, numerous studies were done on exploring the economics and energy of renewable sources of liquid fuels to replace the dwindling fossil fuels. Bioethanol is one of the alternatives of the traditional fuels, which has remarkable growth of late. However, this growth faces a lot of challenges and cannot be sustained. More importantly, there is an increasing in farmland use for corn ethanol resulting in food prices dramatic rise. In fact, to produce 5-gallon of biofuel for a full tank of car, 450 pounds of corn is needed. This amount of cereals produced from the corn has sufficient calories to feed an adult for 12 months [1]. Lignocellulosic biomass is an abundant biopolymer in nature and is a by-product of the agricultural industry. It is considered a promising raw material to produce biofuels and chemicals as it has remarkable sugar content.

Unfortunately, lignocellulosic materials are very recalcitrant in nature with typical lignocellulosic biomass components of cellulose (38-50 %), hemicellulose (23–32 %), and lignin (15–25 % w/w) [2]. Lignin is the most recalcitrant component. It is a protective barrier that prevents plant cell degradation both by chemicals and enzymes. Meanwhile, the crystallinity of cellulose, its accessible surface area, degree of cellulose polymerisation and degree of acetylation of hemicelluloses are the main factors considered as affecting the rate of biological degradation of lignocellulose by enzymes [3]. The pretreatment process can destroy or alter hemicellulose or lignin structure; thus, it reduces the cellulose crystallinity and increases the accessible area for the hydrolysis step [4]. Proper pretreatment is required to loosen the lignocellulosic structure to facilitate chemical and enzymatic hydrolysis and enhance the digestibility for ethanol or biogas production [5]. Generally, the pretreatment process is the most expensive step of bio-alcohol production which arouses the concerns of researchers. Currently, various methods including physical pretreatment by mechanical utilities; chemical pretreatment by alkali, dilute acid, oxidising agents, and organic solvents; steam explosion; (supercritical) hot water; ammonia; supercritical CO_2 explosion; ionic liquid; biological pretreatment; electrical pretreatment; or a combination of these, have been proposed for the pretreatment of lignocellulosic biomass [6]. However, these technologies suffer from relatively low sugar yields, severe reaction conditions and high processing costs [7]. Therefore, it is necessary to develop new approaches to pretreat the biomass.

Microwaves (MW) are electromagnetic waves spanning a frequency range from 300 (3×108 cycles/s) to 300 GHz (3×1011 cycles/s), with most industrial and household microwave systems operating at either 900 or 2.45 GHz [8]. Microwaves interact with polar molecules and ions in a material, and result in both thermal and non-thermal effects that drive physical, chemical or biological reactions [9]. Microwave irradiation has been commonly used in chemistry because it has high heating efficiency and can, in some cases, increase reaction rate and reduce reaction time. There are many examples of application of microwave irradiation in the field of organic synthesis [10], chemical catalysis [11], and solid state reactions [12]. A number of industries have benefited from the distinction between microwave heating and conventional heating such as in food processing field. Especially, energy conversion of microwave irradiation lead to volumetrically heat generation with the target material rather than through the surface of the material, as is the case with conventional heating [13]. Microwave irradiation can affect in a positive way in biomass digestion. Therefore, many studies have been accomplished to investigate the appropriate operational parameters of the microwave pretreatment so as to optimise the conditions for a further efficient hydrolysis of biomass [14-16].

This work reviews the effect of microwave pretreatment and discusses various key operating parameters on different types of lignocellulosic biomass. An emphasis is placed on how microwave/physical and microwave/chemical pretreatment processes affect lignocellusic materials and its enzymatic hydrolysis and the sugar recovery from the pretreatment liquor after the pretreatment processes.

2. Combination Mechanical - Microwave Pretreatment

Mechanical pretreatment is an important way to reduce cellulose crystallinity and increase delignification. Milling or grounding the biomass to reduce particle size positively reflects on the pretreatment process. It leads to increased available specific surface and enhance enzyme accessibility for the subsequent enzymatic hydrolysis step [17]. Bernardo et al. [18] suggested that necessary particle sizing needs to be determined in the context of thermochemical pretreatment employed for lignocellulose conversion because mechanical pretreatment by itself is insufficient to attain economically feasible biomass conversion. It was stated by Chen et al. [7] that the optimum lignin removal occurred with particle size 1–2 mm. It was provided the best results in terms of highest delignification and lowest loss of sugar. Hu [19, 20] observed lignin removal ratio of 63–70% with various particle size ranges of 1.0–2.0, 0–0.5, 0.5–0.25, and <0.25 mm of switchgrass used in microwave-assisted alkali pretreatment but the energy was intensive, thus increased the pretreatment cost. Karunanithy et al. [21] grounded switchgrass and big bluestem, the particle size ranged between 0.3 and 1.2 mm for switchgrass and for big bluestem 0.4 and 0.8mm. Single screw extruder was used to extrude the two feed stocks. The combination of extrusion and microwave pretreatment has improved recovery of glucose, xylose and total sugar by 27.0%, 16.7%, and 21.4%, respectively for switchgrass. While 17.3%, 24.9%, and 19.7% increased for big bluestem were found as compared to non-microwave pretreated samples after enzymatic hydrolysis of the pretreated samples. Though microwave heating shows a high interaction with powder samples to increase recovery sugar yield but there is still concern no cost of energy. Therefore, using controlled condition of microwave pretreatment will reduce the energy consumption and allow for higher product due to the selective target heating reduces the unnecessary waste. Write the subsections as below.

3. Combination Microwave-Chemical Pretreatment

The combined microwave-chemical pretreatment of different feedstock resulted in higher sugar recovery. Alkaline solution removes lignin, while the acidic solution removes hemicellulose. Several chemical were used in microwave/chemical pretreatment such as microwave-assisted dilute ammonia [7], microwave-assisted $FeCl_3$ [22] and the two most commonly studied chemical methods in the pretreatment of lignocellulosic biomass are the microwave assisted-alkaline and microwave-assisted acid pretreatments. This paper will discuss these two later types of pretreatments for single and multiple pretreatment stages.

3.1. One-stage microwave-chemical pretreatment

One-stage microwave-chemical pretreatment is generally carried out by addition one of the chemicals to the lignocellulosic matter during microwave. NaOH aqueous solution and sulfuric acids are the most common chemicals. Table 1 shows the summary of some recent research done on the use of microwave – chemical pretreatment of biomass for bioethanol production for one-stage.

Table 1. Summary of Recent Research has done on the Use of Microwave-Chemical Pretreatment of Biomass for Bioethanol Production.

Raw Material	Pretreatment condition	Results	References
S. spontaneum* and *A.donax	One-stage 5 % NaOH, 80 °C,5 min for *S. spontaneum* and120 °C,5 min for *A. donax*	One-stage Max. yield of monomeric 6.8 g/100 g for both feedstocks	Komolwanich et al. [23]
	Two-stage 5 % NaOH, 200 °C,10 min for *S. spontaneum* 0.5 %H_2SO_4,180°C, 30 min for *A. donax*	Two-stage 33.8 g/100 g *S. spontaneum* 31.9 g/100 g *A. donax*	
Empty Fruit Bunch	One-stage 3% NaOH, 180 W, 12 min	One-stage reducing sugar 411mg/g	Nomanbhay et al. [24]
Sugarcane Bagasse	One-stage 1% NaOH, 600W, 4 min	One-stage 0.665 g/g dry biomass	Binod et al. [25]
Miscanthus Sinensis	One-stage 1.0% NH_4OH, 300W,15min	One-stage Monomeric sugar yields 2.93 g/100 g biomass	Boonmanumsin et al. [26]
	One-stage 1.63% H_3PO_4, 300W, 30 min	One-stage 62.28g/100g biomass	
	Two-stage 1.0% NH_4OH, 300W, 15min 1.78% (v/v) H_3PO_4 300W, 30min	Two-stage 71.64g/100g biomass	
Switchgrass	One-stage 3% NaOH, 250W, 10 min	One-stage Highest yield of reducing sugars 30 mg/mL	Keshwani et al. [15]

3.1.1. One-stage microwave-alkali pretreatment

Komolwanich et al. [23] reported that the microwave-assisted NaOH pretreatment of *S. spontaneum* and *A. donax* positively affected the cellulose content while hemicellulose and lignin contents declined and the maximum yields of monomeric sugar was 6.8 g/100 g at 5 % NaOH. Pretreatment oil palm empty fruit bunch fiber (EFB) was done using the combination of MW and NaOH and it was found that the enzymatic saccharification of EFB was significantly improved by the removal of more lignin and hemicellulose and enhancing cellulose accessibility during the pretreatment. The results indicated that 3% NaOH at microwave power of 180 W for 12 minutes are the optimum pretreatment conditions, achieving 74% of lignin and 24.5% holocellulose removal [24].Microwave-alkali pretreatment of sugarcane bagasse using 1% NaOH solution at 600 W for 4 min followed by enzymatic hydrolysis produced reducing sugar yield of 0.665 g/g dry matter [25]. Vani et al. [27] compared the pretreatment of cotton plant residue by alkali assisted microwave at 300W for 6 min with high pressure reactor pretreatment (180 °C, 100 rpm for 45 min). They found that hydrolysis of solid fractions resulted in maximum reducing sugar yield of 0.495 g/g, requiring energy of 108 kJ for microwave-assisted alkali pretreatment while, 540 kJ of energy was need in the high pressure reactor pretreatment, an reduction of 5-fold. Zhu et al. [28] attributed that to solubilisation of hemicellulose and lignin concentration in NaOH solution. Consequently, dilute NaOH pretreatment improves the enzymatic digestibility because it effectively removes lignin and enlarges the surface area and pore size of the substrate, as a result of decreased crystallinity of cellulose, and cleaved the structural bonds between lignin and other carbohydrates [29]. Zhu et al. [16] also reported that using microwave-assisted alkali to pretreat wheat straw proved that removing more lignin and hemicellulose from biomass took less pretreatment time than the alkali/conventional heating this confirmed by Zhao et al. [30]. They have mentioned that pretreatment of rice hulls by NaOH solution in a microwave environment, it has increased accessibility of the substrates due the rupture of the rigid structure of rice hulls. The reducing sugar content was increased by 13% compared to the samples without microwave pretreatment.

3.1.2. One-stage microwave-acid pretreatment

Palmarola-Adrados et al. [31] used dilute sulfuric acid solution heated in microwave to pretreat starch-free wheat fibers. It was demonstrated that the biomass pretreatment using microwave heating was able to produce a higher sugar yield than the steam explosion pretreatment. The impact of dilute acid concentration (up to 2% sulfuric acid) coupled with microwave-assisted heating reduced the hemicellulose content from 29.9 to 10.1% when compared to neutral solution (distilled water). It is worthy to note that an increase in acid concentration intensifies the depletion of hemicellulose so that the relative content of hemicellulose drops to around 1% once the acid concentration is larger than or equal to 0.015 M. Accordingly, it is realised that 79.8 and 97.8 wt% of hemicellulose contained in the raw bagasse were hydrolyzed using distilled water and 0.02 M sulfuric acid, respectively. It was also observed that the relative content of cellulose declines slightly by increasing acid concentration. With regards to lignin, similar behavior was also exhibited when the acid concentration was lifted from 0.015 to 0.02 M. [32]. It is known that dilute acid pretreatment is able to convert hemicellulose to soluble sugars and facilitates the subsequent enzymatic hydrolysis of cellulose [33-35]. Binod et al. [25] found the amount of reducing sugar yield was 0.091 g/g pretreated sugarcane bagasse with microwave-assisted 1% sulfuric acid at 600 W for 4 min followed by enzymatic hydrolysis. The sugar yield was increased to 0.665 g/g pretreated biomass by changing H_2SO_4 with 1% NaOH at the same conditions. It was outlined that the difference with acid pretreatment, the lignin present in the solid fraction blocks enzymatic accessibility which in turn reduces the hydrolysis efficiency [36]. Alkali pretreatment, in contrast can remove lignin from the lignocellulosic materials.

3.2. Two-stage microwave-chemical pretreatment

Table 1 shows summary of some recent research done on the use of microwave – chemical pretreatment of biomass for bioethanol production for two-stage. As shown previously, one-stage pretreatment methods have some limitations. For example, combination microwave-alkali pretreatment removes most of the lignin from biomass and the remaining solid residue on enzymatic hydrolysis results in the production of a mixture of hexose and pentose sugars, which need complex co-fermentation methods for comprehensive sugar utilisation. With acid pretreatment, the lignin present in the solid fraction constrains enzymatic hydrolysis which decreases the hydrolysis efficiency [25]. Two-stage microwave-chemical pretreatment is one of the solutions to overcome some limitation of single-stage microwave–chemical pretreatment. [37]. Binod et al. [25] reported that the pretreatment of sugarcane bagasse via sequential microwave-alkali-acid treatment with 1% NaOH and 1% sulfuric acid. The recovery of fermentable sugars from sugarcane bagasse was improved with an overall yield 0.83 g/g dry biomass, as compared to microwave/alkali only pretreatment with reducing sugar yield of 0.665 g/g dry biomass, at microwave power of 600 W and 4 min pretreatment time. Obviously, these results indicate a combined microwave-alkali-acid pretreatment for short duration improved the fermentable sugar yield. Zhu et al. [16] subjected rice straw to microwave/alkali and microwave/acid/alkali for its enzymatic hydrolysis for xylose recovery from the pretreatment liquid. They observed that xylose could not be recovered by the microwave/alkali pretreatment process, but could be recovered as crystalline xylose by the microwave/acid/alkali. This is probably, due to the high lignin-derived impurities in the pretreatment liquors.

4. Combination of Microwave-Steam Explosion Pretreatment

Steam explosion (SE) are used in the fractionation of biomass components. In this method, biomass is exposed to pressurised steam and then the pressure is suddenly reduced. Due to pressure fluctuation, the materials undergo an explosive decompression [38]. A novel process includes using a combination of steam explosion and microwave irradiation methods (SE–MI) was accomplished by Pang et al. [39]. They investigated and compared SE-MI with steam explosion only treatment. The corn stover was irradiated under 540 W microwave power for 3 min. Both of the two pretreatment methods were achieved at 170–210°C for 3-15min. Results demonstrated that compared to SE alone process, SE–MI process improved the enzymatic hydrolysis yields of glucose and xylose, and slightly enhanced the total sugar yield. The maximum glucose yield, xylose yield and total sugar yield of the process were 57.4%, 17.8% and 75.2% (corresponding to 28.0 g glucose, 8.7 g xylose and 36.7 g total sugar were generated from100 g raw feedstock), respectively, found at 200°C for 5 min. SE–MI pretreatment showed clear advantage in inhibiting the increase of biomass crystallinity. The crystallinity after SE–MI pretreatment was 19% less than that resulting SE pretreatment at 190°C for 5 min.

5. Operating Parameters Affecting Sugar Recovery

5.1. Biomass loading

Biomass loading is an important factor affecting microwave pretreatment efficiency. Selecting the suitable substrate concentration can enhance the pretreatment output by accelerating biomass dissolution. Lu et al. [40] examined rape straw with various solid loadings of 30 (LTS), 50 (MTS), and 90% (HTS) at 900 W microwave power for a min. They found that the maximum glucose yield of 53.5% was attained at the solid loading of LTS, but this value is similar to that of MTS (48.6%). Thus at the expense of a small decrease in sugar yield, more straw can be pretreated and less energy is needed overall. Furthermore, both cellulose and hemicellulose saccharification was shown to improve with a simultaneous increase in substrate concentration at the middle levels where the optimum substrate concentration was 75 g/L achieving maximum saccharification under 680 W microwave power for 24 min [41]. While a further rise in the level of substrate concentration results in a gradual decrease in saccharifications. It might be caused by the different "energy effect" with different substrate concentration. In other words, the samples with a high biomass loading (and thus relatively low water loading) will receive less energy absorbed by water due to oscillation of water molecules [42], which is not beneficial to the structure disruption of rice straw. As a result, a higher straw digestibility was obtained for samples at a relatively low biomass loading.

5.2. Microwave power of pretreatment

Unlike conventional heating sources, microwave irradiation produces higher power densities, which positively reflects to increase production rates and shrink production costs of bio-alcohol. Xu et al. [43] observed that microwave power level positively affected glucose recovery from alkali assisted pretreatment of wheat straw (although the results for xylose were mixed). On the other hand, Binod et al. [25] reported that microwave-acid pretreatment of sugarcane bagasse had no increase in sugar yields when microwave power levels were varied as shown in Fig. 1. It shows the maximum reducing sugar yields for microwave-assisted acid (MA), microwave-assisted alkali (MAL) and microwave-assisted alkali/acid (MAA) pretreatment at different microwave power. For MA pretreatment, it was observed that there is an inverse relationship between the increasing microwave power and reducing sugar yield. The highest reducing sugar was shown at 100 W microwave powers. For MAL and MAA pretreatment, the highest reducing sugar was produced at 600 W power level. Furthermore, it was observed that the pretreatment time can be reduced by increasing the microwave power level with some limitations. As the temperature rises, the degree of polymerisation of cellulose declines, long cellulose chains collapse to shorter groups of molecules, it release glucose that degrade to hydroxymethyl furfural [44].Thereby, it is essential to find a proper microwave power to avoid unnecessary waste in energy or degradation some useful components. It was reported that microwave power of 180 W is optimum to allow for sufficient lengths of pretreatment time without drastic volumetric losses of the liquid phase [24].

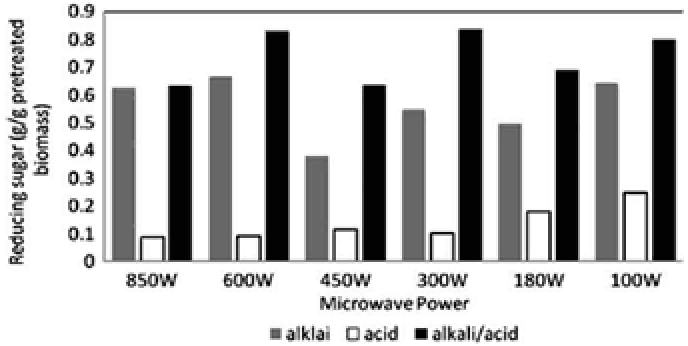

Fig. 1. Maximum Reducing Sugar Yield for MA, MAL and MAA Pretreatment at Various Microwave Power [25].

5.3. Irradiation time

Irradiation time (reaction time) is one of the main factors that have been reported to influence the pretreatment severity [45, 46]. It was found that the interactive effect between irradiation time and microwave power level significantly influenced the biomass digestibility [41] by enhancing hemicellulose removal and cellulose digestibility [47]. Moreover, an extended exposure time with a higher microwave power may led to a decline biomass digestibility, as increase in irradiation time and microwave power cause high temperature within the sample which could initiate decomposition of released sugar in pretreatment process [47]. For instance, dissolved xylose can be decomposed into furfural at high temperature, consequently reducing the total xylose yield. Furfural is an undesirable by-product which plays negative role by inhibiting fermentation processes [48].

In contrast, Karunanithy et al. [21] pretreated switchgrass and big bluestem via sequential extrusion-microwave pretreatment and compared to the extrusion-only as a control. They observed that the recovery of all sugars increased by 15.2% for switchgrass and 14.2% for big bluestem when the samples exposed to microwave irradiation for 2.5 min compared to control. However, they reported increasing the microwave exposure time to 10 min had only modest effects on sugar recovery. In the case of switchgrass, glucose yields were not affected, while xylose and total sugar recovery dropped slightly. Hu and Wen [20] reported that microwave treatment time did not affect glucose recovery from switchgrass at 400 W power level of microwave-alkali pretreatment. Nomanbhay et al. [23] reported that the highest reducing sugar yields was obtained at 12 minutes after pretreatment of oil palm fruit via microwave-assisted 3% NaOH solution at 180 W for exposure time varied at 3-21 min. Komolwanich et al. [22] reported that there is a decreasing trend in the yields of monomeric sugar at increased temperatures. The comparison between reaction time and temperature revealed reaction temperature is the most significant parameter in the release of monomeric sugars. These findings are consistent with the pretreatment results for switchgrass by the microwave [49].Thus, the suitable reaction time and temperature should be investigated to obtain the maximum monomeric sugar yields.

6. Formation Inhibitors

Most of the feed stocks were exposed to microwave pretreatments (particularly with chemicals), necessitate feedstock washing after pretreatment to eliminate fermentation inhibitors. The major types of fermentation inhibitors are furfural and hydroxymethyl furfural (HMF), weak acids, and phenolic compounds. Maiorella et al. [50] reported that the concentrations of acetic acid 0.5-9 g/l, formic acid 0.5–2.7 g/land lactic acid 10–40 g/l inhibited *Saccharomyces cerevisiae* yeast growth in the fermentation process due to interference of the acids with functions involved in cell maintenance. Meanwhile, glycerol at a concentration of 450 g/l alters the cell's osmotic pressure [50], and furfurals at concentrations of 3 g/l are considered antagonistic to cell growth [51]. Karunanithy et al. [21] reported 0.12 g/l of acetic acid was the only fermentation inhibitor found after pretreatment switchgrass by combination extrusion-microwave pretreatment. Higher acetic acid concentrations were found after pretreatment of Kans grass and Gaint reed via microwave-assisted NaOH and two-stage microwave/NaOH/H_2SO_4 but the furfural was untracable [22]. It was recorded there were 0.7 g/l acetic acid, 0.04 g/l lactic acid, 2.3 g/l glycerol, 0.14 g/l formic acid, less than 0.1 g/l HMF and furfurals from pretreated sorghum bagasse by microwave-assisted dilute ammonia [7]. However, the quantities of these chemicals were insufficient to generate any inhibitory effect. Steam explosion-microwave pretreatment of corn stover aggravated furfural, HMF, formic and acetic acids formation when compared to steam explosion pretreatment alone [39]. Pang et al. [52] observed an increase in acetic acid concentration from 2.14 to 2.94 g/100 g matter with microwave power and exposure time for combination steam explosion- microwave pretreatment of corn stover. The presences of these amounts of inhibitors indicate of the severity of the pretreatment. Therefore, pretreatment optimisation is the best way to prevent the formation of many of these compounds or make their levels far below inhibitory levels.

7. Conclusions

The recent application of microwave pretreatment of lignocellulosic biomass for high sugar yield was reviewed. Combining microwave with physical or chemical pretreatment method showed positive effect to increase the reducing fermentable sugar yields prior to the hydrolysis step through the removal of lignin or altering the recalcitrant biomass components. Optimisation of various operating pretreatment parameters that affects the reducing sugar yields and inhibitors formation such as biomass loading, microwave intensity, and irradiation time is also important. An added advantage for microwave pretreatment is that the quantities of inhibitor formed during the pretreatment process compounds were found to be insufficient to generate any inhibitory effect for the fermentation process.

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