**Thermochemical pretreatments of maize stem for sugar recovery: comparative evaluation of microwave and conventional heating**

Zongyuan Zhu1\*, Yanbing Liu1, Leonardo D. Gómez2, Tao Wei1, Xinglin Yang1, Rachael Simister2, Simon J. McQueen-Mason2, Duncan J. Macquarrie3

1 School of Energy and Power Engineering, Jiangsu University of Science and Technology, No. 2 Mengxi Road, Zhenjiang, Jiangsu Province, China, 212003

2 Centre for Novel Agricultural Product, University of York, Wentworth Way, York, UK, YO10 5DD

3 Green Chemistry Centre of Excellence, University of York, Heslington Road, York, UK, YO105DD

\*Corresponding author

Email: [*zongyuan.zhu@just.edu.cn*](mailto:zongyuan.zhu@just.edu.cn)

**Abstract**

Microwave (MW) heating is attracting great attention in biorefinery processes, because of its special dipole rotation heating mechanism. In the current study, MW and conventional heating methods were employed to assist the thermochemical pretreatments (H2O, H2SO4 or NaOH) of maize stem biomass. Their influences on sugar release and biomass compositions during pretreatments were comparably evaluated. Compared to conventional heating pretreatment, MW thermochemical pretreatments are highly efficient in sugar recovery, contributing to 4.3 times higher amount of sugar release (1.25 *vs* 0.30 μmol/mg biomass) with reaction time 8 times shorter (5 *vs* 40 min) and selectively producing glucose as the major constituent (0.75 μmol/mg biomass) using 0.2 M H2SO4 as pretreatment media. MW thermochemical pretreatment also effectively removed lignin (up to 91.6%) within 5 min, which was significantly higher than conventional heating pretreatment (51.2%). Conventional heating pretreatment successfully removed hemicellulose and converted the crystalline cellulose into amorphous cellulose, which is probably due to its longer heating time. Rapid MW thermochemical pretreatments efficiently fractionated hemicellulose and removed lignin content while keeping the crystalline cellulose structure. MW and conventional heating pretreatments led to similar digestibility of biomass solid residues. Overall, MW thermochemical pretreatment represents an energy efficient alternative strategy, as it consumed 25-34 folds less energy than conventional heating pretreatment for effective biomass fractionation and value-added chemical production.

**Key words:** Microwave heating; conventional heating; thermochemical pretreatment; maize stem; sugar recovery; lignin removal.

1. **Introduction**

World energy consumption has been rising as a consequence of a number of reasons, including population growth, industrialization, economic growth, and transportation of people and goods. Besides the dwindling reserves of fossil fuels, great concern is associated with its utilization due to the irreversible deterioration of the environment and human health (Gu et al., 2018; Xu et al., 2017). Therefore, second generation bioenergy is gaining support in an attempt to sustain the future energy demand and meet the needs for a greener energy system(Cong et al., 2020; Zhu and Xu, 2020). Maize is the third most important grain after wheat and rice. According to data from the United States Department of Agriculture, global maize production was 1114,753 Thousand metric tons (TMT), with the U.S. as the largest producing country (347,048 TMT), followed by China (260,770 TMT) and Brazil (101,000 TMT) (USDA Foreign Agricultural Service, 2020). A large number of agricultural residues are produced after harvesting, which can be converted into a spectrum of marketable products (i.e. energy, fuel, material, and chemicals) *via* suitable conversions within the concept of biorefinery. Most agricultural residues after maize harvest are lignocellulosic biomass, which is composed of cellulose, hemicellulose, and lignin, forming a recalcitrant structure to protect plants from degradation by microorganism or insects in the natural environment (Gu et al., 2018; Zhang et al., 2019). Being a linear homopolysaccharide, cellulose comprises β-D-glucopyranose units that are linked together by β-1,4-glycosidic bonds. Hemicellulose is a heteropolysaccharide comprising xylans, xyloglucans, xyloglactans, and mannans that have β-(1-4)-linked backbones(Jacobs et al., 2003). Compared to cellulose, hemicellulose has a more diverse structure and lower molecular weight with different functional groups, making it more digestible (Zhu et al., 2020). Lignin is composed of cross-linked polymers of phenolic monomers, acting as a binder to hold the lignocellulosic matrix together (Kumar et al., 2009; Moran-Mirabal, 2013). The complex structure of lignocellulosic material hinders extractions of digestible sugars and value-added chemicals from the biomass. Hence, appropriate pretreatments are necessary to disrupt this rigid structure, eliminate lignin, depolymerize hemicellulose and reduce the crystallinity of cellulose (Zhu et al., 2016). Pretreatments can be energy consuming and expensive, thus developing economically viable and efficient pretreatment alternatives is paramount. Over the last decades, microwave (MW) pretreament has been gaining interest and is considered as an energy efficient method. Heat exchange through the surface is not involved. It also benefits from volumetric heating, shorter heating time, low solvent consumption and easy control of reaction parameters (Bundhoo, 2018). Additionally, MW radiation selectively heats the polar parts of biomass at faster heating rates, leading to the “explosion” effect and disrupting the rigid structure of the biomass matrix, hence contributing to higher extraction yields (Taqi et al., 2020; Zhu et al., 2020). Apart from thermal effects (biomass heating and pressure increase), non-thermal effects possibly occur during MW radiation of biomass material, but such non-thermal effects of MW heating are still controversial (Asomaning et al., 2018).

In most of the previous studies, MW pretreatment of biomass is followed by enzymatic hydrolysis to produce reducing sugars, which is not only time consuming, but also costly (Jin et al., 2018; Kumar et al., 2019a; Kumar et al., 2019b; Sewsynker-Sukai and Gueguim Kana, 2018). In the present work, efficient and effective sugar recovery during pretreatment eliminates the need for enzymatic hydrolysis process and is highly economically and technically favourable. In our previous studies on MW pretreatment of *Miscanthus* at different pretreatment temperature (130-200 oC), 180 oC was the optimum temperature to maximize lignocellulosic material fractionation and minimize sugar degradation (Zhu et al., 2015a). In the current study, maize stem was used as the feedstock for the MW pretreatment at 180 oC with water and 0.2-0.4 M NaOH or H2SO4 for 5-20 min. As a benchmark of our MW pretreatments, conventional thermochemical pretreatments using water, NaOH or H2SO4 were performed at 180 oC for 40 min, as 40 min of reaction time can effectively depolymerize lignocellulosic materials (Gómez et al., 2014; Ibbett et al., 2011) . The effects of MW and conventional thermochemical pretreatments on the reducing sugar production during the pretreatment process, compositions, digestibility and morphological features of pretreated maize stem residues were comparatively evaluated. Energy consumptions of MW and conventional pretreatments were also calculated and compared.

**2. Material and methods**

**2.1 Material**

Maize stems with leaves were obtained from Lousignan, France, which were firstly dried (50 oC, 40 h) in an oven and then milled by knife milling. The average particle size is 325 mm × 98 mm. The maize stem was composed of cellulose (20 ± 1%wt), lignin (30 ± 1.2%wt), hemicellulose (52 ± 2%wt) and ash content (4.9 ± 0.14%wt).

2.2 Microwave and conventional heating thermochemical pretreatments of dried maize stems

Dried maize stem (0.4 g) and 16 ml H2O, H2SO4 (0.2 M and 0.4 M) or NaOH (0.2 M and 0.4 M) solution were put in 35 ml Pyrex® vials with a magnetic stir bar. CEM monomode microwave machine (CEM Discover SP-D, US) was used to perform MW Pretreatment at 180oC for 5-20 min. The IR temperature probe of the CEM microwave machine was calibrated at 180 oC by following the CEM operating instructions before each group of experiments. Each pretreatment condition was performed in triplicate.

An acid digestion vessel (Parr Instruments, Moline, IL) was used to perform the conventional heating pretreatment, which was heated in a convection oven (power: 1550 W). Dried maize stem (0.4 g) and pretreatment media (16 ml of H2O, 0.2 M NaOH or H2SO4) were mixed in the acid digestion vessel. The pretreatment temperature was 180oC, and the reaction time was 40 min. Each pretreatment condition was performed in triplicate.

After MW and conventional pretreatments, the pretreatment liquors and biomass solid fraction were separated by centrifugation. Prior to monosaccharides compositions analysis of the pretreatment liquid fraction, it was neutralized to pH 7 with 1 M HCl or 150 mM Ba(OH)2. The biomass solid residue was rinsed with 10 ml ethanol for three times and dried at 50oC overnight for following biomass composition, chemical structure, morphological studies and digestibility analysis.

2.3 Monosaccharides compositions analysis of pretreatment liquid fraction

The monosaccharides compositions of the pretreatment liquid fraction were analysed by High Performance Ion Exchange Chromatography with an electrochemical detector (DionexICS-3000PC, Thermo Scientific, USA) (Jones et al., 2003).

2.4 Lignin content of biomass solid fraction

3.5 mg of maize stem sample was mixed with acetyl bromide and glacial acetic acid solution (25% v/v). The mixture was heated at 50 oC for 3 h and transferred into a 5 ml volumetric flask, followed by adding 175 µl hydroxylamine HCl, 1 ml of 2 M NaOH and acetic acid. The solution was then diluted 10 times. UV (VARIAN 50Bio) was used to measure the absorbance at 280 nm and the acetyl bromide soluble lignin percentage (ABSL) of biomass was determined using the equation (Foster et al., 2010a):

Lignin content = ABSL×400 mg

A280 = Absorbance at 280 nm (blank corrected), total volume = 5 ml, coefficient = 17.75 g-1 L cm-1, path length = 1 cm

2.5 Hemicellulose percentage of biomass solid fraction

Maize stem (4 mg) were mixed with trifluoroacetic acid (0.5 ml, 2 M) in sample vials, followed by flushing dry argon. The biomass was hydrolysed for 4 hours at 100 oC. After cooling, trifluoroacetic acid was fully removed in a Speedvac centrifugal evaporator. The solid residue was then rinsed with 200 μl of isopropanol for two times, followed by evaporation. 200 μl ultrapure water was added into the biomass sample and mixed well. Then the liquid and biomass residue were separated by centrifuge. After 20 times dilution, the supernatant was re-suspended in 150 μl of ultrapure water and filtered. Dionex ICS-3000 was used to analyse the monosaccharides compositions of hemicellulose.

2.6 Crystalline cellulose percentage of biomass solid fraction

Firstly, trifluoroacetic acid (500 µl, 2 M) was used to hydrolyse 10 mg of maize stem sample at 100 oC for 4 h. Then, 1 ml of nitric acid: acetic acid: water (1: 8: 2 v/v) was added for further hydrolysis at 100 oC for 30 Min. After completion, the solid residue was crystalline cellulose, which was decomposed into glucose using 175 µl of concentrated H2SO4  at room temperature for 45 min. Then the H2SO4 solution was diluted with ultrapure water to 3.2% and kept at 120°C for 2 h, followed by a further dilution of 10 times. Corresponding glucose content was quantified by using Anthrone Reagent (2 mg anthrone/ml concentrated H2SO4) (Foster et al., 2010b).

2.7 Digestibility analysis of biomass solid fraction

The digestibility of maize stem was measured on a high throughput saccharification robotic system. Enzymatic hydrolysis was performed using an enzyme cocktail with a 1:4 (v/v) Novozyme 188 and Celluclast that was filtered by a Hi-Trap desalting column. Four mg of biomass were hydrolysed with 250 μl of enzyme cocktail at 50 oC for 8 hours, buffered by sodium acetate solution (250 ml, 25 mM, pH 4.5). Glucose was quantified by 3-methyl-2-benzothiazolinonehydrazone (MBTH) (Gomez et al., 2010).

2.8 Fourier transformed infrared spectrometry analysis (FT-IR) of biomass solid fraction

The chemical compositions of maize stem were analysed and compared by Fourier transformed infrared spectrometry (FT-IR) (VERTEX 70, Bruker). The spectra were recorded between 650 - 2000 cm-1, which was measured under 64 scans with a spectral resolution of 4 cm-1.

2.9 Morphological study of biomass solid fraction

The morphology features of maize stem were measured using a scanning electron microscope (JEOL, JSM-6490LV, Japan). Biomass samples were coated with 7 nm Au/Pd and measured under vacuum condition, with a secondary electron detector and 5 kV accelerating voltage.

2.10 Energy consumption calculation

The energy consumptions of MW and conventional heating pretreatments were calculated and compared. The MW heating profiles were exported from CEM software and imported into Auto CAD 2016. The energy consumptions of MW pretreatments with different reaction time (5-20 min) were calculated based on each stage and then summed up. The energy consumptions of conventional heating pretreatments were calculated from the oven power parameter (1550 W) and heating time (40 min). According to Issi and Kaplan (Issi and Kaplan, 2018), the active working time of heating resistor was 38.71% of the total running time of domestic oven that operated at 180oC. Meanwhile, the energy consumption for oven operation (lighting, fan, and electronic components) was 19.95% of total energy consumption during active heating. The total energy consumption was composed of energy consumption during active heating and energy consumption during none active heating.

Energy consumption (active heating) = 1550 J/s × 2400 s × 38.71% = 1440.01 KJ

Energy consumption (none active heating) = 1550 J/s × (2400 × 61.29%) s × 19.95% = 454.86 KJ

Therefore, total energy consumption during conventional heating was 1894.86 KJ.

1. **Results and discussions**

**3.1 Monosaccharides in the pretreatment liquid fraction**

Under thermochemical pretreatment conditions, hemicellulose and cellulose can be depolymerized to different extents, contributing to the production of several different monosaccharides during the pretreatment. Figure 1 shows the sugar release during MW or conventional heating pretreatments of biomass by using H2O, NaOH or H2SO4 as pretreatment media. Galactose, arabinose, xylose, glucose, and mannose are presented in the pretreatment liquor, indicating the depolymerization of hemicellulose. Using MW H2O or NaOH pretreatments, (Figure 1(a-c)), similar yields of xylose and glucose were obtained under each condition, suggesting that both glucan and xylan were the major constitutes of hemicellulose. In the case of conventional heating pretreatment (Figure 1(d)), only glucose was the major sugar component under H2O and NaOH pretreatments, whilst both xylose and glucose were the major products under H2SO4 pretreatment, indicating that glucan was easier to be deconstructed than xylan. When reaction time was 5 min, MW 0.2 M H2SO4 pretreatment gave the highest sugar production of 1.25 μmol/ mg biomass with glucose as the major constituent (0.75 μmol/ mg biomass). The highest sugar production can be explained by effective hemicellulose and cellulose depolymerization, as well as minimized sugar degradation. According to the hemicellulose composition study (Figure 2), the glucose content in hemicellulose fraction of untreated maize stem was 14.4% (0.8 μmol/mg biomass), and the glucose content of the hemicellulose fraction in the solid residue after MW 0.2 M H2SO4 pretreatment was 8.86% (0.49 μmol/mg biomass), suggesting that effective depolymerizations of both hemicellulose and cellulose took place after MW 0.2 M H2SO4 pretreatment. MW H2O pretreatment produced a sugar yield of 0.89 μmol/ mg biomass, which is higher than NaOH pretreatment. Under MW heating condition, water molecules dissociation occurs and generates OH3+ that will facilitate biomass decomposition (Yakunov et al., 2017). In addition, acidic functional groups were released from hemicellulose during pretreatment, promoting the hydrolysis process of biomass substrate (Olorunsola et al., 2018). The acidity generated in water pretreatments is lower than that of 0.2 M H2SO4. However, with MW 0.4 M H2SO4 pretreatment, the sugar production was reduced to 0.86 μmol/ mg biomass, because of sugar degradation under strong acidic condition. When reaction time was 10 min (Figure 1(b)), MW 0.2 M H2SO4 pretreatment led to a sugar production of 1.08 μmol/ mg biomass with high glucose production (0.78 μmol/ mg biomass). Significant sugar degradation took place when the acid concentration raised from 0.2 to 0.4 M, as the sugar release was reduced to 0.32 μmol/ mg biomass. In the case of MW 0.2 M NaOH pretreatment, the sugar production was slightly increased with longer reaction time (5 *vs* 10 min), whereas it was reduced with higher NaOH concentration (0.4 M). When the reaction time was 20 min, sugar degradation occurred under all MW pretreatment conditions, particularly in the case of MW H2SO4 pretreatment. Glucose was decomposed into 5-hydromethyl-2-furaldehyde, and xylose was decomposed into furfural, which may undergo polycondensation to form humin that is a complex and recalcitrant carbonaceous substance (Tsilomelekis et al., 2016). Under conventional pretreatments (Figure 1(d)), the amounts of sugar release for H2O and NaOH pretreatments were very small, only 0.12 and 0.08 μmol/ mg biomass respectively. It was noted that conventional heating H2O pretreatment contributed to monosaccharides mixture with a high purity of glucose, which eliminated hazardous chemicals usage and required easier separation process. Conventional heating H2SO4 pretreatment gave a slightly better performance for sugar release (0.30 μmol/ mg biomass) than H2O and H2SO4, but it was still considerably lower than that of MW H2SO4 pretreatment. Figure 1 (a-c) and (d) show that MW pretreatments were much more effective and efficient than conventional thermochemical pretreatments in biomass decomposition and sugar release at 180 oC. In this case, the total sugar release was 4.16 times higher than conventional thermochemical pretreatment with 8 times shorter reaction time (5 *vs* 40 min). Glucose was selectively produced as the major product under dilute H2SO4 pretreatment. The glucose recovery was 38% by using MW 0.2M H2SO4 pretreament for 5 min. However, longer reaction time and higher acid concentration contributed to a fast degradation of sugars and seriously reduced sugar yield. Hence, acid concentration and reaction time should be carefully controlled for optimum sugar release.

**3.2** **Hemicellulose percentage in the maize stem solid fraction**

According to the aforementioned results, reaction time of 5 min was able to effectively fractionate biomass material and extract fermentable reducing sugars, especially glucose. Hence, the hemicellulose percentages of MW pretreated biomass samples for 5 min were compared with that of conventional heating pretreated biomass samples for 40 min (Figure 2). The hemicellulose percentage in maize stems was 52% in the untreated biomass material and was composed of arabinose, fucose, glucose, galactose, mannose, xylose, glucuronic acid, and galacturonic acid. With MW H2O and NaOH pretreatments for 5 min, about 19-23% of hemicellulose was extracted from the maize stem. In accordance with previous discussion, hemicellulose was efficiently removed under acid pretreatment condition, about 8.2% of the hemicellulose remained in the solid fraction after 0.2 M H2SO4 pretreatment. It was completely removed using 0.4 M H2SO4. Compared with other hemicellulose components, mannose presented a more obvious and sudden reduction after pretreatment, indicating it was easier to be removed. Other hemicellulose components showed proportional decrease. In agreement with previous reported work, the degree of hemicellulose hydrolysis was enhanced by increasing the pretreament intensity (Li et al., 2015; Xiao et al., 2017 ).

Under conventional heating thermochemical pretreatment at 180oC for 40 min, hemicellulose was effectively removed from biomass material, which was similar to previously reported work (Gómez et al., 2014; Lima et al., 2014). Only 1.5 - 3% hemicellulose presented in the biomass solid residues. In other words, from 1 mg biomass material, 490-505 μg hemicellulose should be in the pretreatment liquor in the form of either monosaccharides, oligosaccharides or degradation products. According to the amount of sugar release (Figure 1(d)), only 0.3 μmol (49 μg) of sugars was produced from 1 mg biomass after 0.2 M H2SO4 pretreatment. Although hemicellulose was almost completely extracted from the biomass using acid, alkali or water pretreatment, the resulting monosaccharides were not completely presented in the liquid fraction, which can be explained by either sugar degradation or hemicellulose hydrolysis to oligosaccharides rather than monosaccharides. According to Gómez et al.(Gómez et al., 2014), a large amount of furfural and hydroxymethylfurfural presented in the pretreatment liquor after conventional H2SO4 pretreatment of lignocellulosic materials under 180oC for 40 min, whereas conventional NaOH pretreatment produced little furfural or hydroxymethylfurfural. Therefore, it can be inferred that conventional heating pretreatments contributed to a more effective hemicellulose decomposition than MW NaOH and H2O pretreatment, but conventional H2SO4 pretreatment led to sever sugar degradation and conventional NaOH pretreatment was unable to fully hydrolyse hemicellulose into its monomers. In comparison, MW pretreatment not only effectively broke down hemicellulose into its constituent monosaccharides but also minimized sugar degradation.

* 1. **Lignin contents in the of maize stem solid fraction**

Lignin acts as a protective barrier by covalently linking to the cellulose and hemicellulose, which strengthens the structure of plants and enhances its recalcitrance (Baruah et al., 2018). Therefore, they must be removed or decomposed for utilizing lignocellulosic material in the concept of biorefinery. Most of the previous studies only reported the relative percentage of lignin in the biomass material. However, the only relative percentage of lignin is not sufficient enough to elucidate the lignin content changing during pretreatment. In our study, lignin content was quantified and its relative percentage was compared in the following discussion. Figure 3 presents the lignin amounts in maize stem after MW or conventional heating pretreatments. The lignin amount in untreated maize stem was 119 mg in 400 mg, and it was effectively removed by MW thermochemical pretreatment. The lignin removal from biomass increased with reaction time when H2O was the pretreatment medium. In MW NaOH and H2SO4 pretreatments, lignin was rapidly removed from biomass with reaction times of 5 Min, resulting in only 10-16 mg lignin presence in the biomass solid residue. That is to say, 86.5-91.6% lignin was removed after 5 min. In conventional heating pretreatment, 0.2 M NaOH showed a stronger lignin removal capacity than H2O and 0.2 M H2SO4, contributing to a lignin content of 58 mg in the biomass solid residue (lignin removal of 51.2%). Compared with conventional thermochemical pretreatment, MW thermochemical pretreatment was rapid and effective in lignin removal, irrespective of the pretreatment media type and concentration. The heat was gradually transferred from the surface to the core under conventional heating, leading to a mild structural change of lignocellulosic material. However, MW heats polar groups in the substrate quickly, while nonpolar parts do not absorb MW radiation, resulting in temperature and pressure difference inside the biomass and causes severe disruption of the physical structure of the lignocellulosic material. The lignin removal in our work was much higher and efficient than previously reported work (Table 1), indicating that MW pretreatment is a highly promising lignin isolation and extraction technique.

* 1. **Crystalline cellulose percentage in maize stem solid fraction**

Polymerization degree and cellulose crystallinity have significant influences on determining the hydrolysis of lignocellulosic material. The more crystalline the structure, the more difficult to hydrolyse the cellulose (Den et al., 2018). Hence, reduction in crystallinity is a common target for pretreatment. The crystalline cellulose in untreated biomass material was 20.8% (Figure 4). Under MW H2O pretreatment, the crystalline cellulose in the solid residue increased with the reaction time (5 - 20 min). This result was in our expectation, given that lignin and hemicellulose were progressively removed, leaving crystalline cellulose as the major constituent of biomass solid fraction. The crystalline cellulose in the biomass solid residue remained around 55% using MW 0.2 M NaOH pretreatment with changing reaction time. It was 52% with MW 0.4 M NaOH pretreatment for 5 min. With prolonged reaction time, it dropped to 21% at 10 min and 26% at 20 min respectively. When the NaOH pretreatment condition was more severe, part of the crystalline cellulose changed into amorphous cellulose (Mittal et al., 2011), reducing the crystalline cellulose fraction. With MW 0.2 M H2SO4 pretreatment, the crystalline cellulose percentage in maize stem increased with 5 min reaction time, followed by significant reductions with longer reaction times (10-20 min). A more severe reduction of crystalline cellulose was induced by using MW 0.4 M H2SO4 pretreatment, which is possibly attributed to crystalline degradation rather than the change to the amorphous structure.

As it was discussed earlier, hemicellulose and lignin were removed from biomass during conventional heating H2O pretreatment. If the crystalline cellulose content remained unaltered, its relative percentage in pretreated maize stem was supposed to be higher than that of untreated maize stem. Nevertheless, the relative percentage of crystalline cellulose in H2Opretreated maize stem kept unchanged (Figure 4), indicating that some crystalline cellulose changed into amorphous cellulose under the conventional H2O pretreatment condition. Its percentage was brought up to 32.9%, using conventional heating 0.2 M NaOH pretreatment, due to hemicellulose and lignin removals during pretreatment. However, the crystalline cellulose percentage was reduced to 16% using 0.2 M H2SO4 conventional heating pretreatment, possibly because of crystalline cellulose modification to amorphous structure and the subsequent degradation.

* 1. **FT-IR analysis of maize stem solid fraction**

Surface chemical modifiactions of MW and conventional heating pretreated biomass samples are qualitatively analysed by FT-IR spectroscopy. Figure 5 presents the IR spectra of biomass solid residues after 5 Min of MW H2O and NaOH pretreatments and Table 2 summarizes the detailed peak information. The absorbances of MW H2O pretreated maize are the same as that of untreated maize samples, indicating that the biomass chemical compositions changed little. C-O-C stretching of β-glycosidic bonds between the glucose caused sharp peaks at 898 cm-1  (Chen et al., 2012) and 1159 cm-1 (Fan et al., 2012). The absorbances at 1101 cm-1 and 1033 cm-1 associate with cellulose (Chen et al., 2012; Liu et al., 2006) and the strong peak at 1033 cm-1 associates to C-O stretching at C-6 (Liu et al., 2006). In Figure 5, absorbances at 1101 cm-1 and 1159 cm-1 are stronger after MW H2O and NaOH pretreatments, suggesting the cellulose characteristics are more distinctive after lignin and hemicellulose removals (Chen et al., 2012). A new peak at 1204 cm-1 is shown up after MW H2O and NaOH pretreatments, which is associated with C-O-C symmetric stretching and OH plane deformation (Fan et al., 2012). It is expected that hemicellulose are successfully deacetylated and ester bonds between lignin and hemicellulose are also broken after MW NaOH pretreatment, given that the absorbance at 1241 cm-1 (C-O stretching of ester and acetyl functional groups) disappears completely (Li et al., 2010). The peak at 1727 cm-1 associates with bonds between lignin and hemicellulose, such as p-coumaroyl and feruloyl groups, and ester-linked acetyl (Boonmanumsin et al., 2012). The absorbance at 1727 cm-1 diminished, indicating that these linkages are damaged by MW NaOH pretreatment. The absorbance at 1321 cm-1 relates to C-H wagging at C-6 of cellulose (Oh et al., 2005). The absorbance at 1371 cm-1 associates with C-H deformation in cellulose and hemicellulose (Li et al., 2010). Lignin has characteristic peaks at 1425 cm-1, 1516 cm-1 and 1606 cm-1 (Chen et al., 2012; Sun et al., 2003) that are presented in untreated and H2O pretreated maize stem samples. The peak at 1425 cm-1 is associated with the methyl groups of lignin (Guo et al., 2009). The absorbances at 1516 cm-1 and 1606 cm-1 are related to aromatic stretches (Kaparaju and Felby, 2010). After MW NaOH pretreatment, peaks at 1516 cm-1 and 1606 cm-1 diminished, suggesting the effective lignin decomposition, which is in agreement with the previous discussion. Nevertheless, the absorbance at 1425 cm-1 is still presented, since several OCH3 groups are unchanged after NaOH pretreatment. A range of phenolates such as ferulic acid, p-coumaric acid, p-hydroxybenzoic acid and syringic acid vanillin can be released during treatment, among which syringic acid possesses two –OCH3 groups (Ju et al., 2011). NaOH pretreatment can remove the first –OCH3 group easily and create a negative charge on the ring, but the second -OCH3 group removal is challenging.

Figure 6 shows the IR spectra of MW H2SO4 pretreated maize stem samples. After pretreatment, the absorbance at 898 cm-1 is more pronounced, indicating enhanced cellulose characteristics. Meanwhile, several new absorbances are presented after MW H2­SO4 (1052 cm-1, 1101 cm-1, 1158 cm-1 and 1200 cm-1), indicating cellulose structure is more exposed (Ju et al., 2011). This is in accordance with the enhanced crystalline cellulose percentage (70%) in the maize stem after MW 0.2 M H2SO4 pretreatment for 5 min. Just like MW NaOH pretreatment, MW H2SO4 also removed acetyl groups of hemicellulose, due to the missing peak 1241 cm-1, and broken the ester bonds between hemicellulose and lignin, due to missing peak at 1727 cm-1. However, the lignin concerning peaks (1424 cm-1, 1512 cm-1 and 1604 cm-1) still present in the spectra. As it is discussed in the following section (Table 3), the biomass residue after MW H2SO4 pretreatments for 5 min showed a higher percentage of lignin (18%) than hemicellulose (8%). The presence of aromatic stretches should be attributed by a more exposed lignin structure in the pretreated biomass residue, as the core cellulose was surrounded by lignin and a small percentage of hemicellulose. In the case of conventional heating pretreatments, the similar performance of H2O, NaOH and H2SO4 were observed (Supplementary Figure 1).

* 1. **Morphological study of maize stem solid fraction**

Figures 7 and 8 present scanning electron microscope images of biomass solid residues of unpretreated and MW pretreated maize stems. The biomass surface features of untreated maize are shown in Figure 7(a-c). The parallel cellulose bundles are tightly packed together (Figure 7(a)). Under the higher resolution, a smooth and flat surface was observed (Figure 7(b-c)). After 5 min MW 0.2 M NaOH pretreatment, the maize stem structure starts to detach (Figure 8(d)) and the surface coating is considerably damaged (Figure 7(e)), thus parallel strips become visible on the biomass surface. Nevertheless, the biomass surface features are showing a compact structure under higher resolution (Figure 7(f)), which is comparable to that of untreated maize. H2SO4 hardly had any effects on biomass surface if the reaction time was too short (Zhu et al., 2015b), thus the performance of 20 min MW 0.2 M H2SO4 pretreatment is studied (Figure 8). After 20 min 0.2 M MW H2SO4 pretreatment, the cellulose bundles are destructed and showing voids between them (Figure 8(a)). Under the higher resolution, the biomass surface presents broken fragments without completely removing the surface coating (Figure 8(b-c)). Therefore, H2SO4 and NaOH have distinctive effects on the surface of biomass. The biomass coating is removed and cellulose fibres bundles are exposed and separated from each other under NaOH pretreatment, but H2SO4 breaks biomass components into fragments. Figure 9 shows SEM images of biomass solid residue after conventional heating pretreatments. Both conventional heating H2SO4 and NaOH pretreatments remove biomass surface coating (Figure 9 (a) and (d)), and the cellulose bundles are exposed (Figure 9 (b) and (e)). With higher resolution, the biomass surfaces present intact structures (Figure 9 (c) and (f)) that are similar to the untreated biomass surface.

* 1. **Digestibility and chemical compositions of maize stem solid fraction**

After MW and conventional heating thermochemical pretreatments, the digestibility of biomass solid residues was determined (Figure 10). The digestibility of untreated maize stem was 128 nmol sugar/mg biomass.hour digestion, which means 128 nmol glucose is yielded from 1 mg biomass during 1 hour enzymatic digestion. Under the 5 min MW H2O pretreatment condition, the digestibility of pretreated biomass gradually increased up to 168 nmol sugar/mg biomass.hour digestion. MW 0.2 and 0.4 M NaOH pretreated biomass solid residues had similar digestibility (150-171 nmol sugar/mg biomass.hour digestion). Nevertheless, the biomass digestibility was speedily reduced by MW 0.2 M H2SO4 pretreatment, even when reaction time was just 5 min. It was further decreased by using longer reaction times or higher acid concentration. H2O and NaOH increased biomass digestibility, since lignin were effectively removed from biomass material and cellulose was more exposed and accessible to enzymes. The acid pretreatments led to low digestibility of biomass solid fraction, owing to significant sugar release during pretreatment procedure and a relative higher percentage of lignin in the biomass solid fraction (Table 2). Under conventional heating conditions, the digestibility of H2O pretreated biomass solid residue did not change significantly. Conventional NaOH pretreatment increased biomass digestibility, whereas H2SO4 pretreatment reduced biomass digestibility. Overall, MW and conventional heating pretreatments contributed to similar biomass digestibility, but the MW pretreatment was considerably faster.

As can be summarized from the above discussions, MW thermochemical pretreatments just for 5 min was enough to release high amounts of sugars into the pretreatment media and increase the digestibility of biomass solid residue. The overall chemical composition changes of biomass solid fractions after MW and conventional heating pretreatments are shown in Table 3. Conventional heating pretreatment remove hemicellulose and convert the crystalline cellulose into amorphous cellulose, probably due to its longer heating time and outside to inside heating mechanism. Rapid MW thermochemical pretreatments efficiently fractionated hemicellulose and removed lignin content while kept the crystalline cellulose structure. With MW H2SO4 pretreatment for longer reaction time or higher concentration, such a crystalline structure was degraded quickly (Figure 4). Although conventional heating thermochemical pretreatments tend to reduce the crystallinity of cellulose, the sugar release during pretreatment was considerably lower and the digestibility of biomass solid residue was comparable with that of MW pretreated biomass solid residues.

* 1. **Energy consumption**

The energy consumptions of MW thermochemical pretreatments (Table 4) were calculated from the heating profiles (Figure 11) with the assistance of CAD software. In comparison with conventional heating pretreatments, MW heating pretreatment consumed 25-34 folds less energy. The energy consumption difference between MW heating for 5 and 10 min was 16.98 KJ, which became rather small (1.67 KJ) for MW heating for 10 and 20 min (Table 3). Figure 11 shows that the major energy input was consumed at the initial stage of pretreatment. Once the reaction reached the target temperature (180 oC), the power used to stabilize the temperature was fairly modest. It is predicted that MW heating thermochemical pretreatment on a larger pilot scale is also energy efficient, as a longer reaction time that is needed for a larger amount of biomass substrate may not significantly enhance the energy input (Asomaning et al., 2018).

1. **Conclusions**

In the current study, maize stem was used as feedstock for MW and conventional heating thermochemical pretreatments. In comparison with conventional heating thermochemical pretreatments, MW pretreatments showed exceptional efficiency, leading to 4.3 times higher sugar release within only 5 min and selectively producing glucose as the major component using 0.2M H2SO4 as pretreatment media. In addition, the lignin removal was up to 91.6% in MW thermochemical pretreatment, which was much higher than that of conventional heating pretreatment. MW thermochemical pretreatment altered the biomass residue compositions by changing pretreatment media. MW NaOH pretreated biomass was composed of 33% hemicellulose and 13% of lignin. Meanwhile, MW H2SO4 pretreatment efficiently deconstructed hemicellulose into its monosaccharides and left biomass solid residue with 70% of crystalline cellulose and 18% of lignin percentage. In comparison with MW thermochemical pretreatment, the conventional heating pretreatment tends to remove hemicellulose and convert the crystalline cellulose into amorphous cellulose, which is probably due to its longer heating time and convection and conduction heating mechanism. Rapid MW thermochemical pretreatments efficiently fractionated hemicellulose and removed lignin content while keeping the crystalline cellulose structure. Further studies should be performed to investigate the mechanism and kinetic behaviour of biomass decomposition during the MW pretreatment. Moreover, the energy consumption of MW pretreatment was 25-34 folds less than conventional heating pretreatment, and possibly scaled up MW pretreatment of biomass that requires longer pretreatment time is presumably energy efficient. Therefore, MW thermochemical pretreatment is a highly effective and efficient approach to fractionate biomass components and to release large amounts of sugars from biomass material with minimal sugar degradation.

1. **Acknowledgements**

The work was funded by the European Community's Seventh Framework Programme (n° 251132). We acknowledge the financial supports from National Natural Science Foundation of China (n° 21701083) and Jiangsu University of Science and Technology (n°1142931706).

1. **Conflicts of interests**

The authors declare no conﬂict of interest.

**References**

Asomaning, J., Haupt, S., Chae, M., Bressler, D.C., 2018. Recent developments in microwave-assisted thermal conversion of biomass for fuels and chemicals. Renew. Sust. Energ. Rev. 92, 642-657. https://doi.org/10.1016/j.rser.2018.04.084.

Baruah, J., Nath, B.K., Sharma, R., Kumar, S., Deka, R.C., Baruah, D.C., Kalita, E., 2018. Recent trends in the pretreatment of lignocellulosic biomass for value-added products. Front. Energy Res.6, 141. https://doi.org/10.3389/fenrg.2018.00141.

Boonmanumsin, P., Treeboobpha, S., Jeamjumnunja, K., Luengnaruemitchai, A., Chaisuwan, T., Wongkasemjit, S., 2012. Release of monomeric sugars from Miscanthus sinensis by microwave-assisted ammonia and phosphoric acid treatments. Bioresour. Technol. 103, 425-431. https://doi.org/10.1016/j.biortech.2011.09.136.

Bundhoo, Z.M.A., 2018. Microwave-assisted conversion of biomass and waste materials to biofuels. Renew. Sust. Energ. Rev. 82, 1149-1177. https://doi.org/10.1016/j.rser.2017.09.066.

Chen, W.H., Ye, S.C., Sheen, H.K., 2012. Hydrolysis characteristics of sugarcane bagasse pretreated by dilute acid solution in a microwave irradiation environment. Appl. Energy 93, 237-244. https://doi.org/10.1016/j.apenergy.2011.12.014.

Cong, W.J., Wang, Y.T., Li, H., Fang, Z., Sun, J., Liu, H.T., Liu, J.T., Tang, S., Xu, L., 2020. Direct production of biodiesel from waste oils with a strong solid base from alkalized industrial clay ash. Appl. Energy 264, 114735. https://doi.org/10.1016/j.apenergy.2020.114735.

Den, W., Sharma, V.K., Lee, M., Nadadur, G., Varma, R.S., 2018. Lignocellulosic biomass transformations via greener oxidative pretreatment processes: access to energy and value-added chemicals. Front. Chem. 6, 141. https://doi.org/10.3389/fchem.2018.00141.

Fan, M., Dai, D., Huang, B., 2012. Fourier Transform Infrared Spectroscopy for Natural Fibres. in: Salih, S. (Ed.), Fourier Transform - Materials Analysis. IntechOpen, Crotia, pp. 45-68. https://doi.org/10.5772/35482.

Foster, C.E., Martin, T.M., Pauly, M., 2010a. Comprehensive compositional analysis of plant cell walls (lignocellulosic biomass) part I: lignin. J. Vis. Exp. e1745. https://dx.doi.org/ 10.3791/1745.

Foster, C.E., Martin, T.M., Pauly, M., 2010b. Comprehensive compositional analysis of plant cell walls (lignocellulosic biomass) part II: carbohydrates. J. Vis. Exp. e1837. https://dx.doi.org/ 10.3791/1837.

Gómez, L.D., Vanholme, R., Bird, S., Goeminne, G., Trindade, L.M., Polikarpov, I., Simister, R., Morreel, K., Boerjan, W., McQueen-Mason, S.J., 2014. Side by Side Comparison of Chemical Compounds Generated by Aqueous Pretreatments of Maize Stover, Miscanthus and Sugarcane Bagasse. BioEnergy Res. 7, 1466-1480. https://doi.org/10.1007/s12155-014-9480-2.

Gomez, L.D., Whitehead, C., Barakate, A., Halpin, C., McQueen-Mason, S.J., 2010. Automated saccharification assay for determination of digestibility in plant materials. Biotechnol. Biofuels. 3, 23. https://doi.org/10.1186/1754-6834-3-23.

Gu, C., Yuan, Z., Sun, S., Guan, L., Wu, K., 2018. Simulation investigation of drying characteristics of wet filamentous biomass particles in a rotary kiln. Fuel Process. Technol. 178, 344-352. https://doi.org/10.1016/j.fuproc.2018.07.001.

Guo, G.L., Hsu, D.C., Chen, W.H., Chen, W.H., Hwang, W.S., 2009. Characterization of enzymatic saccharification for acid-pretreated lignocellulosic materials with different lignin composition. Enzyme Microb. Technol. 45, 80-87. https://doi.org/10.1016/j.enzmictec.2009.05.012.

Ibbett, R., Gaddipati, S., Davies, S., Hill, S., Tucker, G., 2011. The mechanisms of hydrothermal deconstruction of lignocellulose: New insights from thermal–analytical and complementary studies. Bioresour. Technol. 102, 9272-9278. https://doi.org/10.1016/j.biortech.2011.06.044.

Issi, F., Kaplan, O., 2018. The Determination of Load Profiles and Power Consumptions of Home Appliances. Energies 11, 607. https://doi.org/10.3390/en11030607.

Jacobs, A., Palm, M., Zacchi, G., Dahlman, O., 2003. Isolation and characterization of water-soluble hemicelluloses from flax shive. Carbohydr. Res. 338, 1869-1876. https://doi.org/10.1016/S0008-6215(03)00308-2.

Jin, L., Yu, X., Peng, C., Guo, Y., Zhang, L., Xu, Q., Zhao, Z.K., Liu, Y., Xie, H., 2018. Fast dissolution pretreatment of the corn stover in gamma-valerolactone promoted by ionic liquids: Selective delignification and enhanced enzymatic saccharification. Bioresour. Technol. 270, 537-544. https://doi.org/10.1016/j.biortech.2018.09.083.

Jones, L., Milne, J.L., Ashford, D., McQueen-Mason, S.J., 2003. Cell wall arabinan is essential for guard cell function. P. Natl. Acad. Sci. USA. 100, 11783-11788. https://doi.org/10.1073/pnas.1832434100.

Ju, Y.H., Huynh, L.H., Kasim, N.S., Guo, T.J., Wang, J.H., Fazary, A.E., 2011. Analysis of soluble and insoluble fractions of alkali and subcritical water treated sugarcane bagasse. Carbohydr. Polym. 83, 591-599. https://doi.org/10.1016/j.carbpol.2010.08.022.

Kaparaju, P., Felby, C., 2010. Characterization of lignin during oxidative and hydrothermal pre-treatment processes of wheat straw and corn stover. Bioresour. Technol. 101, 3175-3181. https://doi.org/10.1016/j.biortech.2009.12.008.

Kumar, B., Bhardwaj, N., Verma, P., 2019a. Pretreatment of rice straw using microwave assisted FeCl3-H3PO4 system for ethanol and oligosaccharides generation. Bioresour. Technol. Rep. 7, 100295. https://doi.org/10.1016/j.biteb.2019.100295.

Kumar, N., Muley, P.D., Boldor, D., Coty, G.G., Lynam, J.G., 2019b. Pretreatment of waste biomass in deep eutectic solvents: Conductive heating versus microwave heating. Ind. Crops Prod. 142, 111865. https://doi.org/10.1016/j.indcrop.2019.111865.

Kumar, P., Barrett, D.M., Delwiche, M.J., Stroeve, P., 2009. Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production. Ind. Eng. Chem. Res. 48, 3713-3729. https://doi.org/10.1021/ie801542g.

Li, C.L., Knierim, B., Manisseri, C., Arora, R., Scheller, H.V., Auer, M., Vogel, K.P., Simmons, B.A., Singh, S., 2010. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. Bioresour. Technol. 101, 4900-4906. https://doi.org/10.1016/j.biortech.2009.10.066.

Li, H., Chen, X., Ren, J., Deng, H., Peng, F., Sun, R., 2015. Functional relationship of furfural yields and the hemicellulose-derived sugars in the hydrolysates from corncob by microwave-assisted hydrothermal pretreatment. Biotechnol. Biofuels 8, 127. https://doi.org/10.1186/s13068-015-0314-z.

Lima, M.A., Gomez, L.D., Steele-King, C.G., Simister, R., Bernardinelli, O.D., Carvalho, M.A., Rezende, C.A., Labate, C.A., deAzevedo, E.R., McQueen-Mason, S.J., Polikarpov, I., 2014. Evaluating the composition and processing potential of novel sources of Brazilian biomass for sustainable biorenewables production. Biotechnol. Biofuels 7, 10. https://doi.org/10.1186/1754-6834-7-10.

Liu, C.F., Xu, F., Sun, J.X., Ren, J.L., Curling, S., Sun, R.C., Fowler, P., Baird, M.S., 2006. Physicochemical characterization of cellulose from perennial ryegrass leaves (Lolium perenne). Carbohydr. Res. 341, 2677-2687. https://doi.org/10.1016/j.carres.2006.07.008.

Mittal, A., Katahira, R., Himmel, M.E., Johnson, D.K., 2011. Effects of alkaline or liquid-ammonia treatment on crystalline cellulose: changes in crystalline structure and effects on enzymatic digestibility. Biotechnol. Biofuels 4, 41. https://doi.org/10.1186/1754-6834-4-41.

Moran-Mirabal, J.M., 2013. Advanced-microscopy techniques for the characterization of cellulose structure and cellulose-cellulase interactions. in: Van De Ven T. (Ed.), Cellulose- Fundamental Aspects. IntechOpen, Rijeka, Croatia, pp. 1-45.

https://doi.org/10.5772/56584.

Oh, S.Y., Yoo, D.I., Shin, Y., Kim, H.C., Kim, H.Y., Chung, Y.S., Park, W.H., Youk, J.H., 2005. Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. Carbohydr. Res. 340, 2376-2391. https://doi.org/10.1016/j.carres.2005.08.007.

Olorunsola, E. O., Akpabio, E.I., Adedokun, M. O., Ajibola, D. O., 2018. Emulsifying properties of hemicelluloses, in: Karakus, S. (Ed.), Science and Technology Behind Nanoemulsions. IntechOpen, London, United Kingdom, pp. 30-42. http://dx.doi.org/10.5772/intechopen.74473

Sewsynker-Sukai, Y., Gueguim Kana, E.B., 2018. Microwave-assisted alkalic salt pretreatment of corn cob wastes: process optimization for improved sugar recovery. Ind. Crops Prod. 125, 284-292. https://doi.org/10.1016/j.indcrop.2018.08.086.

Sombatpraiwan, S., Junyusen, T., Treeamnak, T., Junyusen, P., 2019. Optimization of microwave-assisted alkali pretreatment of cassava rhizome for enhanced enzymatic hydrolysis glucose yield. Food Energy Secur. 8, e00174. https://doi.org/10.1002/fes3.174.

Sun, J.X., Sun, X.F., Sun, R.C., Fowler, P., Baird, M.S., 2003. Inhomogeneities in the chemical structure of sugarcane bagasse lignin. J. Agric. Food Chem. 51, 6719-6725. https://doi.org/10.1021/jf034633j.

Tan, L., Liu, Z., Zhang, T., Wang, Z., Liu, T., 2020. Enhanced enzymatic digestibility of poplar wood by quick hydrothermal treatment. Bioresour. Technol. 302, 122795. https://doi.org/10.1016/j.biortech.2020.122795.

Taqi, A., Farcot, E., Robinson, J.P., Binner, E.R., 2020. Understanding microwave heating in biomass-solvent systems. Chem. Eng. J. 393, 124741. https://doi.org/10.1016/j.cej.2020.124741.

Tsilomelekis, G., Orella, M.J., Lin, Z., Cheng, Z., Zheng, W., Nikolakis, V., Vlachos, D.G., 2016. Molecular structure, morphology and growth mechanisms and rates of 5-hydroxymethyl furfural (HMF) derived humins. Green Chem. 18, 1983-1993. https://doi.org/10.1039/C5GC01938A.

USDA Foreign Agricultural Service, 2020. World corn production, consumption, and stocks <https://apps.fas.usda.gov/psdonline/app/index.html#/app/downloads>. (accessed 14 June 2020)

Xiao, L., Song, G., Sun, R., 2017. Effect of Hydrothermal Processing on Hemicellulose Structure. in: Héctor A. Ruiz, M.H.T., Heather L. Trajano (Ed.), Hydrothermal Processing in Biorefineries. Springer Cham, Switzerland, pp. 45-94. https://doi.org/10.1007/978-3-319-56457-9\_3.

Xu, H., Yin, B., Liu, S., Jia, H., 2017. Performance optimization of diesel engine fueled with diesel–jatropha curcas biodiesel blend using response surface methodology. J. Mech. Sci. Technol. 31, 4051-4059. https://doi.org/10.1007/s12206-017-0753-5.

Yakunov, A.V., Biliy, M.M., Naumenko, A.P., 2017. Long-term structural modification of water under microwave irradiation: low-frequency Raman spectroscopic measurements. Adv. Opt. Technol. 5260912. https://doi.org/10.1155/2017/5260912.

Zhang, Z., Zhu, Z., Shen, B., Liu, L., 2019. Insights into biochar and hydrochar production and applications: A review. Energy 171, 581-598. https://doi.org/10.1016/j.energy.2019.01.035.

Zhou, L., Budarin, V., Fan, J., Sloan, R., Macquarrie, D., 2017. Efficient method of lignin isolation using microwave-assisted acidolysis and characterization of the residual lignin. ACS Sustain. Chem. Eng. 5, 3768-3774. https://doi.org/10.1021/acssuschemeng.6b02545.

Zhu, Z., Liu, Y., Yang, X., McQueen-Mason, S.J., Gomez, L.D., Macquarrie, D.J., 2020. Comparative evaluation of microwave-assisted acid, alkaline, and inorganic salt pretreatments of sugarcane bagasse for sugar recovery. Biomass Convers. Biorefin. https://doi.org/10.1007/s13399-020-00680-7.

Zhu, Z., Macquarrie, D., Simister, R., Gomez, L., McQueen-Mason, S., 2015a. Microwave assisted chemical pretreatment of Miscanthus under different temperature regimes. Sustain. Chem. Process. 3,15. https://doi.org/10.1186/s40508-015-0041-6.

Zhu, Z., Rezende, C.A., Simister, R., McQueen-Mason, S.J., Macquarrie, D.J., Polikarpov, I., Gomez, L.D., 2016. Efficient sugar production from sugarcane bagasse by microwave assisted acid and alkali pretreatment. Biomass Bioenerg. 93, 269-278. https://doi.org/10.1016/j.biombioe.2016.06.017.

Zhu, Z., Simister, R., Bird, S., McQueen-Mason, S.J., Gomez, L.D., Macquarrie, D.J., 2015b. Microwave assisted acid and alkali pretreatment of Miscanthus biomass for biorefineries. AIMS Bioeng. 2, 449-468. https://doi.org/10.3934/bioeng.2015.4.449.

Zhu, Z., Xu, Z., 2020. The rational design of biomass-derived carbon materials towards next-generation energy storage: A review. Renewable Sustainable Energy Rev. 134, 110308. https://doi.org/10.1016/j.rser.2020.110308.

Zijlstra, D.S., De Santi, A., Oldenburger, B., De Vries, J., Barta, K., Deuss, P.J., 2019. Extraction of lignin with high β-O-4 content by mild ethanol extraction and its effect on the depolymerization yield. J. Vis. Exp. 143, e58575. https://doi.org/10.3791/58575.

Table 1 Lignin removal of previous and current studies

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Feedstock | Pretreatment condition | Temperature  (oC) | Pretreatment media | Lignin removal (%) | Reference |
| Maize stem | MW, 300 W, 5 min | 180 | 0.2 M NaOH | 91.6 | This work |
| Maize stem | Conventional heating, 40 min | 180 | 0.2 M NaOH | 51.2 | This work |
| Cassava rhizome | MW, 300 W, 5 min | n.a. | 5% w/v NaOH | 13.58 | (Sombatpraiwan et al., 2019) |
| Cassava rhizome | MW, 900 W, 10 min | n.a. | 7% w/v NaOH | 71.16 |
| Mixed softwood pellet | MW, 300 W, 10 min | 190 | 0.2 M H2SO4 | 82.31 | (Zhou et al., 2017) |
| Beech | Conventional heating, 5 h | 120 | 80:20 ethanol/water mixture, 0.24 M HCl | 73.9 | (Zijlstra et al., 2019) |
| Poplar | Conventional heating, 5 min | 200 | Water | 29.53 | (Tan et al., 2020) |

Table 2 Chemical composition changes in the biomass

|  |  |  |
| --- | --- | --- |
| Peak position (cm-1) | Assignment | References |
| 898 | C-O-C stretching of β-glycosidic bonds | (Chen et al., 2012) |
| 1033 | C-O stretching at C-6 of cellulose | (Liu et al., 2006) |
| 1101 | related to cellulose | (Chen et al., 2012; Liu et al., 2006) |
| 1159 | C-O-C stretching of β-glycosidic bonds | (Fan et al., 2012) |
| 1204 | C-O-C symmetric stretching, OH plane deformation | (Fan et al., 2012) |
| 1241 | C-O stretching of ester and acetyl functional groups | (Li et al., 2010) |
| 1321 | C-H wagging at C-6 of cellulose | (Oh et al., 2005) |
| 1371 | C-H deformation in cellulose and hemicellulose | (Li et al., 2010) |
| 1425 | methyl groups of lignin | (Guo et al., 2009). |
| 1516 | aromatic ring vibrations of lignin | (Kaparaju and Felby, 2010) |
| 1606 | aromatic ring stretching of lignin | (Kaparaju and Felby, 2010) |
| 1727 | ester-linked acetyl groups | (Boonmanumsin et al., 2012) |

Table 3 Varied maize stem chemical compositions after MW and conventional heating thermochemical pretreatments

|  |  |  |  |
| --- | --- | --- | --- |
| Pretreatment conditions | Crystalline cellulose  (%) | Hemicellulose  (%) | Lignin  (%) |
| Untreated maize | 20 ± 1 | 52 ± 2 | 30 ± 1 |
| MW H2O, 5 min | 43±4 | 33 ± 0.01 | 22±1 |
| MW 0.2 NaOH, 5 min | 59 ±1 | 33 ±0.01 | 13 ±2 |
| MW 0.2 H2SO4, 5 min | 70 ± 6 | 8±0.007 | 18±1 |
| Conv H2O, 40 min | 16 ±1.6 | 3±0.12 | 22±1.8 |
| Conv 0.2 NaOH, 40 min | 20 ±3 | 2±0.017 | 13±0.0066 |
| Conv 0.2 H2SO4, 40 min | 33 ±5 | 1.6±0.016 | 22±0.0014 |

Table 4 Energy consumption of MW and conventional heating thermochemical pretreatments

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Pretreatment | MW 5 min | MW 10 min | MW 20 min | Conv Heating 40 min |
| Energy consumption  (KJ) | 55.80 | 72.78 | 74.45 | 1894.86 |



Figure 1 Monosaccharides compositions of pretreatment liquors from MW thermochemical pretreatments of maize stem at varied reaction time, (a) 5 min, (b) 10 min, (c) 20 min and (d) conventional thermochemical pretreatments of maize stem for 40 min



Figure 2 Hemicellulose percentages in maize stem after MW pretreatment (reaction time: 5 min) and conventional heating pretreatment (reaction time: 40 min)

aConv: conventional heating



Figure 3 Lignin amounts in maize stem after MW and conventional heating pretreatments



Figure 4 Crystalline cellulose percentages in maize stem after MW and conventional heating pretreatments



Figure 5 FT-IR analysis of maize stem after 5 Min MW H2O and NaOH pretreatments



Figure 6 FT-IR analysis of maize stem after 5 min MW H2SO4 pretreatment



Figure 7 SEM images of untreated maize stem (a. x250; b. x1000; c. x5000) and 5 min MW 0.2 M NaOH pretreated maize stem (d. x250; e. x1000; f. x5000)



Figure 8 SEM images of 20 min MW 0.2 M H2SO4 pretreated maize stem (a. x 250; b. 1x1000; c. x5000)



Figure 9 SEM images obtained from conventional heating 0.2 M NaOH pretreated maize stem (a. x250; b. x1000; c. x5000) and 0.2 M H2SO4 pretreated maize stem (d. x250; e. x1000; f. x5000); reaction time was 40 min



Figure 10 Digestibility of biomass solid residue after MW or conventional heating pretreatments



Figure 11 Typical heating profiles of MW thermochemical pretreatments of maize stem at 180 oC for (a) 5 min, (b) 10 min and (c) 20 min