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CHEMICAL ENGINEERING | RESEARCH ARTICLE

Development of non-derivatizing hydrate salt pre-treatment solvent for pre-treatment and fractionation of corn cob

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Abstract: Major concern in beneficiating lignocellulose is overcoming biomass recalcitrance through pre-treatment. Molten hydrate salts (MHS) is a green solvent with ability to swell and dissolve cellulose and biomass in a non-derivatizing way. Over the last decade, MHSs have been used for isolated cellulose dissolution, however very few studies have been reported on their effectiveness in pre-treating lignocellulosic biomass. Therefore, effectiveness of their application as solvent for pre-treating and fractionating corn cob is presented in this article. In this study, seven molten hydrate salt pre-treatment solvent systems such as unary, binary and ternary mixtures of ZnCl2.4H2O, LiClO4.3H2O and Urea were investigated for their ability to pre-treat and fractionate biomass. The pre-treatment experiments were carried out in a shaking incubator at 70°C for 60 minutes at a biomass: solvent ratio of 1:10. The surface chemistry of the biomass was checked before and after pre-treatment using Fourier Transform infrared spectroscopy. X-ray diffraction and scanning electron microscopy were employed to check the crystallinity and surface morphology of the biomass. Physicochemical analysis consistently indicated a disruption in the structure of corncob due to removal of lignin and hemicellulose during the pre-treatment process. Additionally, results showed a decrease in crystallinity and a change in surface morphology after the pre-treatment using all the seven solvent systems (MHS solvents). The use of ZnCl2.4H2O/ Urea solvent displayed 100% recovery of cellulose, 42% recovery of hemicellulose and 44% recovery

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PUBLIC INTEREST STATEMENT

Pre- treatment is a crucial but expensive processing step in the biochemical conversion of lignocellulosic biomass to basic sugars and finally to fuels and chemicals. Thus, it is essential to fractionate lignocellulosic biomass and make the major components of biomass (cellulose, hemicellulose and lignin) more accessible to enzymatic activities to convert them to simple sugars. However, the degree of fractionation to the desired fractions depends on the effectiveness of the pre-treatment method to separate the biomass to the desired major components. Molten hydrate salts are able to do this, but further research is required to improve on their effectiveness. This study describes the effect of different molten hydrate salts systems composing of $LiClO_4.3H_2O$, $ZnCl_2.4H_2O$ and Urea on the pre-treatment and fractionation of corn cob.

of lignin from the corn-cob when compared to the performance of the other proposed solvent systems in this study.

Keywords: Molten hydrate salts; pre-treatment; fractionation; corn cob
Subjects: Chemical Engineering; Biochemical Engineering; Bioconversion; Bioenergy

1. Introduction

In view of environmental concerns (e.g., global warming) resulting from overuse of fossil fuels, there is a need to produce platform chemicals, materials and fuels from renewable lignocellulosic resources via biochemical/biotechnological methods. Lignocellulosic biomass is the most abundant plant material on the planet (Wilson, 1988). The use of lignocellulosic biomass has been proven to give promising yields in processes designed to produce fuels, chemicals and materials. Lignocellulosic feedstock makes the process cheap, viable as well as eco-friendly. These feedstocks can be derived from woody biomass, municipal waste and agricultural waste (Chang, 2007). Corn cob waste, a type of agricultural waste, is the residue left from removing the maize grains. Cobs make up about 20 wt. % of the yield of the corn residue and corn cob residues are sufficiently available in South Africa and are produced by the maize industry in large quantities of approximately 14.5 million tons annually (Lee, 1997; Mohlala et al., 2016).

All sources of lignocellulosic biomass consist of three fractions (lignin, hemicellulose, and cellulose), which are confined in a hetero-matrix (Lee, 1997). Optimal utilisation of all these fractions in bioprocessing could be instrumental to improving overall economy and viability of bioconversion process. One of the steps in bioconversion of lignocellulosic biomass is the hydrolysis of cellulose and hemicellulose, fractions of this biomass, to fermentable reducing monomeric sugars such as hexose and pentose; and the simple sugars are then fermented and further processed to biofuels and (bio)chemicals (Demirbas, 2009). However, main mitigating factors to efficient hydrolysis include porosity (accessible surface area), cellulose crystallinity, cellulose sheathing by hemicellulose and lignin content in the biomass (Arantes & Saddler, 2011). To overcome these shortcomings, a pre-treatment process is be employed to remove lignin fraction and decrease crystallinity of cellulose in the biomass, thereby increasing its surface area for accessible binding of enzymes (Galbe & Zacchi, 2007). Currently, a variety of fractionation and pre-treatment processes including chemicals, physical and biological pre-treatment methods are investigated in academia and industry (Alvira et al., 2010). Examples of pre-treatment methods that have been investigated and used include; oxidative delignification, acid and alkali hydrolysis (Jacobsen & Wyman, 2000) ionic liquid (Zhu, 2008), hydrothermal (Garrote et al., 2002), inorganic salt immersion, steam explosion(Liu et al., 2013), microbial (Wan & Li, 2011). However, these pre-treatment processes are either economically non-feasible; result in formation of undesired fermentation inhibitory by-products or are ineffective (Bhatia et al., 2012). Furthermore, for environmental sustainability, biomass utilisation will heavily depend on the successful deployment of innovative-green chemistry. Green chemistry is defined as the efficient use of raw materials (preferably renewable), the elimination of waste and avoidance of hazardous or toxic reagents and solvents in chemical processes (Capolupo & Faraco, 2016). Examples of these green solvents are cheap, eco-friendly and recyclable molten hydrate salt (MHS) systems. Molten hydrate salts (MHSs) are aqueous solutions of inorganic salts at extraordinarily high concentration, which varies for each salt, depending on the coordination number of the salt cation (Sen et al., 2013). MHSs have cations that are highly hydrated (coordinated with water), while the anion is coordination-free in the system. This nature gives molten salt hydrates some unique properties such as high boiling point, low vapour pressure and liquid status at moderate temperature, MHS are even able to swell and dissolve cellulose and biomass in a non-derivatising manner (Sen et al., 2013). They have been used as solvent and reaction medium in various chemical reactions and processes including biomass conversion, because of similar properties and performance with ionic liquids (de Almeida et al., 2010). In addition, molten hydrate salts are often known as inorganic ionic liquids. However, molten hydrate salts usually have lower cost, lower viscosity and lower toxicity when compared to other organic ionic liquids. Examples of MHSs are $LiClO_4 \cdot 3H_2O$, $LiSCN{\cdot}2H_2O$, $LiI_2 \cdot 2H_2O$, $ZnCl_2 \cdot 4H_2O$, and their mixtures have been proven to enable the dissolution of cellulose at relatively mild conditions (Sen et al., 2013). Most molten salt hydrate systems which are capable of dissolving cellulose contain Li^+ or Zn^{2+} ions. However, it is noteworthy to mention that all of these ions are not efficient in solubilizing cellulose. Molten salt hydrates such as $ZnCl_2{\cdot}H_2O$ and $LiClO_4{\cdot}H_2O$ are able to solubilize cellulose by the interaction between hydroxyl groups and ionic species and breaking the network of hydrogen bonds (Leipner et al., 2000). In these interactions, water is an important factor. Effect of water of crystallization on the dissolution efficiency of Zinc Chloride MHS was studied by Awosusi et al. (Garrote et al., 2002), and the authors reported that $ZnCl_2 .4H_2O$ was most effective in the pre-treatment of corn cob with 43% glucan and 95% of xylan obtained after the pre-treatment (Awosusi et al., 2017). Fractionation of lignocellulosic biomass into cellulose, hemicelluloses and lignin components by pretreatment has been proposed as the first stage of refining biomass to high value—added products. Therefore, a major desirable property of a solvent during pretreatment is the ability to fractionate the components to the desired fractions. In most strategies, the cellulose rich solid residue is separated from the hemicellulose-lignin liquid fraction by filtration. Then the hemicellulose and lignin are recovered and separated via efficient methods to produce value added products.

The establishment of sustainable production of biofuels, biochemical and biomaterials in the future depends on the integration of low environmentally friendly technologies and green chemistry into biorefinery. Green chemistry is a set of principles which govern the manufacture and application of products with the aim of eliminating the use and generation of environmentally hazardous chemicals (Capolupo & Faraco, 2016). The development of processes and technologies which are both innovative and sustainable is mandatory in achieving the shift towards bio-based production of fuels, chemicals and materials. The addition of co-solvents to solvent pre-treatment could reduce the overall cost and increase the sustainability of the pre-treatment process. In the case of ionic liquid (IL) pre-treatment, various studies have reported using water, DMSO or glycerol as co-solvents (Lou et al., 2016; Varga et al., 2003). These co-solvents were either inefficient, toxic or expensive. NaOH/Urea mixture was studied in the pre-treatment of *miscanthus* at room temperature and approximately 70% glucose yield was achieved at optimized conditions. In addition, it was reported that the cellulose content in the biomass increased with increasing urea concentration (Lou et al., 2016). Urea addition also removed large amount of lignin (Lou et al., 2016). To date, there have been limited research reports on the effect of co-solvents during molten hydrate salt pre-treatment. This study, therefore, investigated the effect of co-solvent during MHS pre-treatment of corn cob. Unary, binary and ternary solvent mixtures containing $ZnCl_2.4H_2O$, $LiClO_4.3H_2O$ and Urea were investigated in this study. The efficacy of the solvent mixture was evaluated in terms of the enhancement of cellulose recovery in the solid fraction and dissolution of lignin and hemicellulose into the liquid fraction. Promising results from this study, as documented in this article, could form the basis for developing greener solvent systems for fractionation of lignocellulosic biomass and its further optimization for commercial application.

2. Materials and methods

2.1. Materials

Raw corn cobs of (*Zea mays*) were collected from domestic farming homes in Mukula Village, Limpopo South Africa. The dried samples were stored in capped plastic bottles tightly and were used shortly after collection. The cobs were cut to size using a band-saw (Mössner August, GmbH Co., Germany) and then milled using a rotor mill (Retsch® SE-200, Germany) with a 640 μm–4 mm sieve. Deionized water produced from Milli-Q water (Millipore) with resistivity of 18 MΩ·cm. $ZnCl_2.4H_2O$ (98%) was bought from Rochelle Chemical Co. Ltd. In addition, H_2SO_4 (98%) analytical-grade, $LiClO_4.3H_2O$ (99%), Urea (99%), Acetone (99%) and glucose (99%) were purchased from Sigma Aldrich Chemical Company.

2.2. Pre-treatment of corn cob

Seven molten salt hydrate pre-treatment systems classified into unary ($ZnCl_2.4H_2O$, $LiClO_4.3H_2O$ and Urea), binary ($LiClO_4.3H_2O/ZnCl_2.4H_2O$, $ZnCl_2.4H_2O$/Urea and $LiClO_4.3H_2O$/Urea) and ternary ($LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea) at a ratio of 1:1, 1:1:1 for the binary and ternary complexes respectively were investigated for the treatment of corncob. The pre-treatment was carried out at 70 °C in a shaking incubator for 60 minutes at agitation speed of 270 rpm. The pre-treatment was done in a 250 ml Erlenmeyer flask at a constant biomass to solvent ratio of 1:10 (5 g dry biomass will be added to 50 g of each solvent). The slurries that were obtained from pre-treatment with each solvent were recovered and separated into solid and liquid fractions using vacuum filtration using a Buchner Funnel of pore size 240 mm. The compositional changes in the hemicellulose, lignin and cellulose were evaluated. In order to evaluate the efficiency of different pre-treatment, with respect to cellulose, hemicellulose and lignin recovery, the multi-level structures of solid residues were characterised by a combination of methods, such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Gravimetric analysis was done with respect to cellulose, hemicellulose and lignin recovery to identify the most efficient system.

2.3. Compositional analysis of the solid and liquid fractions of the corn cob

2.3.1. Solid fraction compositional analysis

The compositional analysis of untreated and MHS-treated biomass was analysed for hemicellulose, lignin, extractive and ash content as documented by the National Renewable Energy Laboratory (NREL) following Laboratory Analytical Procedures (LAP TP-510-42,618, 42,619, 42,622). The analysis is summarised in Figure 1.

2.3.2. Quantitative evaluation of efficiency of the solvents systems

To quantitatively evaluate the effects of various pre-treatment methods on each component (cellulose, hemicellulose and lignin), recovery ratio of each component was estimated. The pre-treatment efficiencies were evaluated based on the recovery of polysaccharides (cellulose and hemicellulose) and lignin. Adequate recovery of hemicellulose and cellulose sugars is important for an ideal pre-treatment. Dry matter yield, which is the amount of dry solid retained after pre-treatment, was calculated as follows (Varga et al., 2003):

$$\text{Dry matter yield}\left(\left[\frac{w}{w}\right]\right) = \frac{\textit{Dry biomass weight after pretreatment}}{\textit{Dry weight of untreated biomass}} \tag{1}$$

Percentage recovery of each component after the pretreatment was calculated as follows (Varga et al., 2003):

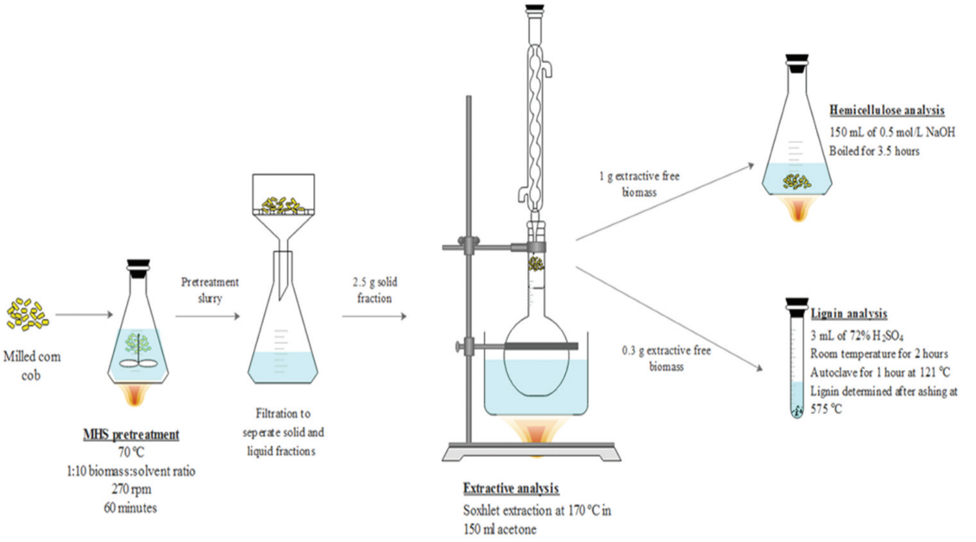


Figure 1. Method of compositional analysis for biomass (Cellulose % = 100%—Extractive%—Hemicellulose%—Lignin%—Ash).

$$\text{Recovery of component}\left(\%\left[\frac{\mathrm{w}}{\mathrm{w}}\right]\right) = \frac{\textit{Component content in pretreated biomass} \times \textit{dry matter yield}\left(\left[\frac{\mathrm{w}}{\mathrm{w}}\right]\right) \times 100\%}{\textit{Total component in untreated biomass}} \tag{2}$$

2.3.3. Total sugar determination of the liquid fraction

About 3 mL of modified 3,5-Dinitrosalicylic acid (DNS) reagent was added to 1 mL of the liquid sample in a test tube with 1 mL of distilled water. The test tubes were then placed in a boiling water bath for 15 minutes and thereafter cooled for 15 minutes. The absorbance of the sample and DNS was then measured at 575 nm. Glucose standard curves were prepared and the values of total reducing sugar for the samples were then read from these glucose curve (Miller, 1959).

2.3.4. Cellulose crystallinity determination using X-ray diffraction (XRD)

The corn cob sample crystallinity was analysed using a D2 advance diffractometer (Bruker, Germany) with a scan rate of 10 min^{-1} from 10° to 90° and Co Kα radiation (1.789 A°) generated at 30 kV and 10 mA. In order to analyse the data, a method developed by Segal et al.(1959) will be used. The crystallinity indices (CrI) were calculated from the XRD patterns using Eq 3:

$$CrI = \frac{I_{002} - I_{amp}}{I_{002}} \times 100\% \tag{3}$$

Where I_{002} is the intensity of 002 lattice diffraction (2θ = 22.6) and I_{amp} represents the intensity of amorphous section (2θ = 18).

2.3.5. Surface chemistry analysis using Fourier transform infrared (FTIR)

Lignocellulosic materials contain alcohols, aromatics, alkanes, ketones, esters and other oxygen-based functional groups which can be analysed using FTIR. Surface chemistry of the raw and pre-treated biomass samples were evaluated by a PerkinElmer Frontier Fourier transform infrared spectrometer (PerkinElmer, USA) using the attenuated total reflectance (ATR) method. Each sample was scanned twice and an average was calculated. A diamond ATR plate with angle of incidence of 45° was used as the internal reflection element. The spectra were obtained in air from a range of 400 to 4000 $\text{cm}^{-1}$and obtained at a resolution of 4 cm^{-1}. The spectra were used to investigate the surface chemistry information of the samples.

2.3.6. Morphological analysis for evaluation of biomass using scanning electron microscope (SEM)

SEM was used to check the surface morphology of the pre-treated and untreated biomass. The dried samples were fixed onto aluminium stubs with the aid of a conductive tape. The samples were then analysed by Carl Zeiss Sigma scanning electron microscope. This was followed by sputter coating with carbon and gold-palladium at five nanometre scale making the fibres conductive, to avoid degradation and charge build-up on the specimen surface. The SEM was operated under a vacuum and the images were captured.

3. Results and discussion

3.1. Biomass compositional analysis

3.1.1. Solid fraction

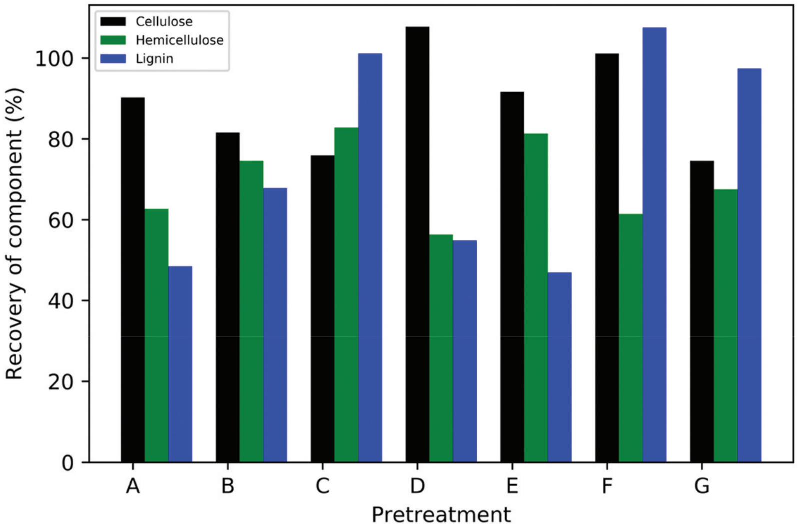
The raw material was characterised in terms of the composition of extractives, ash, cellulose, hemicelluloses and lignin. The characterisation is necessary to determine the extent of the chemical compositional changes resulting from the pre-treatment. From the compositional analysis of the biomass, the percentage recovery was calculated using Equation (2). Evaluation of the extent of recovery of biomass components in the solid fraction is necessary to evaluate the effectiveness of each pre-treatment system on the corn cob and these results are presented in Figure 2.

The recovery was calculated using Equation (1) and Equation (2). The MHS solvent systems pre-treatment was predicted to separate the lignocellulosic biomass into a liquid fraction which contains mostly solubilised hemicellulose as monomers and a solid fraction which is enriched with mostly oligomeric cellulose components. Therefore, a high recovery of cellulose and a low recovery of hemicellulose and lignin are required. Cellulose recovery in the solid fraction was over 80% for all the tested biomass samples except pre-treatment G ($LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea) and C (Urea.). The highest recovery of cellulose was approximately 109% and was recovered by pre-treatment D ($ZnCl_2.4H_2O$/ Urea). Martin et al. (2007) in comparison treated sugarcane bagasse biomass using wet oxidation at alkaline pH, 195°C and 15 min and was able to achieve 70% cellulose recovery (Martin et al., 2007). Hemicellulose recovery was within the range of 55–80% with the lowest being D ($ZnCl_2.4H_2O$/Urea), F ($LiClO_4.3H_2O$/Urea) and G ($LiClO_4.3H_2O/ZnCl_2.4H_2O$/ Urea) with 56%, 61%, 67% recovery respectively. Georgieva et al. (2008) recovered 93% of cellulose and 72% of hemicellulose from wet explosion pre-treatment of wheat straw at 35% (v/v) hydrogen peroxide and 185°C for 15 min, which is in range with the results from this study, this was achieved at much higher operating temperatures and for shorter time (Georgieva et al., 2008). The cellulose recovery in this study is higher than the cellulose recovery obtained from Georgieva et al (2008), while the hemicellulose recovery is within the same range. The increase in the cellulose recovery observed in Georgieva et al compared to this study, could be attributed to higher temperature at which their experiment was conducted.

Lignin recovery was lowest for pre-treatment A, D and E with 48%, 54%, 46% recovery, respectively. The high recovery of cellulose (109%) and low recovery of hemicellulose (58%) and lignin (54%) in the biomass samples pre-treatment in sample D ($ZnCl_2.4H_2O$/Urea) gave an indication that this is the most efficient solvent of the seven investigated for the fractionation of corn cob. These results are in good agreement with formic acid pre-treatment by Zhang et al. (2010) who under mild reaction conditions removed a relatively high ratio of hemicellulose (85%) and lignin (70%), while obtaining almost all the cellulose in the solid residue (M. Zhang et al., 2010). This type of pre-treatment produces toxic by-products such as acetic acid and furfural which are usually unavoidable in pre-treatment using acid solvents, however the furfural can also be recovered to produce value added products (Wyman, 1994).

The pre-treatment in this study using MHSs occurred at a constant temperature of 70°C and the results from the solid and liquid recovery reveal an efficient separation of the hemicellulose from cellulose as well as a low degradation of cellulose to by-products such as hydroxymethylfurfural

Figure 2. Recovery of polysaccharides cellulose, hemicellulose and lignin after pre-treatment (A): $ZnCl_2.4H_2O$. (B): $LiClO_4.3H_2O$. (C): Urea. (D): $ZnCl_2.4H_2O$/Urea. (E): $LiClO_4.3H_2O/ZnCl_2.4H_2O$ (F):$LiClO_4.3H_2O$/ Urea. (G): $LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea.



HMF and acetic acid during the pre-treatment process. These by-products are inhibitory to downstream biochemical processes if the by-products are not the target products. The inhibitory effects become even more severe as a result of recirculation of process water as the process continues (Jönsson & Martín, 2016). Furfural is an extremely important molecule in biofuel production, therefore it can be filtered from the mixture being fermented rather than avoid its generation completely. The reduction in inhibitory product formation is due to the non-derivatizing nature of the solvents. It has been observed that $ZnCl_2.4H_2O$/ Urea solvent system is an excellent solvent for biomass pre-treatment due to its fractionation abilities. This is as a result of the interaction of the chloride anion (Cl^-) and the zinc cation (Zn^{2+}) of the solvent with the hydrogen atoms (H) and oxygen atoms (O) of the cellulose hydroxyl groups, respectively and the hydrogen bond formation with cellulose (Fischer et al., 2002). According to Zhang et al., the mechanism in which urea separates cellulose is by functioning as a hydrogen bond donor and receptor between solvent molecules and preventing the re-association of cellulose molecules, therefore leading to the molecular dissolution of cellulose (L. Zhang et al., 2002).

The relatively high lignin recovery in the solid fraction shows that only a small fraction of lignin was solubilised under the low pre-treatment temperature conditions which caused minimal formation of low molecular weight lignin compounds. This shows that although delignification occurs, it is not as prominent in this type of pre-treatment.

3.1.2. Liquid fraction

Depending on the pre-treatment solvents, some of the cellulose and hemicellulose fractions will form sugar monomers in the liquid fractions. Figure 3 shows the yield of total sugars after pre-treatment.

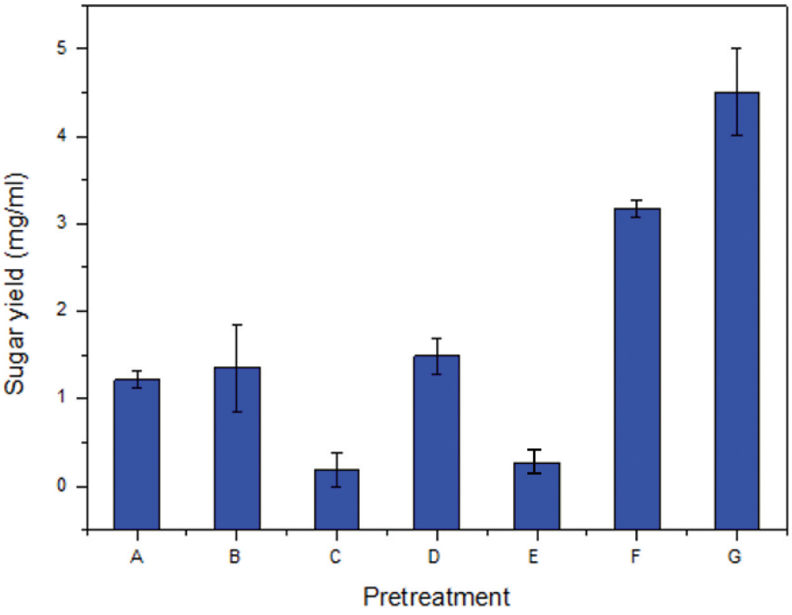
The highest total sugar quantities were found in pre-treatment G ($LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea) at levels of 4.5 mg/mL. For all the other pre-treatment methods except pre-treatment F ($LiClO_4.3H_2O$/Urea), the total sugar concentrations were significantly lower in comparison. The lower sugar formation in pre-treatment solvent A ($ZnCl_2.4H_2O$), B ($LiClO_4.3H_2O$), C (Urea) and E ($LiClO_4.3H_2O/ZnCl_2.4H_2O$) hydrolysates correlate with the results found in Figure 3 which shows these pre-treatment solvents as having the highest hemicellulose recovery in the solid fraction. The higher sugar formation observed in Pre-treatment D ($ZnCl_2.4H_2O$/Urea), F ($LiClO_4.3H_2O$/Urea) and G ($LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea), is mainly due to the fact that lower amounts of oligomeric hemicellulose were retained in the solid fractions which shows that solubilisation of hemicellulose to monomers was more severe in the liquid fraction of these pre-treatment solvents. Hemicellulose is easily soluble. It is able to dissolve in water at low temperatures compared to lignin and cellulose fractions (Nabarlatz et al., 2004).

3.2. Crystallinity and surface chemistry determination

3.2.1. XRD spectra

XRD analysis is used for checking the crystallinity of the material and considers disordered cellulose, hemicellulose and lignin. Cellulose accounts for the highest proportion of the crystalline structure therefore, the XRD spectra is usually an indication of the cellulose crystallinity. The XRD spectra and Crystallinity index (CrI) values for the effect of MHS pre-treatment on corn cob are shown in Figure 4 and Table 1, respectively. In this study, all samples presented the same diffraction patterns. Three typical diffraction peaks which correspond to (101), (002), (040) peaks were observed at $2\theta = 15°$, 22.5° and 33°~ 35 °, respectively. The highest peak observed at 002 was observed for spectra D ($ZnCl_2.4H_2O$/ Urea) which also happens to have one of the highest cellulose recoveries in Figure 2 while Urea which has one of the lowest cellulose recoveries has a low peak intensity shown as spectra C in Figure 4. The peaks at 040 lattice plane also correspond to crystalline regions, the lattice planes which were not observed could be due to interference from other biomass components (Sathitsuksanoh et al., 2011).

Figure 3. Yield of total sugars in liquid fraction after MHS pre-treatment. Average values and standard deviations reported for duplicates. (A): $ZnCl_2.4H_2O$. (B): $LiClO_4.3H_2O$. (C): Urea. (D): $ZnCl_2.4H_2O$/Urea. (E): $LiClO_4.3H_2O$/ $ZnCl_2.4H_2O$ (F):$LiClO_4.3H_2O$/Urea. (G): $LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea.



3.2.2. FTIR spectra

The FTIR technique was used to check the chemical nature of the fractions and residue after the pre-treatment. Figure 5 depicts the FTIR spectra of the pre-treated biomass using different MHS. The main chemical bond vibrations of lignocellulosic materials are present between 800 and 1800 cm^{-1}.

The band observed at 2900 cm^{-1} in Figure 5 could be attributed to C-H stretching. The results show a reduction and broadening out in these peaks for all the pre-treatment results except pre-treatment D, E and G. which show increase in these peaks. Urea appears to disrupt the methyl groups as seen in C and F treatments this is due to its ability to prevent the re-association of cellulose molecules, therefore leading to the molecular dissolution of cellulose. The broadening and reduction of the peaks indicate the rupture of the methyl/methylene groups of cellulose. This characteristic increase in band intensity at 2900 cm^{-1} has been reported by Ciolacu et al. (Ciolacu et al., 2011) and Kumar et al. (Kumar et al., 2009) and the authors concluded that corn stover and poplar solids became more amorphous upon pretreatment. Furthermore, noticeable differences were observed at 3400 cm^{-1} for most of the pre-treated samples attributable to absorption of moisture from air because the FTIR analysis was not carried out in a moisture-controlled environment.

In Figure 5, the band at 1670 cm^{-1} could be attributed to an unconjugated C = O stretch of ester, acetyl or carboxylic acid groups in hemicellulose components and linkages between lignin and carbohydrates within this region is expected. FTIR intensity at this region increased after pre-treatment F (i.e. for $LiClO_4.3H_2O$/Urea) and G (i.e. for $LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea), but the peaks diminished in samples A, B, C after the pretreatment. The peaks at 1670 cm^{-1} show slight changes in the hemicellulose content after $ZnCl_2.4H_2O$/ Urea pre-treatment, and low hemicellulose removal after pre-treatment using E ($LiClO_4.3H_2O/ZnCl_2.4H_2O$) and G ($LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea). The observation from these spectra further corroborates the results presented in Figure 2 where the highest percentage loss of hemicellulose was recorded in samples treated with $LiClO_4.3H_2O$/Urea and $LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea. This also confirms breakage of the carbohydrate and lignin linkages. For lignin, major functional group is aromatic compound (phenolic hydroxyl group) with

Figure 4. XRD spectra of (A): $ZnCl_2.4H_2O$. (B): $LiClO_4.3H_2O$. (C): Urea. (D): $ZnCl_2.4H_2O$/Urea. (E): $LiClO_4.3H_2O/ZnCl_2.4H_2O$ (F):$LiClO_4.3H_2O$/Urea. (G): $LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea.

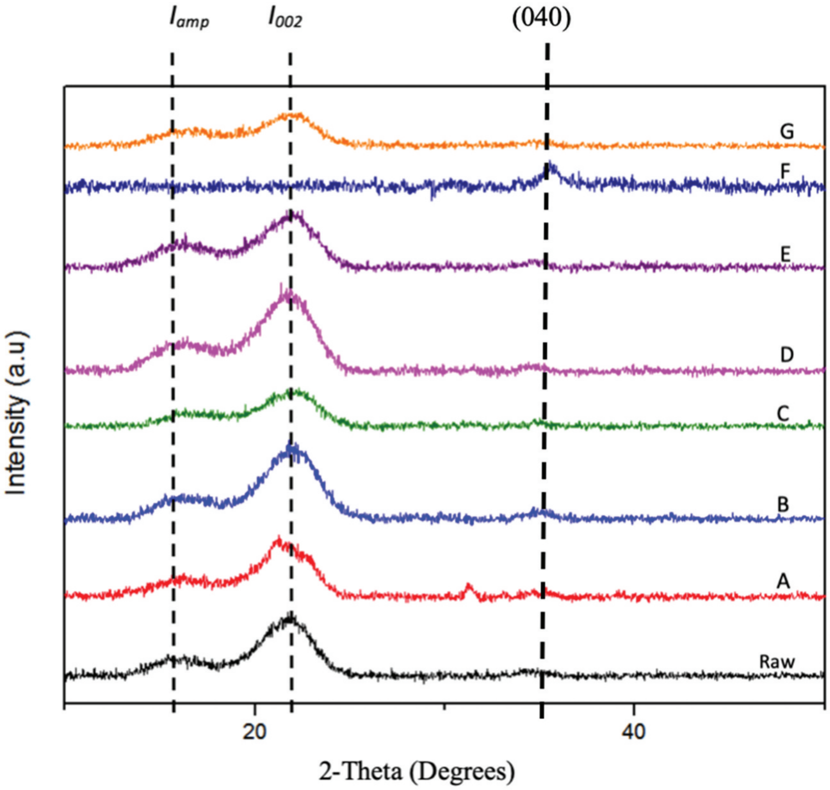


Table 1. Band assignments for the FTIR spectra

2900	C–H stretching (related to rupture of methyl/ methylene group of cellulose)
1050	C–O stretching vibration (cellulose and hemicellulose)
1300	Aliphatic C-H stretching in methyl and phenol OH (Lignin)
1670	unconjugated C = O stretch of ester
900	Removal of amorphous cellulose

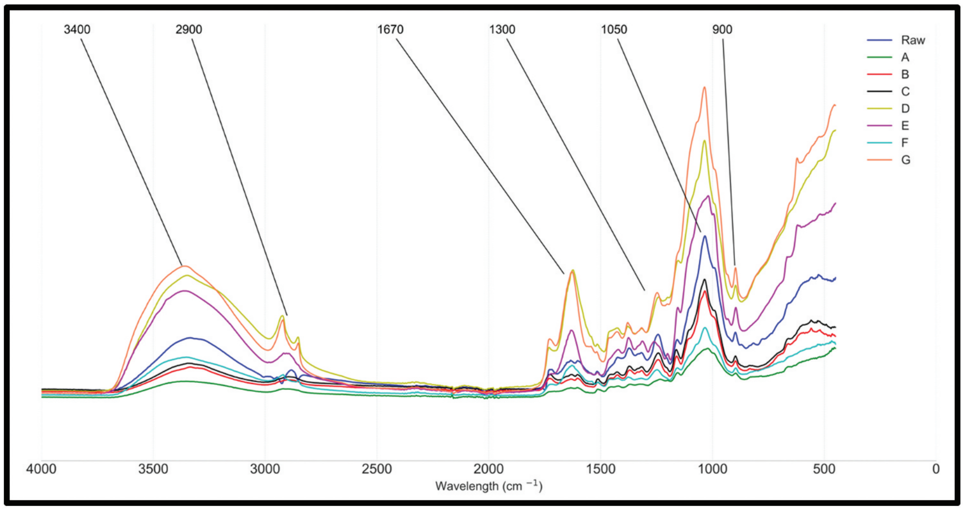
a benzene ring. Structural change in lignin and loss of aromatic compounds were indicated by the change in intensity at 1300 cm^{-1} band. Samples pre-treated with ($ZnCl_2.4H_2O$) [A], with ($LiClO_4.3H_2O$) [B], with (Urea) [C], with ($LiClO_4.3H_2O/ZnCl_2.4H_2O$) [E], and with ($LiClO_4.3H_2O$/Urea) [F] displayed a decrease in peak intensity of 1300 cm^{-1} band.

3.2.3. Crystallinity index (CrI)

Research reports have surfaced in literature in which CrI has been obtained from XRD patterns using Equation (2) (Ling et al., 2017; Yoshida et al., 2008). The same approach was used in this study to obtain the CrI reported in Table 2.

From Table 2, it could be observed that CrI of corncob residues changed approximately proportionally to the amount of cellulose recovered. Crystallinity is strongly influenced by the biomass composition. It was initially hypothesized that the crystallinity of the biomass would decrease due to the pre-treatment, however since XRD measures all components and not just cellulose, there

Figure 5. FTIR Spectra of (A): $ZnCl_2.4H_2O$. (B): $LiClO_4.3H_2O$. (C): Urea (D): $ZnCl_2.4H_2O$/Urea (E): $LiClO_4.3H_2O/ZnCl_2.4H_2O$ (F):$LiClO_4.3H_2O$/Urea. (G): $LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea.



were interferences from the other amorphous components (hemicellulose, lignin). Therefore, the concept of "apparent crystallinity" is preferred as the amorphous regions are not only from cellulose but from other parts of lignocellulose as well. The raw sample presented the lowest apparent crystallinity (CrI), because it has a higher content of hemicellulose and lignin, which are amorphous (Xu et al., 2007). The results thus show an increase in crystallinity with pre-treatment due to the removal of the lignin and amorphous hemicellulose fractions. The samples with lower content of lignin and hemicellulose in the compositional analysis were the samples that presented higher crystallinity, as can be noticed for the pre-treatment experiments (C, D and E). Due to the lack of regular crystalline structure in hemicellulose and lignin, the interpretation of the crystallinity of cellulose through XRD analysis is possibly hindered by the hemicellulosic and lignin fractions. The crystallinity index obtained from XRD also shows low crystallinity for $LiClO_4.3H_2O$/Urea. There are three crystalline peaks, but only the highest peak (002) was used in the calculation. This results in an exclusion of the other crystallinity peak at (040) which may have contributed to the overall crystallinity of this sample, thereby resulting in disparity in the results obtained from FTIR spectra and XRD patterns. However, the CrI obtained from the FTIR spectra and XRD pattern qualitatively suggests a reduction in crystallinity of cellulose in corn cob during the pre-treatment using MHS solvent system. As put forward by Li et al. (Li et al., 2010), it could be speculated that the decrease of CrI was because of the rapid precipitation of water that prevented the dissolved lignocellulose from rearranging into the original crystalline structure, thereby resulting in biomass with more amorphous structure.

Table 2. Crystallinity index of raw and pre-treated biomass

Pretreatment	CrI
Raw	48.044
$ZnCl_2.4H_2O$	62.081
$LiClO_4.3H_2O$	71.260
Urea	67.747
$ZnCl_2.4H_2O$/Urea	72.764
$LiClO_4.3H_2O/ZnCl_2.4H_2O$	54.134
$LiClO_4.3H_2O$/Urea	15,095
$LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea	63.626

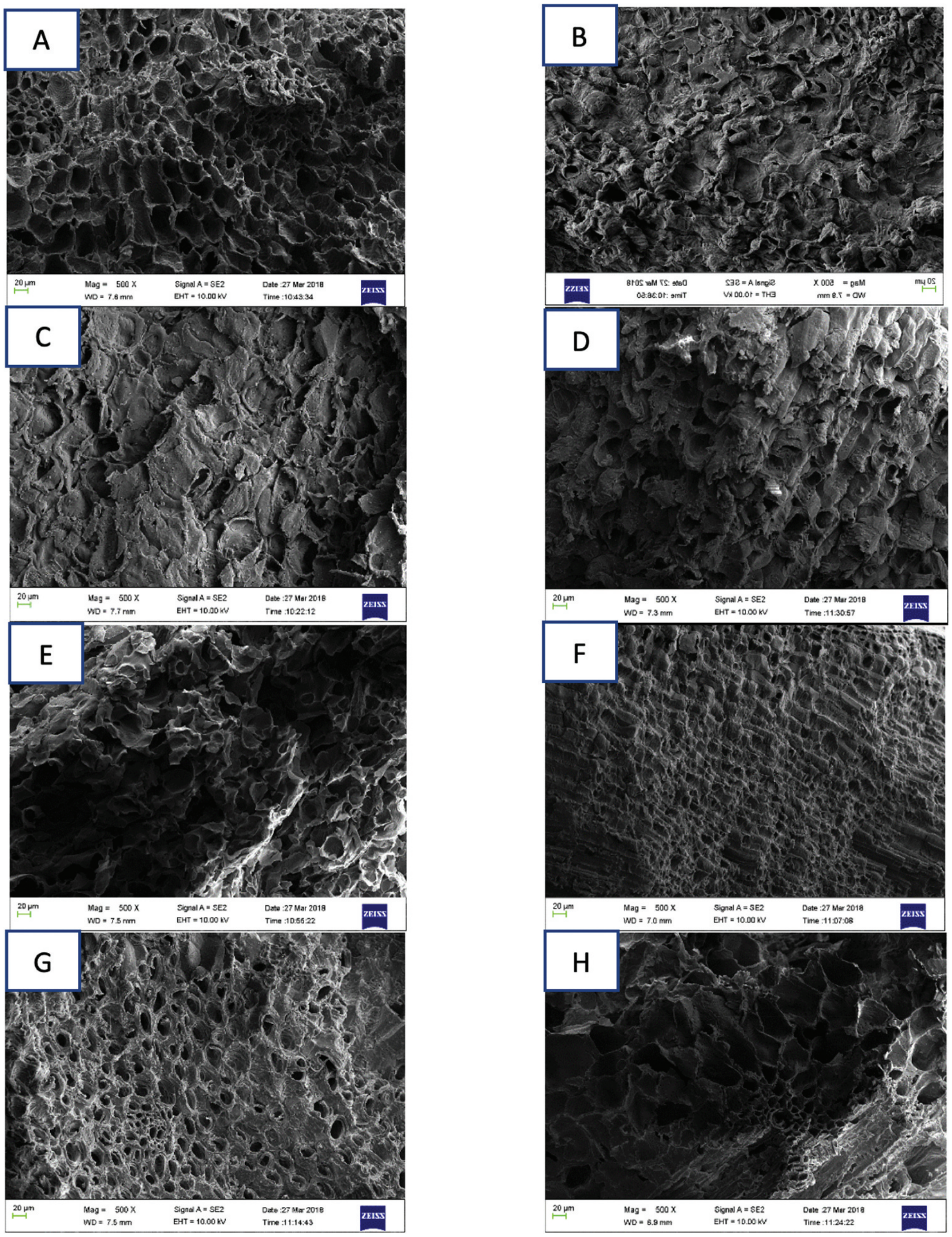


Figure 6. Scanning Electron micrograph of untreated and pre-treated corn cob (at 500X Magnification). untreated(A); $ZnCl_2.4H_2O$ treated (B); $LiClO_4.3H_2O$ treated(C); Urea treated (D); $ZnCl_2.4H_2O$/Urea treated(E); $LiClO_4.3H_2O/ZnCl_2.4H_2O$ treated (F); $LiClO_4.3H_2O$/Urea treated (G); $LiClO_4.3H_2O/ZnCl_2.4H_2O$/Urea treated(H). (I) Magnified C at 2000 X magnification (Red circles indicate globular structures).

3.3. Surface morphology of the biomass

To understand the significant changes in corn cob after pre-treatment, the morphology of the untreated and pre-treated corn cob samples was investigated by SEM, as presented in Figure 6.

SEM results for the raw samples shows an intact lamellar structure where hemicellulose and lignin wraps around the cellulose in a hetero-matrix. In addition, the structure of the raw sample is visibly ordered; however, the molten hydrated salt treated (Figure 6B to Figure 6H) corncob samples showed disrupted lamellar structures due to the removal of hemicellulose and lignin. The surface morphology of the corn cob was changed in Figure 6B to Figure 6H, in addition, there was damage in the intact cell structure as well as a more exposed internal cell structure. The most obvious change from the original fibre can be noted in the Figure 6B. These samples were not homogenous therefore; quantification based on surface deconstruction cannot be done. The

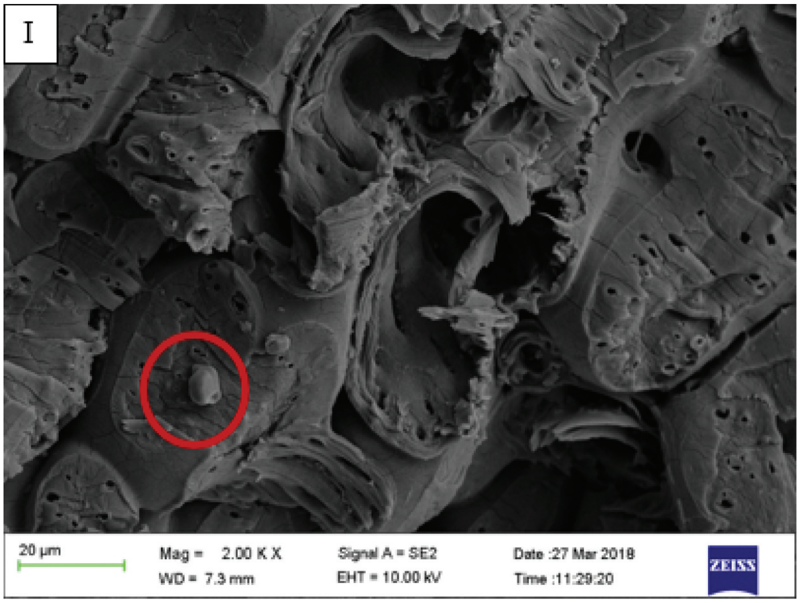


Figure 6. (countined)

change in surface morphology is in agreement with the finding of (Selig et al., 2009)) which showed that there was similar change on the biomass surface structure occurs when corn stover is pre-treated and delignified using alkaline peroxidase (Selig et al., 2009).

Further proof of modification, which occurred after pre-treatment, and another interesting feature of some of these samples is the presence of globular structures (see sample C which in Figure 6I). These globular structures are associated with lignin condensation that was observed on the surface of the corn cob after pre-treatment. The formation of these lignin agglomerates on the surface have been observed in many other types of lignocellulosic biomass when they undergo organosolv steam-explosion and diluted acid pre-treatment (Donohoe et al., 2008). This droplet phenomenon has been related to the severity of pre-treatment conditions in previous studies. The droplets were observed in the corn cob samples pre-treated with (B) $ZnCl_2.4H_2O$ (C) $LiClO_4.3H_2O$ (D) Urea. The more severe the pre-treatment and its conditions, the more droplets formed on the surface. The lignin molecules liquefy and then coalesce. Once the lignin phase transition is reached, droplets are formed within the cell wall matrix. Due to the hydrostatic pressures within the layers of the cell wall, some of the lignin fractions are forced to the outer surface of the biomass samples. The small droplets bind to the pre-treatment mass and are then re-deposited on the biomass surface when the samples are cooled (Ghaffar & Fan, 2013).

Biomass morphology is a major factor that contributes to effective hydrolysis. The higher the surface area of the biomass; the better the accessibility of the solvent into the plant cell wall. Consequently, this translates into an enhanced efficiency of the fractionation of main fibres into fibrils and strands. Results of the SEM analysis corroborated the results from FTIR and XRD analyses in this regard, indicating reduction in crystallinity of the biomass during the MHS pre-treatment

4. Conclusions

Over the last decade, molten hydrate salts have been used in dissolution of pure cellulose, however a few studies have been reported to check their ability in deconstructing lignocellulosic biomass during pre-treatment. As far as cold be ascertained, this article reports, for this first time, the application of MHSs and their mixtures as solvent for pre-treatment and fractionation of corn cob. From the results, it can be concluded that all the seven MHS solvent systems investigated in this study were effective in altering the biomass crystallinity. Images from the SEM revealed a loose and disordered structure of biomass after post pre-treatment. FTIR analysis indicated that MHS-treated biomass exhibited a decrease in the overall crystalline. It can be concluded that the seven MHS solvents proposed in this study are promising green solvents to deconstruct biomass (i.e. altering surface chemistry, textural property, morphology, etc.) and reduce cellulose crystallinity. The decrease in crystallinity and increase in surface area after the pre-treatment will enhance the digestibility of the biomass during enzymatic hydrolysis, and in turn increases sugar yield for bioconversion to value-added products (e.g., biochemical and biofuels). Among the pre-treatment solvents studied, $ZnCl_2.4H_2O$/ Urea solvent system displayed the highest effectiveness in terms of cellulose recovery, hemicellulose recovery in the liquid fraction, and lignin removal. It is expected that this pre-treatment solvent can improve the utilisation of biomass significantly due to the significant recovery of cellulose and lignin in the solid fraction and hemicellulose in the liquid fraction. Interestingly, this promising results were obtained at relatively mild conditions (e.g., temperature of 70°C) using an environmentally friendly solvent ($ZnCl_2.4H_2O$/ Urea), promoting therefore sustainability in energy and environment

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References

Alvira, P., Tomás-Pejó, E., Ballesteros, M., & Negro, M. J. (2010, July). Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology*, *101*(13), 4851–4861. https://doi.org/10.1016/j.biortech.2009.11.093

Arantes, V., & Saddler, J. N. (2011, February). Cellulose accessibility limits the effectiveness of minimum cellulase loading on the efficient hydrolysis of pretreated lignocellulosic substrates. *Biotechnology for Biofuels*, 4 (1), 3. https://doi.org/10.1186/1754-6834-4-3

Awosusi, A. A., Ayeni, A., Adeleke, R., & Daramola, M. O. (2017, March). Effect of water of crystallization on the dissolution efficiency of molten zinc chloride hydrate salts during the pre-treatment of corncob biomass. *Journal of Chemical Technology & Biotechnology*, *92*(9), 2468–2476. https://doi.org/10.1002/jctb.5266

Bhatia, L., Johri, S., & Ahmad, R. (2012, December). An economic and ecological perspective of ethanol production from renewable agro waste: A review. *AMB Express*, *2*(1), 65. https://doi.org/10.1186/2191-0855-2-65

Capolupo, L., & Faraco, V. (2016). Green methods of lignocellulose pretreatment for biorefinery development. *Applied Microbiology and Biotechnology*, *100*(22), 9451–9467. https://doi.org/10.1007/s00253-016-7884-y

Chang, M. C. Y. (2007). Harnessing energy from plant biomass. *Current Opinion in Chemical Biology*, *11*(6), 677–684. https://doi.org/10.1016/j.cbpa.2007.08.039

Ciolacu, D., Ciolacu, F., & Popa, V. (2011, January). Amorphous cellulose - Structure and characterization. *Cellulose Chemistry and Technology*, *45*(1-2), 13–21.

de Almeida, R. M., Li, J., Nederlof, C., O'Connor, P., Makkee, M., & Moulijn, J. A. (2010). Cellulose conversion to isosorbide in molten salt hydrate media. *ChemSusChem*, *3*(3), 325–328. https://doi.org/10.1002/cssc.200900260

Demirbas, A. (2009, September). Biofuels securing the planet's future energy needs. *Energy Conversion and Management*, *50*(9), 2239–2249. https://doi.org/10.1016/j.enconman.2009.05.010

Donohoe, B. S., Decker, S. R., Tucker, M. P., Himmel, M. E., & Vinzant, T. B. (2008, December). Visualizing lignin coalescence and migration through maize cell walls following thermochemical pretreatment. *Biotechnology and Bioengineering*, *101*(5), 913–925. https://doi.org/10.1002/bit.21959

Fischer, S., Thümmler, K., Pfeiffer, K., Liebert, T., & Heinze, T. (2002, September). Evaluation of molten inorganic salt hydrates as reaction medium for the derivatization of cellulose. *Cellulose*, *9*(3/4), 293–300. https://doi.org/10.1023/A:1021121909508

Galbe, M., & Zacchi, G. (2007). Pretreatment of lignocellulosic materials for efficient bioethanol production. *Advances in Biochemical Engineering/biotechnology*, *108*, 41–65. https://doi.org/10.1007/10_2007_070

Garrote, G., Domínguez, H., & Parajó, J. C. (2002). Autohydrolysis of corncob: Study of non-isothermal operation for xylooligosaccharide production. *Journal of Food Engineering*, *52*(3), 211–218. https://doi.org/10.1016/S0260-8774(01)00108-X

Georgieva, T. I., Mikkelsen, M., & Ahring, B. (2008, April). Ethanol production from wet-exploded wheat straw hydrolysate by thermophilic anaerobic bacterium thermoanaerobacter BG1L1 in a continuous immobilized reactor. *Applied Biochemistry and*

Biotechnology, *145*(1–3), 99–110. https://doi.org/10.1007/s12010-007-8014-1

Ghaffar, S. H., & Fan, M. (2013, Oct). Structural analysis for lignin characteristics in biomass straw. *Biomass and Bioenergy*, *57*, 264–279. https://doi.org/10.1016/j.biombioe.2013.07.015

Jacobsen, S. E., & Wyman, C. E. (2000, March). Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes. *Applied Biochemistry and Biotechnology*, *84*(1), 81–96. https://doi.org/10.1385/ABAB:84-86:1-9:81

Jönsson, L. J., & Martín, C. (2016, January). Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects. *Bioresource Technology*, *199*, 103–112. https://doi.org/10.1016/j.biortech.2015.10.009

Kumar, R., Mago, G., Balan, V., & Wyman, C. E. (2009). Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies. *Bioresource Technology*, *100* (17), 3948–3962. https://doi.org/10.1016/j.biortech.2009.01.075

Lee, J. (1997, July). Biological conversion of lignocellulosic biomass to ethanol. *Journal of Biotechnology*, *56*(1), 1–24. https://doi.org/10.1016/S0168-1656(97)00073-4

Leipner, H., Fischer, S., Brendler, E., & Voigt, W. (2000, Oct). Structural changes of cellulose dissolved in molten salt hydrates. *Macromolecular Chemistry and Physics*, *201*(15), 2041–2049. https://doi.org/10.1002/1521–3935(20001001)201:15<2041::AID-MACP2041>3.0.CO;2-E

Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H. V., Auer, M., Vogel, K. P., Simmons, B. A., & Singh, S. (2010, July). Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. *Bioresource Technology*, *101*(13), 4900–4906. https://doi.org/10.1016/j.biortech.2009.10.066

Ling, Z., Chen, S., Zhang, X., Takabe, K., & Xu, F. (2017, August). Unraveling variations of crystalline cellulose induced by ionic liquid and their effects on enzymatic hydrolysis. *Scientific Reports*, *7*(1), 1–11. https://doi.org/10.1038/s41598-017-09885-9

Liu, Z.-H., Qin, L., Pang, F., Jin, M.-J., Li, B.-Z., Kang, Y., Dale, B. E., & Yuan, Y.-J. (2013, January). Effects of biomass particle size on steam explosion pretreatment performance for improving the enzyme digestibility of corn stover. *Industrial Crops and Products*, *44*, 176–184. https://doi.org/10.1016/j.indcrop.2012.11.009

Lou, H., Hu, Q., Qiu, X., Li, X., & Lin, X. (2016, March). Pretreatment of miscanthus by NaOH/Urea solution at room temperature for enhancing enzymatic hydrolysis. *BioEnergy Research*, *9*(1), 335–343. https://doi.org/10.1007/s12155-015-9695-x

Martin, C., Klinke, H. B., & Thomsen, A. B. (2007). Wet oxidation as a pretreatment method for enhancing the enzymatic convertibility of sugarcane bagasse. *Enzyme and Microbial Technology*, *40*(3), 426–432. https://doi.org/10.1016/j.enzmictec.2006.07.015

Miller, G. L. (1959, March). Use of dinitrosalicylic acid reagent for determination of reducing sugar. *Analytical Chemistry*, *31*(3), 426–428. https://doi.org/10.1021/ac60147a030

Mohlala, L. M., Bodunrin, M. O., Awosusi, A. A., Daramola, M. O., Cele, N. P., & Olubambi, P. A. (2016, September). Beneficiation of corncob and sugarcane bagasse for energy generation and materials development in Nigeria and South Africa: A short overview. *Alexandria Engineering Journal*, *55*(3), 3025–3036. https://doi.org/10.1016/j.aej.2016.05.014

Nabarlatz, D., Farriol, X., & Montané, D. (2004, July). Kinetic modeling of the autohydrolysis of lignocellulosic biomass for the production of hemicellulose-derived oligosaccharides. *Industrial & Engineering Chemistry Research*, *43*(15), 4124–4131. https://doi.org/10.1021/ie034238i

Sathitsuksanoh, N., Zhu, Z., Wi, S., & Zhang, Y.-H. P. (2011, March). Cellulose solvent-based biomass pretreatment breaks highly ordered hydrogen bonds in cellulose fibers of switchgrass. *Biotechnology and Bioengineering*, *108* (3), 521–529. https://doi.org/10.1002/bit.22964

Segal, L., Creely, J. J., Martin, A. E., & Conrad, C. M. (1959, Oct). An empirical method for estimating the degree of crystallinity of native cellulose using the x-ray diffractometer. *Textile Research Journal*, *29*(10), 786–794. https://doi.org/10.1177/004051755902901003

Selig, M. J., Vinzant, T. B., Himmel, M. E., & Decker, S. (2009, March). The effect of lignin removal by alkaline peroxide pretreatment on the susceptibility of corn stover to purified cellulolytic and xylanolytic enzymes. *Applied Biochemistry and Biotechnology*, *155*(1–3), 397–406. https://doi.org/10.1007/s12010-008-8511-x

Sen, S., Martin, J. D., & Argyropoulos, D. S. (2013). Review of cellulose non-derivatizing solvent interactions with emphasis on activity in inorganic molten salt hydrates. *ACS Sustainable Chemistry & Engineering*, *1* (8), 858–870. https://doi.org/10.1021/sc400085a

Varga, E., Schmidt, A. S., Réczey, K., & Thomsen, A. B. (2003, January). Pretreatment of corn stover using wet oxidation to enhance enzymatic digestibility. *Applied Biochemistry and Biotechnology*, *104*(1), 37–50. https://doi.org/10.1385/ABAB:104:1:37

Wan, C., & Li, Y. (2011, August). Effectiveness of microbial pretreatment by Ceriporiopsis subvermispora on different biomass feedstocks. *Bioresource Technology*, *102* (16), 7507–7512. https://doi.org/10.1016/j.biortech.2011.05.026

Wilson, J. L. (1988). Biochemistry; Third edition (Stryer, Lubert). *Journal of Chemical Education*, *65*(12), A337. https://doi.org/10.1021/ed065pA337

Wyman, C. E. (1994, January). Ethanol from lignocellulosic biomass: Technology, economics, and opportunities. *Bioresource Technology*, *50*(1), 3–15. https://doi.org/10.1016/0960-8524(94)90214-3

Xu, Z., Wang, Q., Jiang, Z., Yang, X., & Ji, Y. (2007, February). Enzymatic hydrolysis of pretreated soybean straw. *Biomass and Bioenergy*, *31*(2–3), 162–167. https://doi.org/10.1016/j.biombioe.2006.06.015

Yoshida, M., Liu, Y., Uchida, S., Kawarada, K., Ukagami, Y., Ichinose, H., Kaneko, S., & Fukuda, K. (2008, March). Effects of cellulose crystallinity, hemicellulose, and lignin on the enzymatic hydrolysis of miscanthus sinensis to monosaccharides. *Bioscience, Biotechnology, and Biochemistry*, *72*(3), 805–810. https://doi.org/10.1271/bbb.70689

Zhang, L., Ruan, D., & Gao, S. (2002). Dissolution and regeneration of cellulose in NaOH/thiourea aqueous solution. *Journal of Polymer Science Part B: Polymer Physics*, *40* (14), 1521–1529. https://doi.org/10.1002/polb.10215

Zhang, M., Qi, W., Liu, R., Su, R., Wu, S., & He, Z. (2010, April). Fractionating lignocellulose by formic acid: Characterization of major components. *Biomass and Bioenergy*, *34*(4), 525–532. https://doi.org/10.1016/j.biombioe.2009.12.018

Zhu, S. (2008, June). Use of ionic liquids for the efficient utilization of lignocellulosic materials. *Journal of Chemical Technology & Biotechnology*, *83*(6), 777–779. https://doi.org/10.1002/jctb.1884

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