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The pretreatment of miscanthus using ionic liquids; a way for biofuel production

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1 Introduction

Biomass, as fuel source, is renewable, environmentally friendly and abundant in the natural world. Lignocellulosic biomass is a potential source of renewable energy for transportation fuels through the conversion of fermentable sugars derived from cellulose and hemicelluloses to biofuels. A lignocellulosic material contains up to 35-50% cellulose which is the most abundant biopolymer on the earth and, thus, it is a valuable source of raw materials [1]. The comprehensive utilization of cellulose resources has drawn much attention from the governments and researchers, and there is an increasing demand to develop new technologies to obtain and dissolve cellulose to overcome the drawbacks of traditional pulping and processing methods. Nevertheless, the highly crystalline nature of cellulose, and the presence of lignin surrounding the cellulose microfibrils, contribute to the slow enzymatic hydrolysis of cellulosic biomass and necessitate pretreatment to increase hydrolysis rates. While mechanical milling, weak and strong acid treatment, ammonia fiber expansion, and other pretreatment methods increase hydrolysis rates [2], by far the most effective pretreatment devised so far is the dissolution and subsequent precipitation of cellulose in ionic liquids [3]. Ionic liquids are organic salts, liquids around or below 100°C. These solvents have unique physicochemical properties such as high thermal stability, wide electrochemical window and negligible vapor pressure and so they are considered to be green solvents. They have been suggested to replace volatile organic compounds in industrial separation processes, as well as applications in chemical synthesis, electrochemistry, polymer chemistry and nanotechnology [4].

In the present study, different imidazolium based ionic liquids were used to dissolve miscanthus and extract cellulose with high purity to be easily converted into biofuels. The influence of different parameters such as miscanthus size, miscanthus weight%, temperature, time, precipitant type, water content and the structure of the IL were evaluated.

2 Methods

2.1 Miscanthus dissolution

Solid-liquid equilibrium phase diagrams of the studied systems were obtained at atmospheric pressure and at temperature ranges starting from 363 to 403 K. The solubility experiments of miscanthus in ILs have been performed in a jacketed glass. The experimental set up consists of a cell with an internal volume of about 200 cm^3. The temperature of the cell was maintained constant using a thermostatic bath (polystat 5D +37, Fisher scientific.) with a precision of ±0.1 K. The internal temperature of the cells was also measured with a calibrated platinum probes Pt100 with an accuracy of ± 0.1 K. The mixtures, with compositions inside the immiscible region of the system, are weighed using a METTLER analytical balance with a precision of ± 0.0001 g.

For the solubility of miscanthus in ILs, dimethyl sulfoxide (DMSO) was added to ILs (20: 80 wt %) to form a clear solution with stirring. In a typical dissolution, desired amounts of IL/DMSO and miscanthus were loaded into a prepared cell. The cell was sealed and connected to the temperature controller. The mixture was vigorously stirred for 6 hours and was then heated very slowly (about $1K.h^{-1}$) until complete dissolution of the miscanthus in the ionic liquid solution. A dark, amber-colored, viscous miscanthus suspension was obtained. The solubility measurements were confirmed by the visual observation of the solution under microscope.

2.2 Cellulose extraction and residue separation

For the extraction of cellulose, A 5 wt % miscanthus was dissolved in IL/DMSO solution, after dissolution, the suspension was filtered through a glass filter to remove the undissolved residue. Water was added to the resulting clear liquors, and a cellulose-rich extract was reconstituted from the liquor. This extract and the undissolved residue were respectively washed with water/DMSO and water until the IL was completely

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removed and then dried overnight in an oven at 373 K prior to use. The percentage of miscanthus dissolved and regenerated as well as the cellulose extraction rate in the material was calculated. The extracted cellulose was characterized using different techniques such as FTIR, NMR XRD, MEB and SEM.

3 Results and disscusion

3.1 Miscanthus dissolution

ILs are capable of dissolving complex macromolecules and polymeric materials with high efficiency by breaking the extensive hydrogen bonding network of polysaccharides and promoting their dissolution [5]. This mechanism has been observed to proceed as follows: The ion pairs in BMIMCl dissociate into individual Cl^- and $Bmim^+$ ions. Free Cl^- ions associate with cellulose hydroxyl protons, and free $Bmim^+$ cations associate with cellulose hydroxyl oxygen groups. These disrupt hydrogen bonding in cellulose and cause its dissolution.

Figure 1 presents the solubility of miscanthus in four ionic liquids. It was found that the solubility of miscanthus is higher in DMIMMPh than other ionic liquids and this maybe related to its high hydrogen bond basicity and polarity.

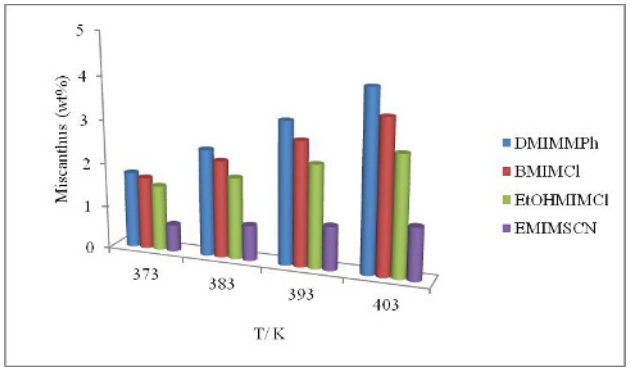

Figure 1. The solubility of miscanthus in ionic liquids.

3.2 Evaluation of process variables

3.2.1 Effect of type of ionic liquid

Table 1 shows the dissolution rate, regeneration rate and cellulose extracted percentages for miscanthus with four ionic liquids.

Table 1. Effect of type of ionic liquid on the dissolution and extraction processes.

IL/ DMSO	Diss. Rate %	Reg. Rate %	Cell. Extr. %
DMIMMPh	58	20	70
BMIMCl	55	18	68
EtOHMIMCl	50	16	67
EMIMSCN	21	7	54

It is obvious that the efficiency of ionic liquids increases in the following order: EMIMSCN < EtOHMIMCl < BMIMCl < DMIMMPh. This can be explained due to the hydrogen bond basicity and polarity of ionic liquids.

3.2.2 Effect of temperature

Brandt et al. [6] concluded that swelling and dissolution in ILs is temperature-dependent, and that better dissolution and regeneration rates are obtained at temperatures beyond 373 K. Figure 2 shows that the dissolution rates increase when the temperature increases from 363 to 403 K. Nevertheless, the regeneration rate increases from 363 to 383 K but at temperature higher than 383 K it decreases due to the degradation occurrence [3].

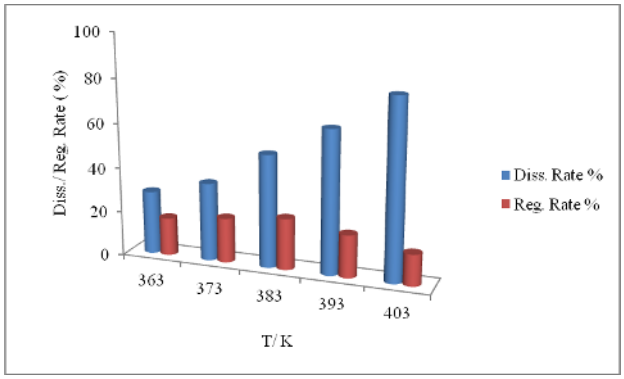

Figure 2. The effect of temperature on the dissolution and regeneration rate % of miscanthus in DMIMMPh.

3.2.3 Effect of time

The kinetics of the miscanthus dissolved in DMIMMPh was studied as a function of dissolution time. Figure 3 shows that the dissolution and regeneration rates increased with increasing reaction time from 3 to 24 hours. The dissolution rate increased by 29%, while the regeneration rate only increased by 12.7% indicating that the polymer degradation occurs with time [3].

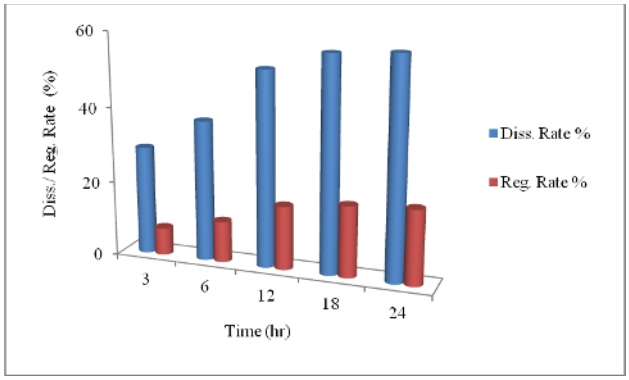

Figure 3. The effect of time (hr) on the dissolution and regeneration rate % of miscanthus in DMIMMPh.

3.3 Analysis of the regenerated cellulose-rich extract and undissolved residues

3.3.1 XRD analysis

The X-ray spectra presented in figure 4 prove that amorphous cellulose is obtained after the regeneration of miscanthus. The untreated miscanthus sample shows two prominent peaks near 2θ of 15° and 22°, indicating the characteristic diffraction pattern of cellulose I. The regenerated cellulose-rich extracts display a slightly broad amorphous diffraction peak near 2θ of 21°, which is the characteristic diffraction pattern of cellulose II. Compared with the diffraction pattern of the original miscanthus, the intensities of the diffraction peaks in the cellulose-rich extracts are smaller, revealing that ILs destroy the inter and intramolecular hydrogen bonds among lignocelluloses, leading to lower crystallinity in the cellulose-rich extract [7].

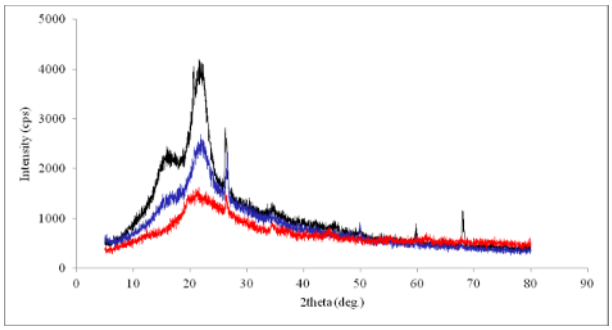

Figure 4. XRD of ■) miscanthus, ■) miscanthus residue and ■) cellulose-rich extract.

3.3.2 Morphological investigation

Figure 5 shows MEB images of original miscanthus, the cellulose-rich extract, and miscanthus residue are analyzed. Compared with the original miscanthus, which has a fascicular texture, the miscanthus residue shows a highly porous structure; this indicates that ILs effectively disrupts the intricate network of non-covalent interactions within lignocelluloses, leading to the dissolution of miscanthus. The morphology of the regenerated cellulose- rich extracts obtained from ILs is homogeneous and dense, and presents uniform macrostructures.

4 Conclusion

This study presents an environmentally friendly method of extracting cellulose from miscanthus, and also provides a new approach for utilizing biomass resources. However, the cellulose extraction method presented shows some limitations. Thus, further studies could be performed. The results presented make the proposed technology highly promising for future applications.

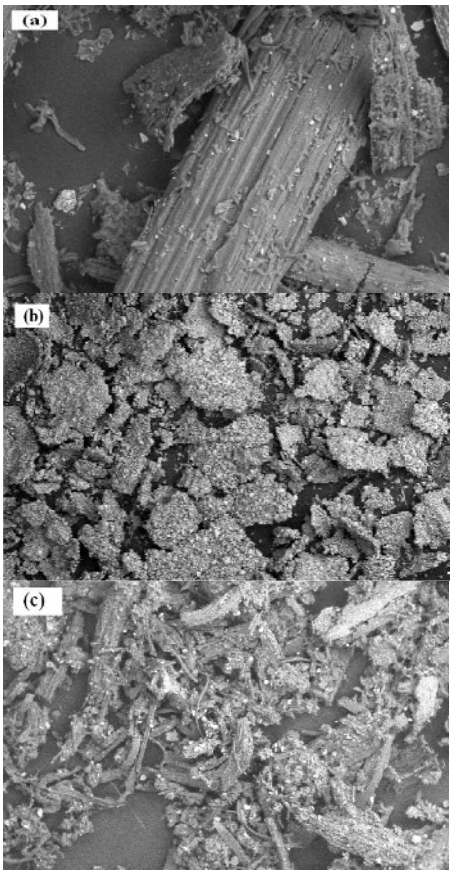

Figure 5. MEB images of (a) original miscanthus, (b) the cellulose-rich extract, and (c) miscanthus residue.

References

1. H. Tadesse and R. Luque, Energy Environ. Sci. **4** (2011) 3913–3929
2. M. Mora-Pale, L. Meli, T.V. Doherty, R.J. Linhardt, J.S. Dordick, Biotechnol Bioeng. **108** (2011) 1229-1245
3. X. Wanga, H. Li, Y. Cao, Q. Tang, Bioresource Tech. **102** (2011) 7959-7965
4. N.V. Plechkova, K.R. Seddon, In. Chem. Soc. Rev. **37** (2008) 123-150
5. R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, J. Am. Chem. Soc. **124** (2002) 4974-4975
6. A. Brandt, J.P. Hallett, D.J. Leak, R.J. Murphy, T. Welton, Green Chem. **12** (2010) 672
7. Z.G. Wang, T. Yokoyama, H.M. Chang, Y. Matsumoto, J. Agric. Food Chem. **57** (2009) 6167-6170