

Cellulose fractionation from real sludge samples through ionic liquid [BMIM][Cl]

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This paper deals with the pre-treatment of bark sludge, bio sludge and fiber sludge by ionic liquid, and the fractionation of these cellulose-based samples into different fractions. Bark sludge, bio sludge and fiber sludge are secondary products and/or waste products in the forest industry, and it is important to find new opportunities to utilize these sludges e.g. in the biofuel production.

The sample pre-treatment was carried out in the ionic liquid, 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), which is a good solvent for cellulose. Before the chemical analysis, the dissolved fiber sludge was extracted into different fractions with liquid-liquid extraction. These fractions were analyzed using mass spectrometry.

The pre-treatment of real samples, e.g. sludges from the pulp mill, is the most challenging step in the utilization of these raw materials in the biofuel production. If the cellulose dissolved from the pulp mill sludge can be successfully converted to sugars through ionic liquids, this opens up new possibilities in the biofuel production and in the utilization of these secondary products of the forest industry.

1. Introduction

Nowadays we need to find new and sustainable fuels for the future. It is important that we take care of the environment by using fuels, that don't cause emission of pollutants into the air. Biofuel production should not compete with food production. Biobutanol is energy effective, do not dissolve in water as much as methanol and ethanol and it is less corrosive than ethanol. Biobutanol is suitable as such in combustion engines due to its air/fuel ratio and it is also suitable for distribution in existing fuel distribution networks due to its low vapor pressure. Biobutanol is energy effective, do not dissolve in water as much as methanol and ethanol and it is less corrosive than ethanol and is therefore better suited for biofuel than ethanol or methanol. Biobutanol can be produced from e.g. waste products from food or forest industry.

Conventional methods to convert lignocellulosic materials to sugars have been acid hydrolysis or the use of high pressures and temperatures. These methods are either

energy-intensive or require the recirculation of acid (Tsao, 1979). There are several solvents which dissolve cellulose, but they usually degrade cellulose upon dissolving (Klemm et al., 1998). Ionic liquids can be used as non-degrading solvent for cellulose (Heinze et al., 2005; Swatloski et al., 2002). Ionic liquids can also be used as re-usable media for pyrolysis of cellulose to anhydrosugars (Sheldrake and Schleck, 2007). Dissolution of cellulose with ionic liquids allows the comprehensive utilization of cellulose by combining two major green chemistry principles: using environmentally preferable solvents and bio-renewable feed-stocks (Holbrey et al., 2003; Zhu et al., 2006). Cellulose can be dissolved, without derivation, in some hydrophilic ionic liquids, such as 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and 1-allyl-3-methylimidazolium chloride [AMIM][Cl] (Fort et al., 2007; Wu et al., 2004). The dissolution process can be accelerated by microwave heating (Aksela and Myllymäki, 2005; Zhu et al., 2006). The regeneration of cellulose from the ionic liquids is possible by the addition of water, ethanol or acetone. After the regeneration, the ionic liquids can be recovered and reused. However, ionic liquids are very expensive and thus this process is not yet economic in the industrial-scale. The commercialization of these processes still need research and has made a great progress in recent years.

Bark sludge, bio sludge and fiber sludge used in this study are all cellulose-based samples from a pulp mill. They are either secondary or waste products in the forest industry. The aim of this study was to study if these cellulose-based real samples from the pulp mill could dissolve in the ionic liquid [BMIM][Cl] into sugars. The second aim was the successful fractionation of samples with liquid-liquid extraction for chemical analysis. The real samples, if suitable for conversion to sugars with high yields and selectivities, could then be utilized in biofuel production.

2. Experimental

2.1 Samples and materials

Samples used in this research (bark sludge, fiber sludge and bio sludge), are real process samples from the pulp mill. The bark sludge is the bark-rich circulation water from the wood processing and a part of the waste water from sludge processing. The fiber sludge, also called primary sludge, consists of waste water from the sulfate mill. Bio sludge is actually living bio sludge, which vital functions are best at pH range 6-8. It is biomass from the active sludge station, which is a part of waste water treatment process.

The cation exchanger used in this research was Amberlite IR-120, which is a strongly acidic cation exchanger, H⁺ form.

The solvent used in this research is the ionic liquid, 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]).

2.2 Sample dissolving in the ionic liquid

The wet samples from the pulp mill were first vacuum filtrated with a Sartorius filtration equipment with medium flow qualitative filter paper and then dried at 100°C for 24 h. After this the samples were crushed or cut to smaller pieces. The average particle weights of bark sludge, fiber sludge and bio sludge were 0,0024 g, 0,0026 g and 0,0129 g respectively. FT-IR spectra were measured from the dry samples by Perkin Elmer Spectrum 100 equipped with the ATR unit.

The ionic liquid, 1-butyl-3-methylimidazolium chloride [BMIM][Cl], was made according to following: 1-Chlorobutane (159.5 g, 1.72 mol) in a 500 ml flask was mixed with 1-methylimidazole (103.0 g, 1.25 mol) and refluxed until all methylimidazole had reacted (24-48 h). The reaction was followed by ESI-MS and ^1H NMR. The crude product was recrystallized from ethyl acetate-acetonitrile mixture (55:45). The yield of white [BMIM][Cl] was 174.8 g (80%). [BMIM]Cl: ^1H NMR (200 MHz, CDCl_3): δ 0.96 (3H, t, $J_{\text{HH}} = 7.3$ Hz), 1.41 (2H, m), 1.89 (2H, m), 4.13 (3H, s), 4.34 (2H, t, $J_{\text{HH}} = 7.3$ Hz), 7.47 (1H, t, $J_{\text{HH}} = 1.8$ Hz), 7.62 (1H, t, $J_{\text{HH}} = 1.8$ Hz), 10.67 (1H, s). MS(ESI $^+$) [m/z (rel. int. (%))]: 139 ([BMIM]). MS(ESI $^-$) [m/z (rel. int. (%))]: 210 (Cl[BMIM]Cl).

The ionic liquid, 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), was dried at 70°C in vacuum and the water content was determined. The water content should be below 0,5 % (m-%). This pre-treatment is necessary to do, to get rid of the water as is an impurity in ionic liquids and to assure the complete dissolving of cellulosic material.

0,1 g (0,5 g) of sludge sample were dissolved in 5 g of the ionic liquid in an oil bath. The oil bath was equipped with the stirrer (stirring rate 150 rpm) was used and the temperature in the oil bath was adjusted to be between 90 and 115°C . The total time for dissolving was on for 3 hours. Samples were taken during the dissolving (one sample/hour) from the ionic liquid. These samples were analyzed by FT-IR.

2.2 Fractionation of samples for analysis

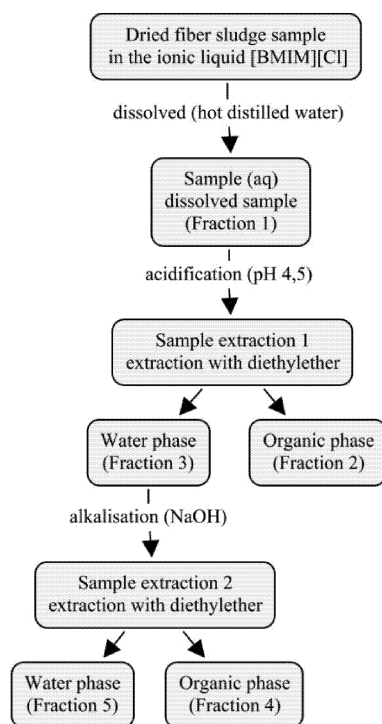


Figure 1. Fractionation scheme

Sample fractionation scheme is presented in Figure 1. The sample (dried fiber sludge dissolved in ionic liquid) was dissolved in 10 – 20 ml of distilled water (step 1) which was added to the vial and the vial was shaken hard. At this step, hot water was used because the ionic liquid solidified in cool water. pH of the solution was measured to be around 4,5 for the fraction sample (aq). After that 10-20 ml of diethylether was added to the reaction solution and the sample was extracted. Organic phase (fraction 2) and water phase (fraction 3) were separated. The water phase was made alkalic (pH 9,8) with sodium hydroxide (NaOH 6 M). After that the sample was extracted with 10-20 ml of diethylether, and the samples were taken from the organic (fraction 4) and water (fraction 5) phases.

The fractions were analyzed by GC-MS, ESI-MS and HPLC. Analysis results showed that the ionic liquid was too dominant i.e. no other components were observed by ESI-MS. To get rid of the ionic liquid, 10 ml of distilled water was added to the sample which was eluted through a cation exchanger (Amberlite).

GC-MS and ESI-MS analyses did still not give wanted results. Though, ESI-MS showed that the complete cation exchange was challenging, there was still ionic liquid left in the sample. HPLC-MS again showed other components, when the concentration of the cation was low after cation exchange.

3. Results and discussion

3.1 Dissolving results

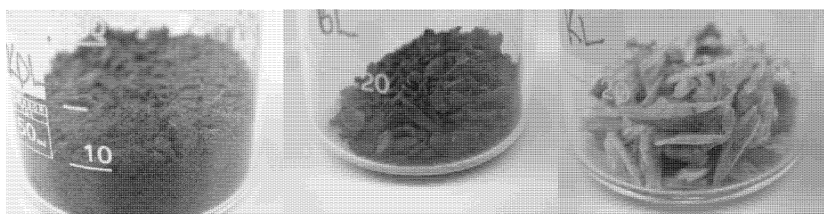


Figure 2. Dry bark-, bio- and fiber sludges, respectively.

Dried sludge samples are presented in Figure 2. The IR spectra from the dried sludge samples were measured (see Figure 3). As can be seen in Fig. 3 the spectrum for fiber sludge (FS) is exactly identical for the reference spectrum (measured from the cellulose filter paper). The other sludge samples, bio sludge (BIS) and bark sludge (BAS), do not follow the same trend (see Figure 4), which gives the evidence that the cellulose concentration in these samples is very low (if any). This is consistent with the other results presented in this paper.

After drying, the samples were dissolved in the ionic liquid, 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), as described in Section 2.1. When the dry fiber sludge was dissolved in the ionic liquid with the molar ratio of 1:10, the viscosity of the samples increased after the cellulose dissolution. The sample volume was changed to 0,1 g and the fiber sludge dissolved totally. Instead, the bio sludge did not dissolve at all and the bark sludge dissolved only partly. Therefore, the dissolving experiments were continued with fiber sludge only. In the next experiments samples

were taken during the dissolving (one sample/hour) from the ionic liquid. These samples were analyzed by FT-IR. It showed that one hour time for dissolving of fiber sludge in the ionic liquid was enough.

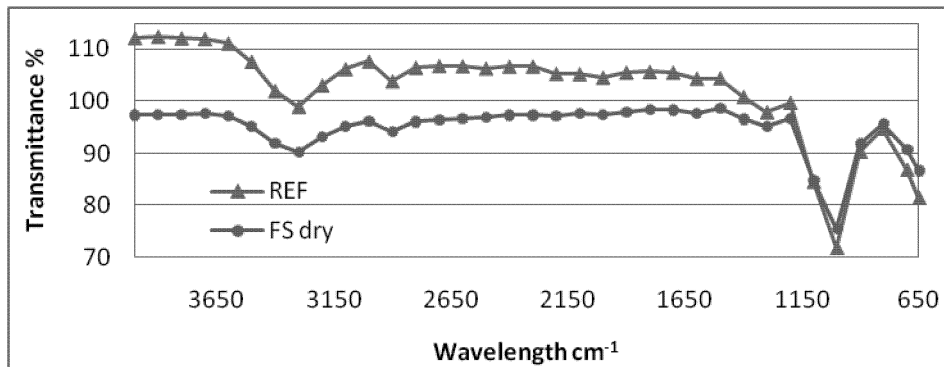


Figure 3. The IR-spectra measured for the dried fiber sludge (FS) and the reference sample (REF), which was cellulose.

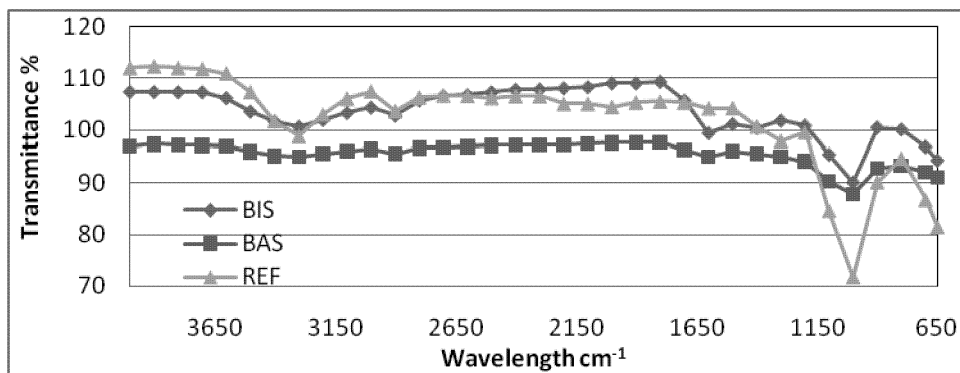


Figure 4. The IR-spectra measured for the dried bio sludge (BIS), bark sludge (BAS) and for the reference sample (REF), which was cellulose.

3.2 Analysis of samples after fragmentation

The fractionation scheme was planned as described in Section 2.3 to involve the dissolving step, acidification step, extraction step, alkalization step followed by the second extraction step (see Figure 1).

Based on the preliminary results, glucose (mass 180 g/mol) was found in some of the dissolved real sludge samples, while all the samples showed the presence of cellulose. The yields of glucose were still low. Acid hydrolysis in ionic liquid would make the glucose conversion efficient (Li et al., 2007).

4. Conclusions

This study aimed at converting lignocellulose-based raw materials to sugars, which can further be converted to bioalcohols (biofuel components) by e.g. fermentation. Based on the results, fiber sludge from the pulp mill seems to be a potential raw material in biofuel production. It can be dissolved in the ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), and convert to sugars. Instead bark sludge and bio sludge did not dissolve in the ionic liquid, a reason why they were not suitable for this purpose. There is a need for the development of pre-treatment procedure in order to get higher yields and better selectivities.

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