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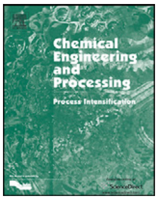

Separation and recovery of the constituents from lignocellulosic biomass by using ionic liquids and acetic acid as co-solvents for mild hydrolysis

Jaap van Spronsen[a], Miguel A. Tavares Cardoso[b], Geert-Jan Witkamp[a], Wiebren de Jong[b], Maaike C. Kroon[a,c,*]

[a] Section Process Equipment, Department of Process & Energy, Faculty of Mechanical Maritime & Materials Engineering, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

[b] Section Energy Technology, Department of Process & Energy, Faculty of Mechanical Maritime & Materials Engineering, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

[c] Separation Technology Group, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands

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ABSTRACT

Previously, ionic liquids were found to partially dissolve lignocellulosic biomass. Here, it is reported that the biomass itself does not dissolve directly, but that it is hydrolyzed first before the constituents (cellulose, hemicellulose and lignin) dissolve into the ionic liquid. By addition of an acidic catalyst, this hydrolysis step can take place at milder conditions. Acetic acid is chosen as a suitable acidic catalyst, because it is already present in lignocellulosic biomass in the form of acetyl groups on the hemicellulose. Here, it is shown that acetic acid also works as co-solvent, increasing the solubility of the constituents of lignocellulosic biomass in the ionic liquid. The milder conditions for hydrolysis result in a higher degree of utilization of the lignocellulosic biomass, whereby all constituents can be fully recovered and further processed and the ionic liquid can be reused.

1. Introduction

The depletion of fossil resources together with the global warming alarms has led to an intensified search for alternative resources to supply the modern society. Biomass has the potential to become a sustainable alternative resource for production of raw materials and fuels with a neutral carbon dioxide balance. Especially interesting in this context is the use of lignocellulosic biomass (wood or straw), because it does not compete with the food chain. However, current processes to convert lignocellulosic biomass to useful materials are highly inefficient. Even the most efficient processes, *i.e.*, the production of paper from wood, show a biomass utilization of only 35% [1]. The rest of the lignocellulosic biomass is burnt to produce heat or ends up as waste.

The aim of this research is convert lignocellulosic biomass into useful raw materials and fuels with a much higher degree of utilization. Lignocellulosic biomass mainly consists of cellulose (35–50%), hemicellulose (20–35%) and lignin (5–30%) [2]. These components are assembled in a complex three-dimensional structure remarkably resistant against chemicals and microbial attack that makes it very difficult to hydrolyze. An effective dissociation of these components and their subsequent separation is needed for the production of high value products from lignocellulosic biomass.

Current processes for biomass dissociation use extreme conditions (high temperature or high acidity), resulting in decomposition of the biomass into undesired low-value products that are difficult to separate from each other [2]. The intention of this work is to dissociate lignocellulosic biomass into its constituents under milder conditions, in order to prevent further decomposition of the cellulose and the lignin. A combination of an ionic liquid with acetic acid as co-solvent at low temperature is used to achieve this goal.

Previously, ionic liquids were found to be able to dissolve a number of monomeric, oligomeric and polymeric saccharides [3–5], including cellulose [6–10]. The dissolved cellulose was further converted into useful products in the ionic liquid phase [11–16]. Examples include the acylation into cellulose acetate [13,14], the hydrolysis into glucose [15] and further dehydration into furan compounds [16].

Many research groups have also tried to dissolve wood into ionic liquids [17–20], resulting in partial dissolution of the biomass. Com-

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* Corresponding author. Tel.: +31 15 2782178; fax: +31 15 2786975.
E-mail addresses: m.c.kroon@tudelft.nl, maaike.kroon@gmail.com (M.C. Kroon).

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plete dissolution of the lignin into an ionic liquid was only achieved when either dimethylsulfoxide was added as co-solvent [19], or when the lignin was already partially decomposed by the Kraft process [20]. Here, it is hypothesized that in these cases the wood itself is not dissolved, but that is hydrolyzed first, followed by dissolution of the hydrolyzed products. This hydrolysis takes place in an ionic liquid with [21] or without addition of an acidic catalyst [22,23]. Addition of an acidic catalyst enhances the rate of hydrolysis and subsequently the rate of dissolution, which can now be carried out at lower temperatures. In this way, further decomposition of the biomass is minimized.

Conventionally, the hydrolysis of biomass is carried out in acidic media with the aim to convert all cellulose into glucose [24]. For the same purpose, strong acids have been added to mixtures of lignocellulosic biomass and ionic liquids [21]. Here, it is suggested to use a weak acid as catalyst instead, so that the biomass can be dissolved by breaking the chemical bonds between the cellulose, hemicellulose and lignin, without further decomposition of cellulose into glucose. Acetic acid is chosen as suitable weak acid, because it is already present in lignocellulosic biomass in the form of acetyl groups on the hemicellulose [2]. Moreover, acetic acid can work as a co-solvent [19], further enhancing the solubility of lignin in the ionic liquid.

In this work, the hydrolysis of pine wood and wheat straw will be carried out first in three different ionic liquids, *i.e.*, 1-ethyl-3-methylimidazolium chloride ([emim][Cl]), 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and 1-ethyl-3-methylimidazolium acetate ([emim][OAc]). Thereafter, the effect of addition of acetic acid to [emim][Cl] on the hydrolysis of pine wood and wheat straw will be investigated. After hydrolysis of the lignocellulosic biomass in the ionic liquid/acetic acid mixture, the constituents will be separated and recovered. The cellulose fraction will be isolated by precipitation with ethanol. Next, the lignin will be isolated by precipitation with water. Finally, the remaining hemicellulose will be analyzed. This hemicellulose fraction could be converted into furfural, and removed from the ionic liquid phase by extraction with supercritical carbon dioxide [25] without any contamination by the ionic liquid [26], but is not further investigated here. This would result in complete recovery of the ionic liquid.

2. Experimental

2.1. Materials

Wheat straw was produced in Spain under controlled conditions. Before usage, the wheat straw was milled using a Tomado stick blender set (Oosterhout, The Netherlands) and sieved with a mesh size < 1 mm. The straw was analyzed by the Klason method [27]. The straw was found to consist of 30% cellulose, 32% hemicellulose and 38% lignin.

Pine wood pellets were purchased from Energy Pellets Moerdijk (Moerdijk, The Netherlands) and were milled using a Retsch ZM-200 ultra centrifugal mill (Dusseldorf, Germany). The wood powder was sieved with a mesh size < 1 mm. Klason analysis [27] indicated the following composition for the wood: 39% cellulose, 26% hemicellulose and 35% lignin.

The ionic liquids [emim][Cl] (≥98%), [bmim][Cl] (≥95%) and [emim][OAc] (≥90%) were purchased from Sigma–Aldrich (Steinheim, Germany). Acetic Acid (≥99.8%) and ethanol (≥99.8%) were purchased from J.T. Baker (Deventer, The Netherlands) and FLUKA (Buchs, Switzerland), respectively. The water used was purified using a PURELAB Maxima from ELGA (Ede, The Netherlands), which delivers water with a resistance of ≥18 MΩ.

Table 1
Dissolution of wheat straw and pine wood in three different ionic liquids: '+' indicates that the solution becomes transparent; '–' indicates that the biomass remains undissolved.

Type of biomass	[emim][OAc]	[emim][Cl]	[bmim][Cl]
Wheat straw	–	+	+
Pine wood	–	+	–

2.2. Experimental procedure

First, dissolution experiments with different ionic liquids were performed: 0.5 g of biomass (wheat straw or pine wood) and 10 g of ionic liquid ([emim][Cl], [bmim][Cl] or [emim][OAc]) were put into a 50 mL Erlenmeyer equipped with a magnetic stirrer. The Erlenmeyer was then heated to 373 K under a nitrogen atmosphere and continuously stirred (200 rpm) during 24 h. Thereafter, 20 mL of water was added to the solution to induce the precipitation of cellulose and lignin The mixture was then cooled down to room temperature and filtered using a 0.22 μm MF-Millipore Membrane Filter (Bedford, USA). The filters were visually inspected. The acidity (pH) of the remaining solution was measured using a pH/Ion meter Radiometer (Copenhagen, Denmark). The acetic acid concentration was also measured using High Performance Liquid Chromatography (HPLC) from Waters, type Waters 510 HPLC pump & Waters Symmetry C_{18}-column (Milford, USA).

Next, the influence of acetic acid addition on the hydrolysis of biomass in [emim][Cl] was investigated: 0.5 g of biomass (wheat straw or pine wood), 10 g of [emim]Cl and different amounts of acetic acid (0, 2, 4 or 6 mL) were weighted into a 50 mL Erlenmeyer equipped with a magnetic stirrer. The Erlenmeyer was heated to the chosen temperature (373 and 398 K) under a nitrogen atmosphere and continuously stirred (200 rpm) for 5 h. Thereafter, 20 mL of ethanol was added to the Erlenmeyer to induce precipitation of cellulose. The mixture was cooled down to room temperature and filtered using a 0.22 μm MF-Millipore Membrane Filter. Next, water was added in a volume ratio of 1:2 with respect to the filtrate in order to induce precipitation of the lignin. The suspension was filtered using a 0.22 μm MF-Millipore Membrane Filter. The different precipitates were analyzed by the Klason method [27] and by Scanning Electron Microscopy (SEM) from JEOL, type JSM-5400 (Tokyo, Japan). The furfural content of the remaining filtrate was analyzed by High Performance Liquid Chromatography (HPLC) from Waters, type Waters 510 HPLC pump & Waters Symmetry C_{18}-column (Milford, USA).

3. Results and discussion

From previous studies on the dissolution of lignocellulosic biomass [17–20] three promising ionic liquids can be identified: (i) [emim][Cl], (ii) [bmim][Cl], and (iii) [emim][OAc]. In this work, the dissolution of the lower lignin containing wheat straw and the higher lignin containing pine wood at 373 K in these three ionic liquids is investigated. Therefore, the biomass is mixed with the ionic liquid, and the obtained mixture is visually inspected. The results for the dissolution experiments are presented in Table 1. Every experiment was repeated at least three times to ensure the reproducibility of the results.

From Table 1 it can be concluded that [emim][OAc] is a poor solvent for lignocellulosic biomass under the applied conditions. The ionic liquid [bmim][Cl] showed better results for straw. The most promising results for both types of lignocellulosic biomass were obtained with [emim][Cl].

Although the mixture of [bmim][Cl] with straw and the mixtures of [emim][Cl] with straw and wood became transparent after 24 h, the biomass did not completely dissolve. When the transpar-