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An efficient process for the saccharification of wood chips by combined ionic liquid pretreatment and enzymatic hydrolysis

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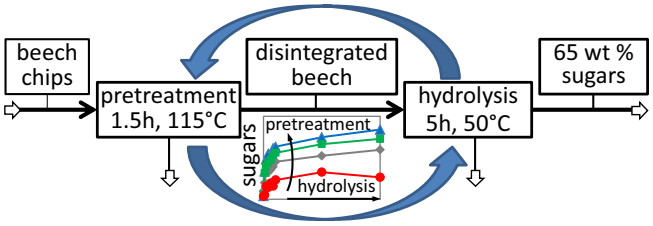
HIGHLIGHTS

- Effective enzymatic hydrolysis of wood chips disintegrated by [EMIM][Ac].
- Pretreated chips of beech provide twice the yield of sugars as compared to spruce.
- Quantitative yield of cellulose and xylan from beech chips pretreated at 115 °C.
- Conversion of more than 70% of cellulose and 65% of wood into sugars within 5 h.
- Longer pretreatment results in degradation products leaching into soluble sugars.

GRAPHICAL ABSTRACT



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ABSTRACT

A process concept combining pretreatment of wood in ionic liquids and subsequent enzymatic hydrolysis to sugars is herein investigated to identify operating conditions which allow for (i) the processing of larger wood chips of 10 mm length, (ii) low temperature, (iii) high sugar yield, and (iv) short processing time. A careful quantitative study of the interaction of pretreatment and hydrolysis reveals that hydrolysis is most effective if beech chips are first disintegrated in [EMIM][Ac] at 115 °C for 1.5 h. The cellulose conversion varies between 70.5 wt% and 90.2 wt% for hydrolysis times between 5 h and 72 h. A complete recovery of cellulose and xylan resulting in a total saccharification of 65 wt% of the wood chips could be demonstrated. It is shown that short pretreatment times are required to enable high sugar yield as well as to limit product degradation.

1. Introduction

The transition from fossil to biobased carbon sources in industrial value chains constitutes one of the global challenges in the face of depleting fossil carbon resources and the negative impact of fossil carbon processing on the global environment. Novel process routes, which aim to preserve the synthesis power of nature by exploiting the variety of native molecular structures present in biomass using combined chemical and biological refunctionalization, have been identified as an attractive alternative to gasification prior to the synthesis of the target molecular products

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(Marquardt et al., 2010; Sanders et al., 2012). Such processing strategies require the depolymerization of carbohydrates under mild processing conditions, avoiding unspecific degradation of the raw material into a multitude of small molecules. The combination of biomass pretreatment under mild conditions and subsequent highly-selective enzymatic hydrolysis offers an attractive strategy to fulfill these objectives. Unfortunately, this strategy is limited because of the high effort required for pretreatment and hydrolysis of biomass, particularly lignocellulosic material.

A novel line of research regarding the pretreatment and hydrolysis of native biomass has been initiated by the finding of cellulose dissolution in ionic liquids (ILs) by Swatloski et al. (2012), ILs are roughly defined as liquid salts with a melting point below 100 °C (Wasserscheid and Welton, 2008). Xiao et al. (2012), for example, showed recently that the dissolution of cellulose in 1-butyl-3-methyimidazolium chloride ([BMIM][Cl]) and its subsequent regeneration enables to complete conversion to sugars in less than 5 h of enzymatic hydrolysis. This promising idea has also been investigated by treating cellulose-rich, native biomass in ILs. Fort et al. (2007) were first to analyze the dissolution of wood in an IL. More recently, Li et al. (2013) reported a fast and nearly quantitative hydrolysis of glucan from pine, eucalyptus, or switchgrass, which was made accessible by pretreatment in 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]) for 3 h at 160 °C. However, some cellulose and a significant fraction of the hemicelluloses are lost at such high pretreatment temperatures and the sugar yield from wood can be as low as 50 wt% (Li et al., 2011; Karatzos et al., 2012).

Temperatures above 110 °C lead to significant loss in sugar yield by depolymerization and degradation of carbohydrates in [EMIM][Ac] (King et al., 2011; Xu et al., 2012). The formation of small and water-soluble molecules under such circumstances is clearly undesirable, because it not only reduces carbon efficiency but would also induce difficult separation problems on an industrial scale.

Furthermore, ILs suffer from thermal degradation and show a decreased long-term stability at higher temperatures, which is not covered by the usual thermogravimetric analyses (Maton et al., 2013). A temperature of 120 °C was identified to mark the start of decomposition for ILs (Meine et al., 2010; King et al., 2011). Any economically viable process concept must clearly avoid procedures leading to the loss of costly solvent. A temperature of approximately 110 °C seems to be a good choice to facilitate high sugar yield (Shill et al., 2012; Auxenfans et al., 2012) while maintaining thermal stability of the IL.

The pretreatment temperature should, however, not be chosen independently of the pretreatment time, since both process parameters significantly affect cellulose conversion. For example, Lee et al. (2009) reported that the yield from wooden cellulose increases from 80 wt% to 95 wt% after pretreatment for 1.5 h in [EMIM][Ac], when the pretreatment temperature is increased from 90 °C to 130 °C. However, similar yields can be obtained at a lower temperature, when a longer pretreatment time is used (Doherty et al., 2010; Labbé et al., 2012). In fact, the recovery of and the yield from hemicellulose seems to be time-critical since a loss of 14 wt% can already occur due to pretreatment for 0.5 h at 120 °C (Qui et al., 2012), and this loss increases to 24 wt% after pretreatment of 3 h at 110 °C (Xu et al., 2012).

Finally, very small wood particles of size less than one millimeter have been utilized in most studies investigating biomass pretreatment with ILs. Not only do they fail to properly represent the heterogeneous morphological structure of wood, but they also include a high energy demand for comminution, which would be unacceptable from an economical point of view for bulk chemical processing (Blanch et al., 2011). Hence, the pretreatment of wood has to focus on larger particles to become economically viable. Larger wood chips have been shown to disintegrate into fibers during pretreatment in ILs prior to their dissolution (Miyafuji and Suzuki, 2011; Viell and Marquardt, 2011). As such, dissolution could possibly be avoided, with the increased specific surface area of the disintegrated wood particle then favoring enzymatic attack during hydrolysis. Up to now, this idea has yet to be explored systematically.

Previous studies indicate that an optimal choice of process parameters could tremendously improve the efficiency of the combined pretreatment and enzymatic hydrolysis of wood chips with large particle sizes. The choice of such parameters must rely on a comprehensive quantitative analysis of the mass balances of the combined pretreatment and hydrolysis process. Choosing ideal operating parameters would also be decisive in achieving an economically viable process, particularly given the high cost of ILs (Klein-Marcuschamer et al., 2011).

In this work, the combined pretreatment and subsequent enzymatic hydrolysis of wood is investigated systematically. Large wood chips are treated with [EMIM][Ac] for the first time with the aim to optimize the sugar yield using a moderate pretreatment temperature and short pretreatment and hydrolysis times. Comprehensive mass balances are established to identify process conditions which allow high-yield conversion and avoid degradation to the extent possible.

2. Methods

The suggested process concept for the saccharification of wood chips by combined ionic liquid pretreatment and enzymatic hydrolysis is depicted in Fig. 1. The process consists of three steps: in the first step, the wood pretreatment with IL deconstructs the wood structure and also achieves partial dissolution. In the second step, a solvent is used to wash off the IL from the undissolved residue; most solvents also result in precipitation of dissolved macromolecules. Hence, dissolved and undissolved wood are both recovered as one solid mass. Molecules that cannot be obtained in the initial precipitation and washing step are discharged as extract with the washing liquor. In the third step, the recovered solids go into hydrolysis, where enzymes convert solid carbohydrates into a water-soluble product. Any remaining solid is collected as residue, which also contains the now inactivated enzymes.

A basic implementation of the concept depicted in Fig. 1 is used first to explore feasibility at small scale. In particular, the dissolved

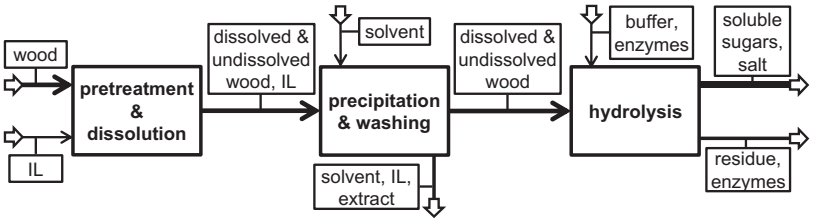

Fig. 1. Block flow diagram of the combined pretreatment and hydrolysis visualizing the process steps and flows. Main process flows are depicted by thick lines.