



Alkaline polyol pulping and enzymatic hydrolysis of hardwood: Effect of pulping severity and pulp composition on cellulase activity and overall sugar yield



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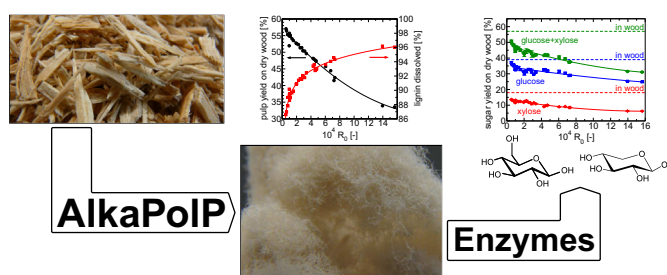
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HIGHLIGHTS

- We present a new pulping process enabling effective saccharification of hardwood.
- The raw material is fractionated in alkaline glycerol at atmospheric pressure.
- 96% of the initial lignin in beech wood were dissolved at short residence times.
- The obtained pulp fraction can easily be hydrolyzed by cellulases.
- Up to 95% conversion of polysaccharides in pulp within 48 h enzymatic digestion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 December 2012

Received in revised form 20 February 2013

Accepted 22 February 2013

Available online 7 March 2013

Keywords:

Pulping
Enzymatic hydrolysis
Lignocellulose
Pretreatment
Glycerol

ABSTRACT

The saccharification of beech wood using alkaline polyol pulping (AlkaPoIP) and enzymatic hydrolysis was investigated. It will be demonstrated that the AlkaPoIP process yields high quality pulps which can easily be hydrolyzed by cellulases. In order to find optimum reaction conditions chips of *Fagus sylvatica* were pretreated by alkaline glycerol at temperatures between 190 and 230 °C for 15, 20, and 25 min. The impacts of temperature and time were expressed using a severity factor R_0 . The dependencies of the conversion during enzymatic hydrolysis on severity, pulp yield, delignification and pulp composition are shown. In further experiments it was investigated if the sugar yields can be increased by the application of ultrasound or surfactants before enzyme addition. Up to 95% of the initial cellulose in wood were converted into glucose using cellulases from *Trichoderma reesei* and β -glucosidase from *Aspergillus niger*.

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1. Introduction

Bioethanol is regarded as a promising renewable energy and raw material source to mitigate the greenhouse effect by decreasing the global petroleum consumption. However, considering the growing world population the production of first generation

bioethanol from sugar and starchy food materials would endanger the food security, especially in Third World countries (Guragain et al., 2011). As main component of lignocellulosic biomass, cellulose is the world's most abundant renewable resource (Klemm et al., 2005) and represents an auspicious sustainable alternative. The production of cellulose-based bioethanol does not compete against food for agricultural area avoiding the "food or fuel" conflict. Prior to ethanol fermentation the cellulose has to be converted into glucose, which is mainly realized with the aid of mineral acids or hydrolyzing enzymes. The latter involve mild

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reaction conditions with low capital costs and high selectivities. However, due to its resistant structure native lignocellulose cannot be efficiently degraded by cellulases. Therefore, an appropriate pretreatment is needed to improve the accessibility of the cellulose by breaking down its tight and recalcitrant matrix (Munoz et al., 2011). Usually this comes along with a dissolution of large quantities of the lignin and hemicelluloses because they are strongly connected among each other. Since conventional sulfurous pulping processes are not applicable to bioethanol production (Chandra et al., 2007) many processes have been developed enhancing the hydrolyzability of lignocellulose over the last few decades such as: non-catalytic pretreatments using steam (Schütt et al., 2011) or hot water (Hu et al., 2008), chemical treatments by acids (Nunes and Pourquie, 1996), alkalis, organic solvents or ionic liquids. Due to differences in feedstock, downstream processes and mass balance approaches it is difficult to compare the published results. However, these processes still involve several obvious drawbacks impeding an industrial application (Guragain et al., 2011; Sun and Chen, 2008 b). If the process works under pressurized conditions, a decompression is necessary causing high exergy losses. Further drawbacks could be caused by corrosive media and the formation of inhibiting degradation products like furfurals. Hence, further research in new pretreatment and biorefinery concepts is still necessary to overcome the remaining obstacles.

As a cheap waste product of the expanding biodiesel production glycerol has gained focus of several research studies during the last years. Because its production now exceeds demand novel economic applications of glycerol need to be explored (Liu et al., 2010). Demirbas (1998) investigated the delignification of wood by aqueous glycerol. He found that lignin and hemicelluloses are dissolved in large quantities while cellulose stays largely preserved. Sun and Chen (2008a) treated wheat straw with aqueous glycerol at 220 °C for 3 h and observed that the subsequent enzymatic hydrolysis gave higher sugar yields than in the case of steam exploded wheat straw. They mentioned four decisive advantages of glycerol as solvent for lignocellulose pretreatment: (1) It can be completely recycled and reused. (2) Being an organic solvent it involves small environmental impact and energy consumption. (3) Operation at atmospheric pressure even at elevated temperatures. (4) Owing to its high polar polyalcohol structure, glycerol easily penetrates into the fiber tissue, providing an effective reaction medium for the delignification of lignocellulosic biomass.

In spite of good progress in the field of lignocellulose pretreatment during the last years it is still a big challenge to find an economic process that completely dissolves lignin and hemicelluloses while preserving the cellulose for enzymatic hydrolysis. These requirements were taken into account in the development of the AlkaPolP process. The application of essentially water-free glycerol in combination with an alkaline catalyst involves decisive advantages. The reaction time is considerably reduced compared to non-catalyzed glycerol pretreatments which take several hours even for lignocelluloses with low lignin content (Guragain et al., 2011; Novo et al., 2011). Moreover, the flexibility of the process regarding the raw material is improved because high catalyst concentrations enable the utilization of more resistant softwood, too. Furthermore, the pulping can be performed at ambient pressure lowering the investment and operating costs. Due to the absence of water the degradation of polysaccharides by hydrolysis and peeling reactions is inhibited resulting in high cellulose yields.

The objective of this contribution is to demonstrate the capability of the developed pulping process to enhance the enzymatic hydrolysis of lignocellulosic biomass. Furthermore, optimum pulping conditions for maximizing the overall sugar yield should be found. Because many authors observed an improvement of hydrolyzability with decreasing residual lignin content of pulp (Nakagame et al., 2011; Jin et al., 2010; Yoshida et al., 2008) it is

elaborated whether it could be used as key predictor for the subsequent enzymatic degradation.

2. Methods

2.1. Materials

Shavings of European Beech (*Fagus sylvatica*) were used as raw material. Prior to pulping experiments the wood was screened in order to obtain several particle size fractions (see Table 1 and Fig. 3). The compositional analysis gave 39.0% cellulose, 18.0% xy-lan, 21.3% lignin and 1.5% extractives on dry weight.

The chemicals used in the pulping experiments were technical glycerol (min. 97%, BDH Prolabo) and potassium hydroxide (min. 85%, BDH Prolabo). The solvents and chromatography standards used in the analyses mentioned below were acetyl bromide (min. 97%, Merck KGaA), acetic acid (99%, Merck KGaA), perchloric acid (70%, Applichem GmbH), sodium hydroxide (min. 97%, BDH Prolabo), sulfuric acid (96%, BDH Prolabo), water (HPLC grade, BDH Prolabo), acetonitrile (HPLC grade, BDH Prolabo), D-xylose (min. 99%, Merck KGaA), D-glucose (min. 99%, Merck KGaA), L-arabinose (min. 99%, BDH Prolabo), D-galactose (min. 99%, Merck KGaA), D-mannose (min. 99%, Merck KGaA), L-rhamnose monohydrate (99%, Alfa Aesar), D-cellobiose (min. 98%, Alfa Aesar). In addition citric acid monohydrate (min. 99.5%, Merck KGaA), polyethylene glycol 400 (for synthesis, Merck KGaA), polyethylene glycol 6000 (molecular biology grade, BDH Prolabo), 3,5-dinitrosalicylic acid (min. 98%, Sigma-Aldrich), phenol (for synthesis, Merck KGaA), sodium sulphite (min. 98%, Merck KGaA), potassium sodium tartrate tetrahydrate (min. 99%, Applichem GmbH), sodium azide (min. 99%, Merck KGaA) and whatman filter paper No. 1 were used for the filter paper assay and preparation of the buffer for enzymatic hydrolysis.

2.2. Alkaline polyol pulping

Pulping experiments were performed in a 2 l batch reactor (spherical reaction vessel with laboratory flange LF 150, Lenz Laborglas GmbH & Co. KG, Wertheim, Germany). The flat flange lid had several necks for temperature measurement (PT100 sensor), feeding, stirring and condensation of gaseous products. For all experiments the solvent mixture, consisting of 1000 g glycerol and 80 g potassium hydroxide, was heated up to the desired temperature using a hemispherical heating mantle. After keeping the system at target temperature for ten minutes the wood was added. At the end of reaction time the residual solids were separated from the black liquor via vacuum filtration at 100 mbar (diaphragm pump ME 1C, Vacuubrand GmbH + Co KG, Wertheim, Germany) using a Büchner funnel and 25 µm filter paper. Afterwards the pulp was suspended in 1 liter distilled water and filtered off three more times. The obtained filter cake was dried at 60 °C, weighted and kept for further analyses as well as for enzymatic hydrolyses.

2.3. Analysis

The residual lignin in wood and pulp samples was determined using the acetyl bromide method described and improved by a number of authors, e.g. Johnson et al. (1961) and Iiyama and Wallis (1988). Samples were ball milled (8 min, 50 Hz, mini-mill pulverisette 23 equipped with a 10 ml zirconium oxide grinding bowl and three 10 mm zirconium oxide grinding balls, Fritsch GmbH, Idar-Oberstein, Germany) making them more homogeneous and improving their solubility in the reagent. The sealed bottles were placed in a tempered water bath to ensure an effective heat transfer. Mixing was performed using small magnetic stirrers avoiding

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