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Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose

Jelle Wildschut, Arjan T. Smit, Johannes H. Reith, Wouter J.J. Huijgen *

Energy Research Centre of the Netherlands (ECN), Biomass & Energy Efficiency, P.O. Box 1, 1755 ZG, Petten, The Netherlands

HIGHLIGHTS

- ▶ Wheat straw biorefining by ethanol organosolv into lignin and digestible cellulose.
- ▶ Major optimization parameters: temperature, ethanol concentration, and acid dose.
- ▶ Biomass particle size and reaction time less influential process parameters.
- ▶ Optimum enzymatic glucose yield of 86% after autocatalytic organosolv.
- ▶ High yields of lignin, furfural, and sugars by acid-catalysed organosolv.

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ABSTRACT

Wheat straw fractionation by ethanol organosolv was studied as pretreatment for enzymatic cellulose hydrolysis. A parametric study focusing on temperature, reaction time, acid catalyst dose, solvent concentration, and particle size was performed to determine their influence on delignification, xylan hydrolysis, and enzymatic cellulose digestibility. Major process parameters were found to be temperature, ethanol concentration, and acid dose. Optimisation of the process towards enzymatic digestibility resulted in a maximum glucose yield of 86% without the use of a catalyst (lignin yield 84%, organosolv at 210 °C, 50% w/w aqueous EtOH). Using 30 mM H_2SO_4 as catalyst resulted in similar glucose and lignin yields at a lower temperature (190 °C, 60% w/w aqueous EtOH). Lowering the pretreatment temperature by using an acid catalyst substantially improved the yield of the hemicellulose derivatives xylose and furfural. A systematic approach in pretreatment optimisation is vital for development of efficient lignocellulosic biorefineries.

1. Introduction

Lignocellulosic biomass is a versatile renewable source of chemicals and fuels, available in large amounts and at relatively low costs (Demirbas, 2007; Huber et al., 2006). Current industrial application for energy purposes is often limited to heat and power generation. However, both the sugar and lignin fractions of lignocellulosic biomass have great potential as a resource for fuels and chemicals production with higher added value (Huber et al., 2006; Kumar et al., 2009; Zakzeski et al., 2010). This can be achieved via the biorefinery approach.

Biorefining is the sustainable processing of biomass into a spectrum of marketable products (food and feed, materials, and chemicals) and energy (fuels, power, and heat) (definition International Energy Agency, Bioenergy Task 42). Appropriate fractionation of the complex lignocellulose material into its constituents is a key operation in a biorefinery. Fig. 1 depicts a possible lignocellulosic biorefinery scheme. In this scheme, lignocellulosic biomass is first fractionated into its major constituents, which are subsequently processed into the desired end-products. The resulting fractions cellulose, hemicellulose and lignin have a variety of potential applications. Cellulose pulp could, for example, be used for paper production or as a carbohydrate source for chemicals or biofuels (e.g., bioethanol or biobutanol by fermentation). Hemicellulose-derived sugars can be used as a substrate for fermentation or anaerobic digestion. Alternatively, sugars derived from the hemicellulose fraction can be (thermo)chemically converted into e.g. furfural (Marcotullio and De Jong, 2011). Furfural, which has many applications e.g. as a solvent, is commercially produced today via thermohydrolysis of biomass residues using mineral acids as catalysts (Zeitsch, 2000). Finally, the lignin fraction is a renewable source of aromatics for a range of chemicals and performance products such as phenolics and ingredients for glues and resins (De Wild et al., 2012; Gosselink, 2011; Zakzeski et al., 2010).

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* Corresponding author. Tel.: +31 224 8162; fax: +31 224 8487.
E-mail address: huijgen@ecn.nl (W.J.J. Huijgen).

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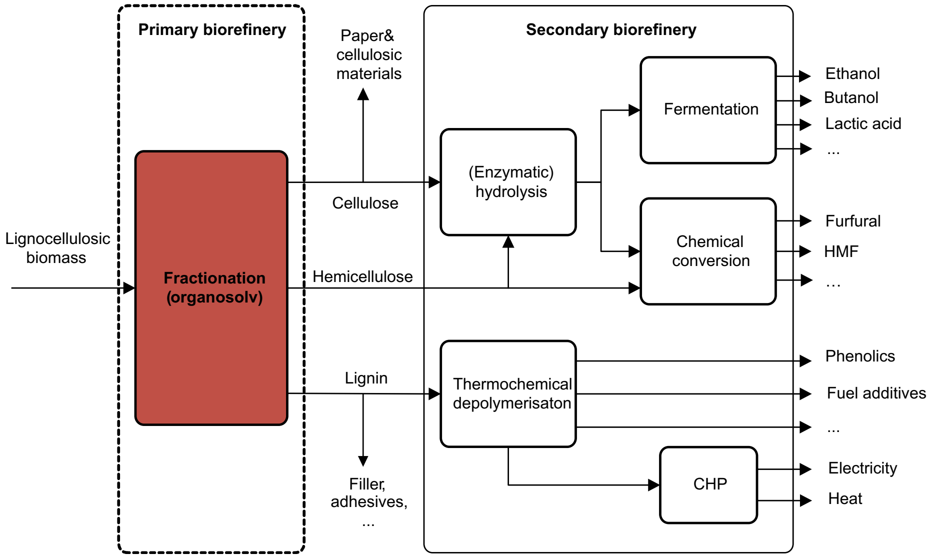

Fig. 1. Organosolv-based lignocellulosic biorefinery (adapted from (De Wild et al., 2012)).

Conversion of cellulose into glucose by enzymatic hydrolysis requires pre-treatment of the lignocellulosic biomass to make the cellulose fraction more accessible to cellulase enzymes. For this purpose several pretreatment techniques are being developed and various overviews can be found in the literature (Alvira et al., 2010; Demirbas, 2007; Hendriks and Zeeman, 2008; Kumar et al., 2009). The current study focuses on organosolv. A key feature of the organosolv process is that it extracts lignin from lignocellulosic biomass prior to enzymatic cellulose hydrolysis in contrast to other common pretreatment technologies such as steam explosion and mild acid pretreatment. Thus, in addition to enzymatically digestible cellulose, lignin with minimum carbohydrate and mineral impurities is produced which facilitates lignin applications with a higher value than heat and power generation e.g. as an ingredient in resins or as feedstock for aromatic chemicals (Zhao et al., 2009; Huijgen et al., 2010, 2012).

Organosolv fractionation consists of cooking lignocellulosic biomass in an (aqueous) organic solvent at elevated temperatures (Zhao et al., 2009). During the process, the hemicellulose is hydrolysed, lignin is dissolved in the liquor and purified cellulose is produced as a pulp. The dissolved lignin can be separated by precipitation by water addition or solvent evaporation. The resulting products are (1) a pulp mainly consisting of cellulose, (2) solid lignin and (3) an aqueous stream containing hemicellulose sugars and derivatives such as furfural (Zhao et al., 2009). Organosolv delignification can be performed with various solvents (e.g. ethanol, acetone, acetic acid) and both autocatalytic (i.e., without any catalyst added) and catalytic. The most well-known autocatalytic organosolv process is the Alcell (now Lignol) process that is based upon autocatalytic ethanol delignification of wood (Pye and Lora, 1991).

Ethanol-based organosolv has been widely studied for pulping as well as for pretreatment purposes. Ethanol is a renewable solvent and its volatility facilitates the extensive recycling required (Zhao et al., 2009). Ethanol-based organosolv pretreatment has been studied for all major types of lignocellulosic biomass including hardwoods (e.g., willow (Macfarlane, 2009), poplar (Kim and Pan, 2010)), softwoods (e.g., lodgepole pine (Pan et al., 2007; Del Rio et al., 2012)), and herbaceous crops (e.g., miscanthus (Brosse et al., 2009)). Wheat straw has been successfully pulped and pretreated using aqueous ethanol in previous studies (Huijgen et al., 2011; Jimenez et al., 1999; Sidiras and Koukios, 2004; Sun et al., 1998; Xu et al., 2007, 2011).

At present, there is growing interest in organosolv fractionation for biorefineries as well as enhanced interest in lignin as a potential industrial source of renewable aromatics. In the current study, wheat straw is fractionated by using autocatalytic and acid-catalysed ethanol organosolv. The aim is to identify the most influential process parameters and to optimize the process towards enzymatic cellulose hydrolysis to glucose. First, a parametric study is performed focusing on temperature, reaction time, catalyst dose, solvent concentration, and particle size in order to gain insight in the effects on delignification, lignin yield, xylan hydrolysis, and enzymatic digestibility. Subsequently, the parametric effects on yield and quality of fractions are summarised in a ‘process product relation scheme’. Finally, the scheme is used to optimize the organosolv fractionation process towards enzymatic cellulose digestibility.

2. Methods

2.1. Biomass

Wheat straw was received ambient-dry from Champagne-Ardennes region, France (harvested summer 2009). The straw was milled with a cutting mill to a particle size smaller than 10 mm (Retsch SM 2000) and stored in closed containers until use. The moisture content of the raw material was determined for each organosolv experiment using a halogen moisture analyser (Mettler Toledo HR83, Columbus, OH) and averaged 7.5 wt.%. The summative composition of the wheat straw was (% w/w dry basis): glucan, 35.4; xylan, 19.8; arabinan, 2.1; galactan, 1.4; lignin, 17.6; ash, 3.5; and extractives, 10.2 (methodology, see Section 2.5). The elemental composition was (% w/w dry basis): C, 47.3; H, 6.4; N, 0.7; and O, 44.6. The acid neutralization capacity of the wheat straw was 0.31 and 0.55 mol H^+/kg dw for pH 4 and 2, respectively ($t = 48$ h, determined according to CEN TS 14 429 (European Committee for Standardization, 2005)). The enzymatic digestibility of the raw material (<10 mm) without organosolv pretreatment was 21% of its theoretical maximum (20 FPU/g dry biomass, see Section 2.6).

2.2. Experimental program

Table 1 shows an overview of the organosolv experiments performed. In the first part of experiments, the influence of individual