

Lignocellulosic biomass fractionation as a pretreatment step for production of fuels and green chemicals

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Abstract

One of the main constraints and the most costly step in the production of lignocellulosic ethanol is its pretreatment that aims at liberating the cellulose by dissolving the lignin and the hemicellulose fractions. For this reason, several different pretreatment methods have been developed that aim at dissolving biomass lignin and hydrolysing the cellulosic part so as to maximize fermentation yields towards ethanol. In this work delignification of a forestry residue took place via a Milox treatment and its variations. Formic acid (FA), Acetic acid (AA) and their mixtures along with Hydrogen peroxide (HP) were used at different temperatures and concentrations as delignifying agents. Additionally, both the untreated and delignified biomass were hydrolysed with hot water (HW) under different pressures and temperatures in an attempt to depolymerize the solid feed. FA delignification was more successful yielding pulps with lignin content as low as 3 wt.%. However, AA delignification was found to be a good alternative since more holocellulose was recovered as solid in the delignified pulp. The HW hydrolysis of the untreated biomass was extremely efficient at dissolving hemicellulose while the hydrolysis of the delignified biomass yielded a liquid with increased sugars concentration. Interestingly, in the cases where Carbon dioxide (CO₂) was used to pressurize the reactor, xylose and glucose yields were increased due to the acidity that CO₂ conferred to the hot water. This allowed for lower temperature reactions which led to the minimization of byproducts such as hydroxymethyl furfural (HMF).

Keywords

biomass delignification, formic acid, hydrogen peroxide, hot water hydrolysis, lignin, cellulose

1. Introduction

Lignocellulosic Bioethanol production is one of the most important processes for the production of biofuels. The Sustainable Integrated Method for the Production of Lignocellulosic Ethanol (SIMPLE) project focuses on the development of a sustainable, high yielding, low cost green process for the production of Lignocellulosic Bioethanol. Process development and optimization focus on the selection, collection and storage methods and the overall potential and availability of biomass (mainly the residues from cotton, maize and cereals cultures and energy crops), the pretreatment of the lignocellulosic biomass, the enzymatic hydrolysis and saccharification steps and the fermentation of the biomass towards Bioethanol. In addition, byproducts such as lignin are upgraded towards fuel additives and activated carbon.

In the case of the pretreatment of lignocellulosic biomass; it has been found to be a much needed step to maximize fermentation yields towards bioethanol which is also the most costly part of the process. Lignin is believed to surround cellulose and hemicellulose, essentially making biomass highly recalcitrant to pathogens, microorganism and enzymes [1]. Different pretreatment methods have focused on delignifying the biomass so as to make holocellulose more accessible to enzymes. Among the pretreatment methods that have attracted interest lately are the organosolv processes, which employ organic solvents for removal of the lignin fraction. A wide variety of processes, solvents and parameters have been investigated ranging from the standard Milox process to combining chemical [2, 3] and physicochemical pretreatment methods [4, 5]. The main advantages of these methods are that they are less risky to the environment, can be recovered and reused thus minimizing liquid wastes, degrade the dissolved fractions far less allowing for their use for production of high added value chemicals such as phenols and hydroxymethyl furfural derived from lignin and hemicellulose respectively and produce pulps that are more easily fermented reducing the overall process cost. The Milox process is based on the effect of in situ generated peroxyformic acid and is considered one of the most important organosolv pretreatment processes. It has been applied on a variety of biomass materials [6].

Another pretreatment method that has been used extensively is the hydrothermal treatment of biomass. The main aim is the hydrolysis of the cellulose that yields sugars and oligosaccharides which may later be fermented towards ethanol. Hydrothermal pretreatment variations include using acidic or basic solutions to depolymerize the holocellulose fraction [7], while others combine chemical with mechanical treatments such ammonia fiber explosion (AFEX) [8]. In all the above cases the main constraints of the technology are (1) the usage of large volumes of chemicals and the subsequent production of large volumes of liquid wastes, (2) the high energy demand in various stages of the process, (3) the need for increasing solid content concentration throughout the process, (4) the yield of monosaccharides and oligosaccharides that is of pivotal importance for the process economics, and (5) the need to

develop a process that can successfully treat different species of biomass. Specifically, chemical usage is one of the main disadvantages of the process because it necessitates the neutralization and handling of large volumes of acidic and/or basic wastes. Acidic hydrolysis of biomass usually employs an inorganic acid such as sulfuric acid (H₂SO₄). A system that has attracted interest lately as an alternative pretreatment medium is CO₂-H₂O mixtures. The addition of CO₂ results in its partial dissolution in H₂O. The dissolved CO₂ reacts with H₂O forming carbonic acid, conferring acidity to the treatment medium which promotes the hydrolysis of biomass [9]. In contrast to conventional acidic mediums, when the CO₂-H₂O mixture is depressurized, CO₂ is immiscible with water, allowing for its easy separation and recycle without the need of downstream treatment of acidic wastes

In this work pretreatment methods were employed for the fractionation of biomass into lignin, hemicellulose and cellulose. The Milox process and its variations were employed so as to delignify the biomass with organic acids and hydrogen peroxide. In a following step hydrolysis with hot water achieved depolymerization of the holocellulose towards sugars and oligosaccharides. Catalysis was introduced in the hot water treatment that allowed for a mild lower temperature hydrolysis to take place by use of CO₂. The lignin was processed with heterogeneous catalytic pyrolysis for production of high added value chemicals such as aromatic hydrocarbons and phenols.

2. Materials and Methods

2.1 Raw material

A commercial wood biomass feed (Lignocel HBS 150-500) originating from beech wood was used in all experiments of the current study. The properties of the biomass feed are shown in Table 1. The feed was dried at 105 °C for 4 hours and kept in a dessicator before it was used in the experimental runs, therefore all results reported in this study are on a dry feed basis.

Table 1. Properties of biomass feedstock (Lignocel HBS 150-500)

Ash/solid residue (wt. %)	1.35
Carbon (wt. %)	45.98
Hydrogen (wt. %)	6.39
Oxygen ¹ (wt. %)	46.28
GHV (MJ/kg)	18.22
Na (mg/kg)	43.8
K (mg/kg)	326
Moisture (wt. %)	8.25

2.2 Milox Pulping

Single stage Milox cookings were carried out in 500 cm³ conical flasks at atmospheric pressures. FA, AA and their mixtures were used at a 10:1 solvent to biomass weight ratio. H₂O₂ was added at concentrations 1 to 3 wt.% on solvent and temperatures ranged from 25 to 90 °C. Typically 30 grams of biomass were treated for each run. The delignified biomasses were filtered and washed with 6 volumes of the corresponding solvent. Finally, the resulting pulp was washed with distilled water and dried in an oven overnight. All solvents used were of analytical grade and were purchased from Sigma-Aldrich.

2.3 Hydrolysis runs

Hot water treatment of biomass and delignified pulps was carried out in a Hatelloy C-276 Parr autoclave with a volume of 975 cm³. 30 grams of solid feedstock were fed into the reactor and 300 grams of distilled water were then poured so as to achieve a liquid to solid ratio of 10:1. The reactor was tightly sealed and pressurized up to 8.5 bars with either N₂ or CO₂. A Parr Model 4848 reactor controller was used to control the temperature inside the reactor. Uniform heating and temperature was ensured by mixing of the suspension with a propeller type agitator rotating at 150 rpm. Temperatures between 150 to 200 °C were studied for a reaction time of 2 hours in all cases. Reaching the desired temperature took typically 15 minutes; this was defined as time zero. After the prescribed reaction time the external heater was removed and the reactor was allowed to cool to room temperature; the cool down time was minimized by cooling the reactor with air externally and internally with water which was circulated through a cooling coil. Typically, 15 minutes was sufficient time for temperature to drop below 50 °C. The reaction mixture was filtered to separate the solid residues from the liquid phase. Distilled water was used to wash the solid residue and the washing water was mixed with the liquid sample received from the hydrolysis. The composition of reaction mixture in the liquid phase was determined using the Dionex chromatography systems (Section 2.3.1). Finally, the solid residue was dried overnight in an oven.

¹ Determined by difference

2.4 Pulp characterization

The biomass samples and the pulp and hydrolysis residues were analyzed for ash, moisture, C and H contents. Elemental analysis was carried out on a CHN-800 elemental analyzer (LECO Corporation, USA) according to the UOP 703 method. For the moisture content, biomass (10.00 g) was weighed in a pre-weighed and dried porcelain crucible, placed in a furnace at 105°C for 15 h. The ash content was calculated by accurately weighing the sample (2.0000 g) in a pre-weighed and dried crucible, and then placing in a muffle furnace for 16 h at 640°C.

Following these preliminary analyses, the hemicellulose, α -cellulose and lignin contents of the untreated and treated biomass samples were determined. Prior to any other analysis, biomass (ca. 10 g) was extracted with a mixture of ethanol and toluene at a ratio of 1:2 for 16 h. The extracted sample, dried in an oven at 105°C for 24 h, was used for the further analyses. The official method TAPPI222 was followed for the determination of the lignin content while the holocellulose content was determined with small modifications of the well-established Wise method. The determination of the cellulose content was based on the official method TAPPI203 and the hemicellulose content of the samples was determined by subtracting the determined α -cellulose content from the holocellulose.

2.5 Sugars determination

The analysis of sugars was performed on an ICS-5000 ion chromatography (Dionex, USA) equipped with a pulsed amperometric detector (PAD), using a CarboPac PA-1 column. The elution was performed with NaOH at 0.6ml/min. The chromatographic method developed allows the qualitative and quantitative analysis of 11 sugars and sugar alcohols and HMF.

3. Results and Discussion

As stated above, commercial Beechwood sawdust (Lignocel) was treated with FA, AA and their mixtures at various temperatures. Hydrogen peroxide was added at 1, 2 and 3 wt.% concentration on solvent. The biomass to solvent ratio was 1:10.

3.1 Milox Temperature effect

Figure 1 presents the effect of temperature on formic acid (FA) delignification. All runs had duration of 60 minutes with the exception of the run presented in figure 1 at 25 °C that had a total duration of 7 hours. Biomass component recoveries refer to the biomass component left in the solid pulp.

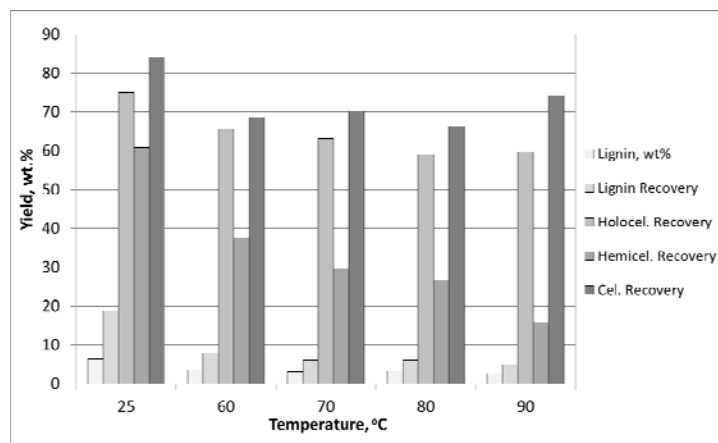


Figure 1. Lignin wt.% in final pulp and lignin, holocellulose, hemicellulose and cellulose recovery from FA/H₂O₂ biomass treatment with temperature.

As temperature increased the delignification was more effective yielding pulps with low lignin concentration. Increasing the temperature from 60 to 90 °C affected only slightly the lignin removal while the effect on hemicellulose removal was more pronounced. At higher temperatures the severity of the pretreatment was such that less hemicellulose was recovered. Cellulose was more resistant and its recovery was unaffected by the increasing severity. The low temperature high reaction time run (25 °C and 7 hrs) yielded a pulp with higher lignin content but also achieved higher holocellulose recovery mostly due to the fact that hemicellulose was retained as a solid in the final pulp due to the very mild treatment conditions. More than 50% and 80% of the hemicellulose and cellulose were recovered with lignin content in the pulp below 6%. At 80 °C lignin content of 4% was achieved, however only around 20% of the hemicellulose was recovered.

3.2 H₂O₂ concentration effect

The effect of H₂O₂ concentration was investigated at 80 °C and 1 hour runs. Figure 2 presents the data.

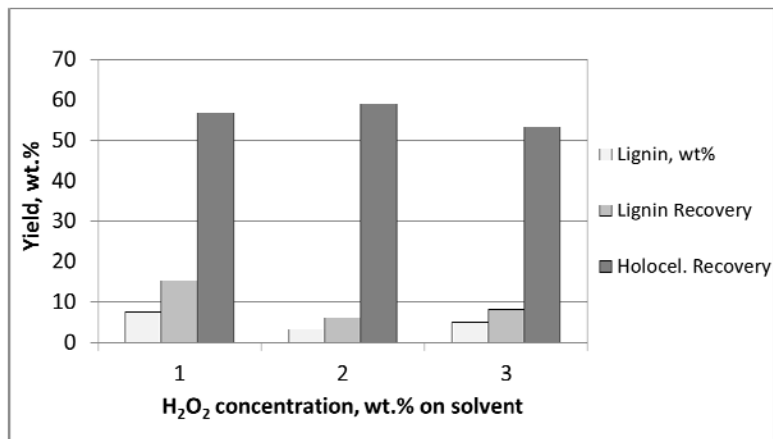


Figure 2. Lignin wt.% in final pulp and lignin, holocellulose, hemicellulose and cellulose recovery from FA/H₂O₂ biomass treatment with temperature.

Even though 80 °C was a high temperature, the run with 1 wt.% H₂O₂ concentration on solvent yielded a pulp with a high lignin content, about 8 wt.%. Increasing the H₂O₂ concentration to 2 wt.% significantly reduced the remaining lignin, lowering the the lignin recovery in the pulp from 16 to 7 wt.% on initial lignin. Further increase of H₂O₂ concentration to 3 wt.% had no effect on lignin dissolution, however the hemicellulose recovery was decreased even further due to the severity of the treatment conditions. Therefore the 2 wt.% H₂O₂ concentration was found to be adequate for effective delignification.

3.3 Hot Water-CO₂ hydrolysis

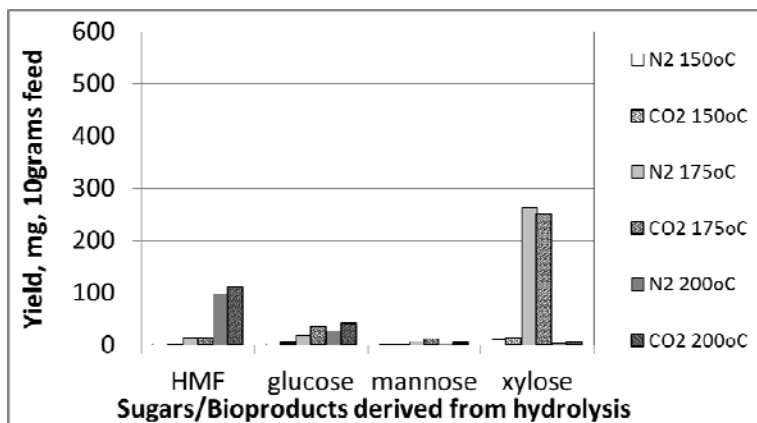


Figure 3. Sugars and HMF detected in aqueous hydrolysis residue after treatment with and without CO₂ of untreated Lignocel

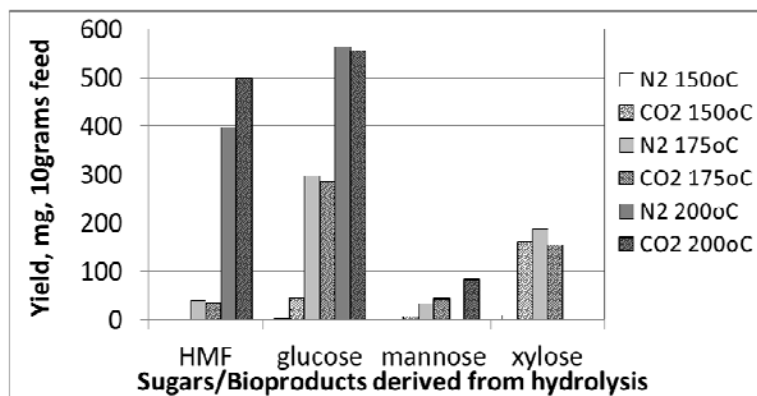


Figure 4. Sugars and HMF detected in aqueous hydrolysis residue after treatment with and without CO₂ of delignified Lignocel with FA, 80 °C, and 2 wt.% H₂O₂ concentration

Hot water treatment with and without CO₂ was performed at temperatures between 150 – 200 and pressures of 12 bar for delignified and untreated biomass. Sugar concentrations in the water after treatment are presented in figures 3

and 4. At 175 and 200 °C no effect of the CO₂ was noted, the temperature was high enough to initiate autocatalytic hydrolysis and further degradation of sugars to HMF. However, at 150 °C the presence of CO₂ resulted in depolymerization of hemicellulose and cellulose towards xylose and glucose respectively without any degradation towards HMF for the case of the delignified biomass. Apparently, the acidity conveyed in the water mixture by the dissolution of CO₂ catalyzed the depolymerization of holocellulose. Finally, comparing delignified and untreated biomass, glucose and xylose yields were much higher for delignified biomass.

3.4 Milox Lignin pyrolysis

Lignin removed with the Milox process was retrieved and pyrolyzed. Product yields are presented in Figure 5. In these preliminary results it was found that catalytic pyrolysis decreased the biooil yield, but also increased its quality which is depicted in the reduction of the biooil O₂ content. Low oil yield was attributed to the degradation of lignin and the presence of hemicellulose degradation products in the solid feed. Optimization of the fractionation process is expected to affect the pyrolysis upgrading process in a positive way.

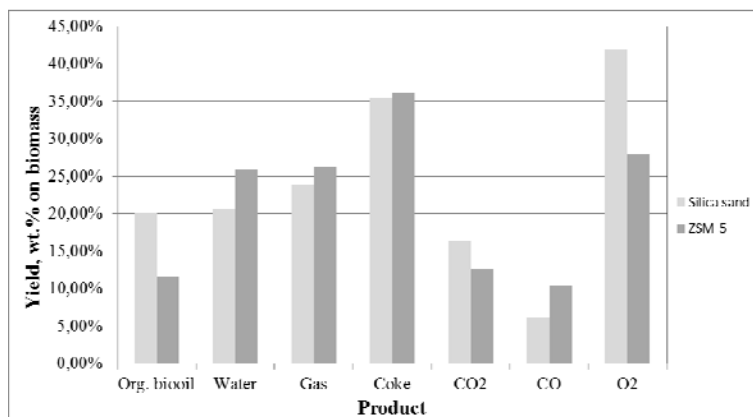


Figure 5. Milox lignin pyrolysis product yields with thermal and catalytic pyrolysis

4. Acknowledgements

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