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Waste Paper as Carbohydrate Source for Biofuel Production: An Experimental Investigation

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A key factor about the use of lignocellulosic materials to produce bioethanol is the pre-treatment step, because the lignocellulosic materials are not easily hydrolyzed by the enzymes if their crystalline structure and the lignin seal are not destroyed before. In this work the treatment of white office paper by means of the Liquid Hot Water (LHW) pretreatment is investigated. Effects of LHW are examined in a laboratory plant, with respect to the solids dissolution and sugar yields after enzymatic treatment.

1. Introduction

Nowadays bioethanol is the most important biofuel for automotive transportation, but in Europe and in the U.S.A. it is commonly produced from starchy materials like corn and wheat. Due to the competition of these crops with food industry the experimental research has recently shifted to lignocellulosic materials. Waste paper constitutes a considerable share of municipal and industrial waste even thought recycling efforts have been strengthened in recent years by legal provisions like the Packaging Directive ($99 \cdot 10^6$ tons of paper were produced in 2008 in the Confederation of European Paper Industries, with a recycling rate of 66%, CEPI, 2008). Although the actual European recycling ratio is relatively high, it has not reached a satisfactory level yet. Moreover, when paper materials are recycled, they are usually turned into lower grade paper products. With further recycling of paper, fiber length in the paper becomes shorter. Since the shortening of paper fibers decreases the quality of paper, the maximum ratio of paper-to-paper recycling is said to be 65% (Ikeda, 2006). This means that a certain fraction of paper would always be sent to disposal. This fraction contains a significant and underutilized source of sugars and could be converted to ethanol and used for energetic proposal achieving both environmental and energy benefits.
Previous research works were focused on enzymatic conversion of waste paper to monomeric sugars using enzymes without any primary treatment (Yamashita *et al.*, 2008; Vynios *et al.*, 2009; Dale and Musgrove, 2005; van Wyk, 2002), with alkali pretreatment (Saxena *et al.,* 1992) and with ultrasonic pretreatment (Ingram and Wood, 2001). Among other possible pretreatments the liquid hot water (LHW) one has the big advantage of requiring no additional chemicals. Consequently, the production of process residues does not occur and the use of low cost construction materials is possible (Lynd,

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1996). Additionally this type of pretreatment is characterized by a low generation of fermentation inhibiting products. These compounds can be further reduced by controlling the residence time of the hydrolysate at high temperature.
Up to our knowledge there are no data yet about the effect of LHW pretreatment to office paper, especially if a semibatch reactor is used.
The objective of our investigation was to determine the best pretreatment conditions (temperature and total reaction time) for the LHW of paper in order to obtain the maximum amount of fermentable sugars after the enzymatic hydrolysis. In particular the effects of LHW pretreatment on white office paper were studied. First the total dissolution of the material as a function of temperature was determined, then the enzymatic hydrolysis of the liquid fraction as well as of the solid residues was performed using cellulases and xylanases commercially available.

2. Materials and methods

2.1 Materials

The treated material was standard white office paper (80 g each A4 sheet) purchased from DiEM. The enzyme complex (Accellerase^{TM} 1000) used for the treatment of both hydrolysate and solid residues from the pretreatment was kindly supplied by Genecor$^{®}$. This enzyme complex is produced by means of a genetically modified strain derived from *Trichoderma reesei,* and has been specifically developed for the treatment of lignocellulosic biomass. The multiple enzyme activities comprise: exoglucanase (2500 CMC U/g), endoglucanase, hemicellulose and betaglucosidase (400 pNPG U/g).

2.2 LHW Pretreatment

The experiments were performed in a laboratory set up specifically designed and depicted in Figure 1, which includes a fixed-bed reactor (77.1 cm^3, ID = 21 mm) filled with the solid material.

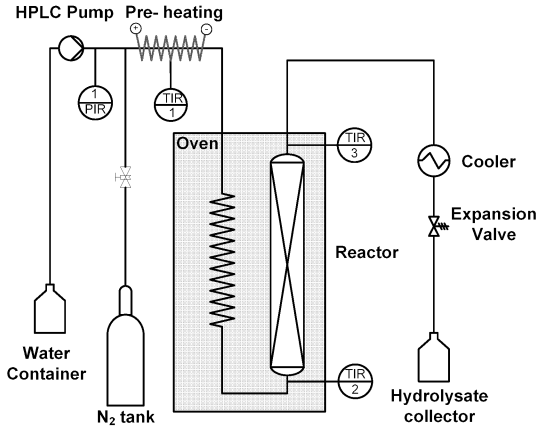


Figure 1. Semi batch reactor.

A glass wool layer and metal filter (1 mm mash size) were placed in the outlet reactor section in order to hold the paper inside.

In all experiments the same amount of paper was treated (28 g) in order to work with the same solid apparent density. The loaded reactor was placed in the oven, pressurized with nitrogen at the desired reaction pressure (60 bar), and preheated for 15 minutes at the reaction temperature. Then the HPLC pump was started and water was pumped through the reactor. All the experiments were carried out at a constant flow rate of 5 mL/min and at the same pressure (60 bar), with temperature ranging from 25 to 250 °C depending on the run. The water temperature was increased up to the reaction temperature first with an electrical resistor and then by an adequate residence time in the inlet pipe placed inside the oven. Temperature and pressure were measured and controlled during the whole experiment. At the oven exit the hydrolysate was cooled down by a water bath and collected. At the end of the reaction time the hydrolysis reaction was stopped simply by depressurising the system: the exit valve was opened to ambient conditions and the reactor was disconnected and immediately quenched in a water bath. Two different fractions were obtained: the liquid ones (hydrolysate) collected during the whole reaction time, and the solids retained in the reactor (solid residue).

2.3 Enzymatic hydrolysis

The hydrolysate fraction as well as the solid residue obtained from the LHW treatment were treated with enzymes to determine the monomeric sugars yield.
Enzymatic treatment (referred to Figure 3a and 3b): 0.1 mL of hydrolysate or 0.03 g of solid samples were added with 0.4 mL of the Accelerase™ 1000 solution and 3 mL of buffer. The enzymatic hydrolysis was carried out at 55 °C for 72 hours in an incubator.
Sensitivity (referred to Figure 4a and 4b): 1 mL of hydrolysate samples or 0.2 g of solid residue were added with different amount of enzyme complex and 2 mL of buffer. The enzymatic hydrolysis was carried out at 55 °C for 24 hours in an incubator.

2.4 Analysis

The dry matter contents of treated solid samples, raw material, and hydrolysate samples were determined by weighting the samples before and after heating at 105 °C until constant weight was reached, according to the standards given by NREL (Sluiter *et al.,* 2008). The composition of the paper was analyzed by the Institute of Wood Technology and Wood Biology (Hamburg, Germany) with the double step acid hydrolysis method.
Samples of hydrolysate were taken after the pre-treatment and were analyzed to measure glucose, and pentoses (xylose and arabinose). Monosaccharide analyses were performed using enzyme kits from Megazyme. The pH of the hydrolysate was measured with a Delta OHM pH meter.

3. Results and discussion

Table 1a shows the result of the double step acid hydrolysis on the raw paper in terms of sugar composition while Table 2b the overall composition calculated from these results. Lignin and ash content are literature data (Foyle *et al.,* 2007) while the polymeric sugars content was calculated from the double step acid hydrolysis as follows:

$$Hemicell\,\% = 0.88\%\,(Xyl + Oth) \quad (1)$$

$$Cellul\,\% = 0.9\%\,Glu \quad (2)$$

where *Xyl* and *Glu* are the monomeric xylose and glucose content of the paper, *Oth* is referred to the other sugars (like mannose, arabinose, galattose etc.) and the 0.88 and 0.9 factors are introduced to convert free sugar residues to anhydrous sugars as present in polysaccharides.

Table 1 Double step acid hydrolysis results (a) and paper overall composition (b).

	Fraction (w/w)
Glucose	70.14
Xylose	13.51
Other sugars	1.08

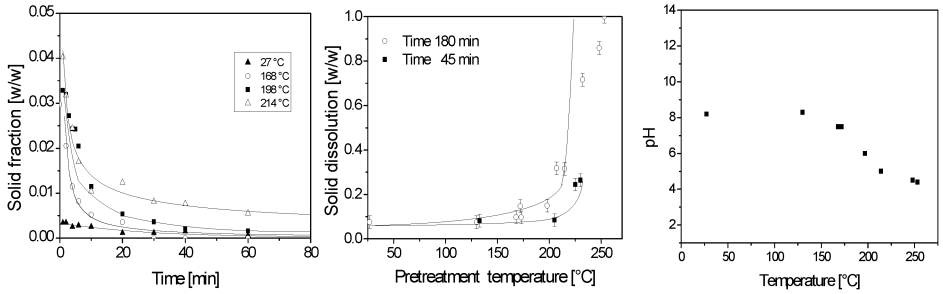
	Fraction (w/w)
Cellulose	63.13
Hemicellulose	11.89
Ash	≈13.99
Lignin	≈9.53

3.1 Hydrolysate instantaneous dissolved solid concentration

Figure 2a shows the instantaneous solid concentration in the hydrolysate. This allows determining the time needed for the dissolution. The concentration of solid in the hydrolysate increases with temperature, a clear sign that dissolution kinetics are faster at higher temperatures. For low temperatures the dissolution is over after 30 minutes, but at higer temperature this process continues for longer time.

3.2 Total solids dissolution and hydrolysate pH

Figure 2b shows the maximum amount of dissolved solid as a function of the pretreatment temperature. The experiments (empty circles) were carried out for 3 hours. Paper, unlike other biomasses, has already been subject to mechanical and chemical treatments so, when pretreated with LHW, it behaves differently.



(a) (b) (c)

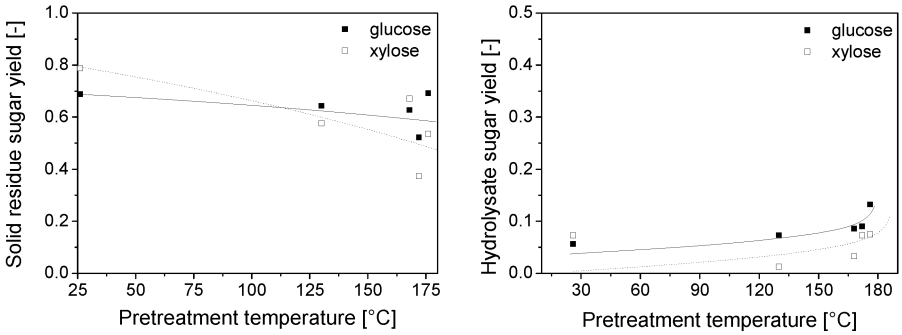
Figure 2. Instantaneous concentrations of solid in the hydrolysate during the reaction time (a) and maximum degree of dissolution at different temperatures (b). Lines represent only trends.

For instance at temperatures above 214 °C the pieces of paper are not recognizable anymore and the treated material is present, in the reactor, as a fine powder. For this reason a total solid dissolution for the points above 214 °C can be assumed. In Figure 2b some of the points above this temperature display a value below 1. This is only due to the fact that after 3 hours some of the fibers are still too big to pass through the metal filter as would happen increasing the reaction time. In Figure 2b the solids dissolved after a treatment of 45 minutes are also shown. Clearly the values are lower. Figure 2c shows the pH values of the total hydrolysate collected during experiments at different temperatures. Increasing the severity of the treatment a decrease of the pH value was

observed. This happens owing to both the formation of degradation products and the release of the acids contained in the hemicellulose.

3.3 Enzymatic treatment

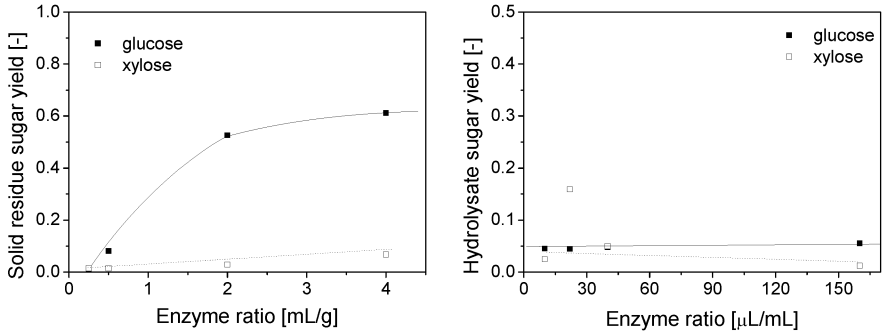
Figure 3a and 3b show the sugar yields obtained by the enzymatic treatment of the solid and of the total hydrolysate after long LHW pretreatments. As the treatment was performed with large amounts of enzymes, long reaction time and diluted condition, these data can be considered as the maximum yield obtainable with enzymes. The sugar yield was calculated as the amount of monomers detected after the enzymatic treatment divided by the total amount of monomers in the raw paper initially loaded into the reactor.



(a) (b)

Figure 3. Sugar yield after enzymatic treatment of the two fractions obtained after the LHW pretreatment: solid residue (a) and hydrolysate (b). Lines show only trends.

At the investigated temperatures only part of the sugars is solubilized. This fraction increases when increasing the temperature. Simultaneously the yield of sugars that can be obtained from the solid residues decreases. The hydrolysate sugar yields are indeed low in accordance with the effect of the LHW pretreatment which is not influenced by temperature in the range investigated. In order to test if the LHW pretreatment is really able to enhance the sugar yield, lower (and more economic in a large scale plant) enzyme/biomass ratio should be used. A sensitivity analysis (Figure 4a and 4b) has been carried out on the solid sample obtained after LHW treatment at 232 °C for 45 minutes.



(a) (b)

Figure 4. Sugar yield after enzymatic treatment as a function of the enzyme ratio. Solid residue (a), hydrolysate (b). Lines show only trends.

4. Concluding remarks

An experimental set up was built to study the LHW pretreatment of lignocellulosic materials. Samples of white office paper were treated in a semibatch reactor. Increasing the temperature a solid dissolution increase was observed. Above 214 °C the complete degradation of the biological material occurred. Similarly the pH of the hydrolysate decreased as a consequence of the release of acids from the hemicelluloses and formation of degradation products. The treatments of the hydrolysate and solid residue with enzymes showed that it is possible to obtain monomeric sugars from paper for a further possible fermentation to ethanol.

5. References

CEPI (Confederation of European Paper Industries), 2008. Key Statistics 2008 European Pulp and Paper Industry.

Dale M.C., Musgrove D., 2004. Continuous conversion of MSW-derived waste paper to bio-ethanol using a 100 L 6-stage continuous stirred reactor separator. In: AIChE Annual Meeting, Conference Proceedings, pp.8237–8242.

Foyle T., Jennings L., and Mulcahy P., 2007. Compositional analysis of lignocellulosic materials: Evaluation of methods used for sugar analysis of waste paper and straw. *Bioresource Technology,* 97, pp. 3026-3036.

Ikeda Y., Park E.Y., Naoyuki O., 2006. Bioconversion of waste office paper to gluconic acid in a turbine blade reactor by the filamentous fungus Aspergillus niger. *Bioresource Technology,* 97, pp.1030–1035.

Ingram L.O. and Wood B.E., 2001. Ethanol production from lignocellulose. United States patent, US 6,333,181 B1.

Lynd R.L., 1996. Overview and Evaluation of Fuel Ethanol from Cellulosic Biomass: Technology, Economics, the Environment, and Policy. *Annu Rev Energy Environ*, 21, pp. 403-465.

Yamashita Y., Kurosumi A., Sasaki C., and Nakamura Y., 2008. Ethanol production from paper sludge by immobilized Zymomonas mobilis. *Biochemical Engineering Journal*, 42, pp.314–319.

Saxena A., Garg S.K., and J. Verma, 1992. Simultaneous Saccharification and Fermentation of Waste Newspaper to Ethanol. *Bioresource Technology,* 42, pp. 13-15.

Sluiter A., Hames B., Hyman D., Payne C., Ruiz R., Scarlata C., Sluiter J., Templeton D., Wolfe J., 2008. Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples. Technical Report NREL/TP-510-42617 January 2008.

van Wyk J.P.H., 2002. Biodevelopment of Wastepaper as a Resource of Renewable Energy: Influence of Enzyme Concentration and Paper Amount on the Bioconversion Process. *Energy & Fuels*, 16, pp. 1277-1279

Vynios D.H., Papaioannou D.A., Filos G., Karigiannis G., Tziala T., Lagios G., 2009. Enzymatic production of glucose from waste paper. *BioResources*, 4, pp.509-521.