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BIOETHANOL PRODUCTION FROM WOOD WASTE

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ABSTRACT. Biomass is a great source of energy and has a special attention as a new raw material for biofuels production. Woody biomass is composed from cellulose, hemicellulose and lignin. Bioconversion of woody biomass to ethanol consists of four stages: pretreatment, hydrolysis, fermentation and ethanol recovery/distillation. In this study, the effect of autohydrolysis pretreatment on cellulose separation followed by enzymatic hydrolysis was investigated. Enzymatic hydrolysis was performed in all cases with *Accellerase 1500* enzymes. Ethanol obtained from wood waste has the potential to be a renewable transportation fuel or, can be used as raw material for bio-hydrogen production.

Key words: *wood, autohydrolysis, enzymatic hydrolysis, bioethanol*

INTRODUCTION

Biomass is a great source of energy and has a special attention as a new raw material for biofuels production (Ballesteros et al., 2006). In addition, agricultural residues, municipal solid waste, industrial solid waste, forestry residues are composed from carbohydrates, which can be further converted into ethanol (Sassner et al., 2008). Ethanol production from varieties species of wood was studied but is not reported the best species of wood for bioethanol production (Mabee et al, 2011).

Woody biomass is composed from cellulose, hemicellulose and lignin. Cellulose is linear homopolymer of glucose; it is rigid and required a hard treatment to break down.

The hemicellulose can be easy converted into oligosugars and monosugars, which can be fermented into bioethanol by yeast (Nakagame et al., 2011). Various methods were tested for hemicellulose, cellulose and lignin separation. Hemicellulose is considered easier to hydrolysed than cellulose, because is very soluble in water. The hemicellulose can be extracted by various extraction procedures, and then can be used for: fermentation for bioethanol production, for furfural and HMF production; in oligomeric form can be used as functional-food ingredients, etc. (Gütsch et al., 2012).

Bioconversion of woody biomass to ethanol consists of four stages: pretreatment, hydrolysis, fermentation and ethanol recovery/distillation.

Pretreatment is the most important stage from entire process of conversion because it is a crucial factor for breaking the structure of wood. Various pretreatments were studied including physic, physico-chemical and biological methods. Eco-friendly pretreatment not involve the use of chemical reagents (Oksman et al., 2011).

Autohydrolysis is an eco-friendly process in which woody biomass is treated with water at high temperature (Feria et al., 2011).

Other challenge of the bioethanol obtaining process from wood waste is represented by the presence of lignin which reduces the bioethanol yield. One of the most used methods for complete lignin removing is delignification (Senila et al., 2014).

Wood waste was converted into bioethanol after pretreatment, delignification, enzymatic hydrolysis and fermentation (Senila et al., 2011). In this study, the effect of autohydrolysis pretreatment on cellulose separation followed by enzymatic hydrolysis was investigated. Enzymatic hydrolysis was performed in all cases with *Accellerase 1500* enzymes. The influence of temperature (180, 190 and 200°C) and pretreatment time (5, 10 and 15 minutes) on the compounds resulting in liquid fraction and in solid fraction were studied. Ethanol obtained from wood waste has the potential to be a renewable transportation fuel or, can be used as raw material for bio-hydrogen production**.**

MATERIALS AND METHODS

Raw material

Wood samples were collected locally. All chemicals were analytical reagent grade. The experimental procedure used to convert wood waste to bioethanol is show schematically in figure 1.

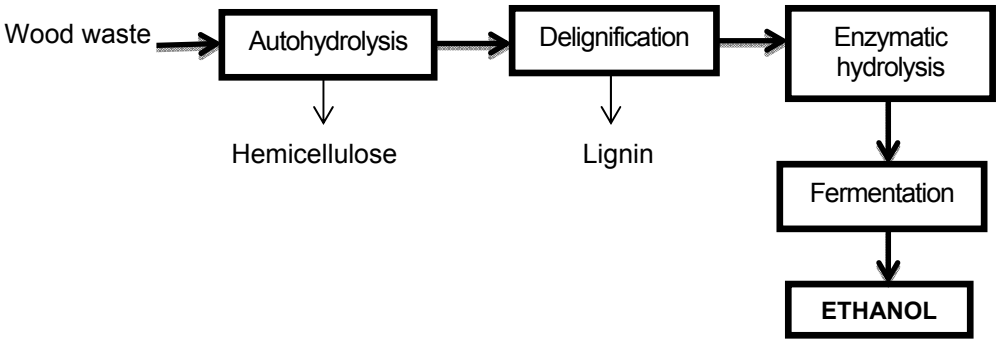

Fig.1. *Schematic representation of different treatments performed for ethanol formation*

Autohydrolysis experiments

The mixture of wood and water was homogenized at the desired proportions (7 kg/kg dry solid) and reacted in a pressurized reactor (Parr Instrument) at 180, 190 and 200°C for 5, 10 and 15 minutes. The pretreated material was separated by filtration into solid and liquid phases. The composition of wood before and after autohydrolysis was determined.

Delignification method

Pretreated material resulted after autohydrolysis pretreatment was delignified with sodium chlorite. The samples was treated with $NaClO_2$ in acetic acid 10%, at 70°C for 1 h (repeated for three times) according to Hallac et al. (2009).

Enzymatic hydrolysis

Enzymatic hydrolysis experiments of solid fraction recovered after delignification of wood were carried out in 500 ml conical flasks containing 0.05 N citrate buffers (pH 5) with 8% (w/v) concentration of pretreated and delignified material. 0.7 ml/g of *Accellerase 1500* were used for all hydrolysis.

Fermentation of sugars

The fermentation of enzymatic hydrolysates was carried out in 1L Erlenmeyer flasks containing nutrients (g/l): KH_2PO_4, 20; $MgSO_4 \cdot 7H_2O$, 10; $(NH_4)_2SO_4$, 20; $MgSO_4 \cdot 1H_2O$, 1; yeast extract, 5; inoculum of *S. cerevisiae* (pH 5) for 72 h at 30°C.

RESULTS AND DISCUSSION

The chemical compositions of wood samples are presented in table 1.

Table 1. *Chemical composition of wood samples (g/100 g wood in oven-dry basis ± standard deviations)*

Compound	Content
Cellulose	46.0 ± 0.30
Xylan	19.0 ± 0.20
Arabinan	1.3 ± 0.07
Acetyl groups	3.7 ± 0.08
Klason lignin	28.4 ± 0.20
Extractives	1.3 ± 0.10
Ash	0.3 ± 0.10

The main constituents of wood waste contain 46% cellulose, 24% hemicellulose and 28% lignin. The high content of cellulose and hemicellulose suggests that wood waste is a potential raw material for bioethanol production.

In this study, autohydrolysis pretreatments were applied to the biomass for separation the components of wood. Through this stage, hemicellulose fraction is recovered in liquid fraction and cellulose and lignin are recovered in solid fraction.

The chemical delignification of wood treated by autohydrolysis was applied in order to enhance the enzymatic hydrolysis and lignin removal. Sodium chlorite acts as delignification agent by depolymerisation of lignin because produce chlorine dioxide. The physic aspects of wood are shown in figure 2.

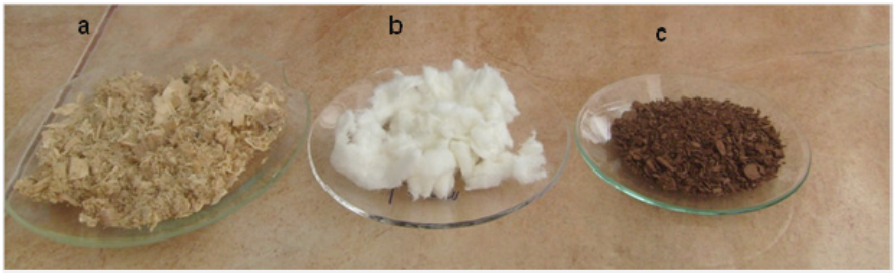

Fig. 2. *Photo of the physical aspects of wood: (a) untreated, (b) cellulosic material obtained after autohydrolyzed delignified wood waste and (c) material obtained after autohydrolysis*

Autohydrolysis pretreatments were carried out at three different temperatures (180, 190 and 200°C) and three different reaction times (5, 10 and 15 min for each temperature). The compositions of wood waste after autohydrolysis pretreatments are presented in table 2.

Table 2. *The solids yields and composition of solids, after autohydrolysis*

Autohydrolysis condition	180°C			190°C			200°C		
	5	10	15	5	10	15	5	10	15
Solid yield (g/100 g raw material, on dry basis)	81.5	79.5	76.5	75.3	74.6	73.6	73.1	72.2	71.9
Solids comp. (g/100 g autohydrolyzed wood, on dry basis)	93.4	96.9	89.4	92.9	98.9	96.9	95.6	98.2	94.4
Cellulose	48.6	56.6	50.6	52.3	57.8	55.9	56.3	59.5	54.9
Hemicellulose	6.2	4.7	4.2	3.8	3.3	2.5	1.1	0.0	0.0
Lignin	38.6	35.6	36.6	36.8	37.8	38.5	38.2	38.7	39.5

Samples treated at 190°C and 10 min reaction time led to the maximal recovery of cellulose in solid fraction. The solid yields varied in the range 71.9 - 81.5g/100 g oven-dry wood. Autohydrolysis solids contained 48.6-59.5 cellulose/ 100 g wood, 0.0-6.2 hemicellulose/100 g wood and 35.6-39.5 lignin/100 g wood. The results presented in table 2 show that the amount of cellulose an lignin are light affected by hydrothermal pretreatment whereas hemicellulose is the most degraded and converted into monomers and oligomers.

The sodium chlorite delignification method was performed to solid material recovered after autohydrolysis pretreatment.

Lignin acts as inhibitor for enzymatic hydrolysis, and the removal of lignin before enzymatic hydrolysis improves enzymatic hydrolysis yields (Nakagame et al., 2011). Taking into account these observations, sodium chlorite delignification was applied for lignin removal before enzymatic hydrolysis.

Fermentation of sugars was performed with *S. cerevisiae* yeast. Final ethanol concentration of 17.9 g/l was obtained for fermentation of sugars that had been obtained by fermentation of substrates (the substrates were obtained after autohydrolysis performed at 190°C and 10 min reaction time).

CONCLUSIONS

This work demonstrates that wood waste is a potential feedstock for production of bioethanol by autohydrolysis, sodium chlorite delignification, enzymatic hydrolysis and fermentation of sugars to bioethanol. Autohydrolysis pretreatment is a green method for cellulose and hemicellulose separation. Temperature was the most important parameter that influences the pretreatment, enzymatic hydrolysis and fermentation.

REFERENCES

Ballesteros I., Negro M.J., Oliva J.M., Cabanas A., Manzanares P., Ballesteros M., 2006, Ethanol production from steam-explosion pretreated wheat straw, *Appl. Biochem. Biotechnol.*, **130**, pp. 496–508.

Feria M.J., López F., García J.C., Pérez A., Zamudio M.A.M., Alfaro A., 2011, Valorization of *Leucaena leucocephala* for energy and chemicals from autohydrolysis, *Biomass and Bioenergy*, **35(2)**, pp. 2224-2233.

Gütsch J.S., Nousiainen T., Sixta H., 2012, Comparative evaluation of autohydrolysis and acid-catalyzed hydrolysis of *Eucalyptus globulus* wood, *Bioresour Technol.*, **109**, pp. 77-85.

Hallac B.B., Sannigrahi P., Pu Y., Ray M., Murphy R.J., Ragauskas A.J.J., 2009, Biomass characterization of Buddleja davidii; a potential feedstock for biofuel production, *Agric. Food Chem.*, **57**, pp.1275-1281.

Mabee W.E., McFarlane P.N., Saddler J.N., 2011, Biomass availability for lignocellulosic ethanol production, *Biomass and Bioenergy*, **35**(**11**), pp. 4519-4529.

Nakagame S., Chandra R.P., Kadla J.F., Saddler, J.N., 2011, The isolation, characterization and effect of lignin isolated from steam pretreated Douglas-fir on the enzymatic hydrolysis of cellulose, *Bioresour. Technol.*, **102**, pp. 4507-4517.

Oksman K., Etang J.A., Mathew A.P., Jonoobi M., 2011, Cellulose nanowhiskers separated from a bio-residue from wood bioethanol production, *Biomass and Bioenergy*, **35(1)**, pp. 146-152.

Sassner P., Martensson C.G., Galbe M., Zacchi G., 2008, Steam pretreatment of H_2SO_4-impregnated *Salix* for the production of bioethanol, *Bioresour Technol*, **99**, pp. 137–145.

Senila L., Gog A., Senila M., Roman C., Silaghi-Dumitrescu L., 2011, Analysis of carbohydrates obtained from wood by gas chromatography-mass spectrometry, *Revista de Chimie*, **62(2)**, pp. 49-153.

Senila, L., Senila, M., Costiug S., Miclean M., Varaticeanu, C., Roman, C., 2014, Autohydrolysis of *Albies alba* wood using adaptive neural fuzzy interference system mathematical modeling, *International Journal of Green Chemistry,* **11**, pp. 1-14.