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Evaluation of Acid and Enzymatic Hydrolysis of Hemicellulose Extracts Produced from Northeast Hardwood

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1. ABSTRACT

At the University of Maine, a hemicellulose pre-extraction technology is now being investigated to improve pulp yields, reduce organic and inorganic load for liquor recovery, and create a feed stream for the generation of new biomaterials.

In this study, we investigate 1. the extent of hemicellulose recovery by pre-extraction using green liquor pretreatment and 2. characterize the hydrolysis of the extract with respect to variable concentration via evaporation and comparing acid and enzymatic hydrolysis.

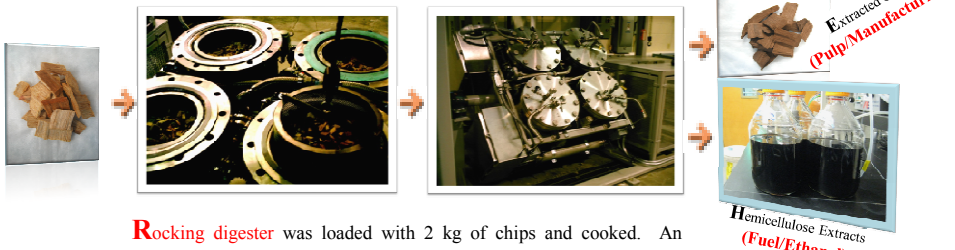
2. INTRODUCTION

Forest biomass is a promising resource for future biofuels and bioproducts. Biorefining wood into paper and chemicals is not as easy as making a single traditional paper product.

Paper is made from the cellulose fraction of wood. Removing lignin and hemicellulose components through a liquid pre-extraction can enhance the quality of the pulp. Pre-extraction of hemicellulose by alkaline (Green Liquor) pretreatment produces a neutral-pH extract containing hemicellulose.

One near term option is to carefully pre-extract the hemicellulose before the main pulping step and then ferment it to bioethanol. A significant difference from other lignocellulosic biomass conversion processes is that the solid fraction has high value to make pulp and paper products and is thus not converted to liquids or boiler fuel.

3. PRE-EXTRACTION PROCESS



Rocking digester was loaded with 2 kg of chips and cooked. An effective Green Liquor of 3 % on chips was used for all cases with liquor to wood ratio of 4:1. This system was agitated (2 rpm) at 160 ◦C for 110 minutes yielding an H-factor of 800.

4. ACID AND ENZYME HYDROLYSIS OF EXTRACTS

The sulfuric acid hydrolysis was conducted with 10 mL hemicellulose extract at various concentration from 2 to 6 %. The temperature ranged from 100 to 160 ºC. The residence time range from 2- to 258-min. All batch Acid hydrolysis experiments were performed using sealed Tubular Reactors (Figure 1). Temperatures of the vessel are adjusted in oil (Heat Transfer Fluid 550, Fisher, Pittsburgh, PA) heating/cooling baths.

Figure 1. Schematic of Acid Hydrolysis Vessel Fitted with Swagelok.

The enzymes 3000 U/g xylanase from *Trichoderma viride* was tested with 10 mL working volume at various loadings from 0.4 to 4 %. The pH ranged from pH 1.5 to 6.0 in increments of one-half pH unit. The agitation (68 RPM), reaction time (96 hours), and temperature (40 ºC) were constant. The pH was adjusted with 1 M NaOH or HCl.

5. CARBOHYDRATE ANALYSIS

Dionex model HPAEC-PAD (LC30 Chromatography, Dionex Corp., Sunnyvale, CA) and Shimadzu model HPLC (LC-10AT Liquid Chromatogram, Shimadzu Corp., Kyoto, Japan) were used for determining the carbohydrates and decomposed products.

6. RESULTS AND DISCUSSION

Table 1. Chemical Composition of Northeast Mixed Hardwood on Dry Basis.

Components	Dry solids (%, w/w)
Glucan	42.1
Xylan	18.3
Mannan	2.2
Galactan	1.9
Arabinan	1.8
Acetyl	3.6
Lignin	24.2
Ash	0.5
Extractives	1.9
Nitrogen	0.26
Uronic Acid	2.39

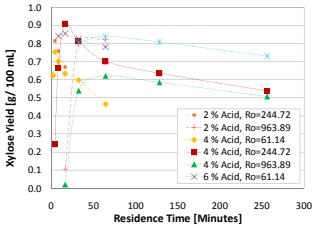


Figure 2. Soluble Xylose Yield from Extracts after Secondary Acid Hydrolysis as Function of Residence Time.

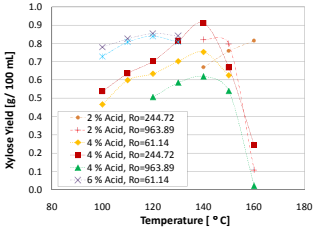


Figure 3. Soluble Xylose Yield from Extracts after Secondary Acid Hydrolysis as Function of Temperature.

The reaction ordinate is given by $R_o = t_r \cdot \exp[(T_r - 100)/14.75]$ in which t_r is the residence time in minutes and T_r is the reaction temperature. The acid hydrolysis conditions are expressed as R_o (severity factor). The data in Figure 2 and 3 indicate that the xylose sugar yield is dependent upon the reaction temperature, time, and H_2SO_4 dose of secondary acid hydrolysis. Figure 2 and 3 present that the maximum yield of xylose was 0.91 g/100mL after dilute acid hydrolysis of 4 % H_2SO_4 (w/v) extracted hemicellulose liquor for 16 min at 140 °C (R_o=244.72).

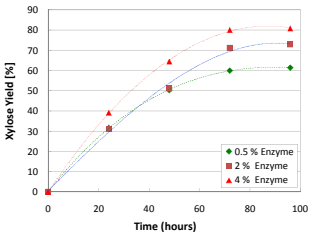


Figure 4. Effect of Xylanase Loading on Xylose Yield (pH=6.0).

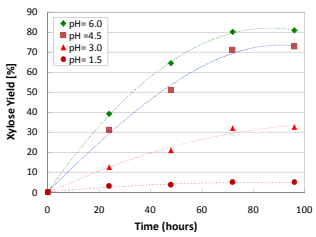


Figure 5. Effect of pH on Xylose Yield (4 % xylanase loading).

Table 2. Comparison of Operating Conditions at the Highest Xylose Yield.

Conditions	Acid Hydrolysis	Enzyme Hydrolysis
Extracts	5.78 % Total Solid	
Temperature	140 ºC	40 ºC
Residence Time	16 min.	72 hr.
Acid/Enzyme	4 % (w/v)	4 % (w/w)
Acid/Enzyme	Sulfuric Acid	Xylanase
pH	0.85	6.00
Xylose Yield	95.8 %	80.1 %
Temperature Controller	Oil bath	Incubator
Reactor	Tubular Reactor	Erlenmeyer Flask

Figure 4 and 5 present the effect of enzyme loading and pH on xylose yield from 5.78 % consistency of extract as function of hydrolysis time at 40 ºC. The range of xylanase loading, from 0.5 to 4 %, was selected for comparison with the xylose yield of the extract. The maximum xylose sugar yield was 80.1 % at the pH 6.0 and 4 % enzyme loading.

7. CONCLUSIONS

The maximum fermentable sugar yield from acid and enzyme hydrolysis of the extract was 0.91 g/100mL (95.5 %) and 0.76 g/100 mL (80.1%) respectively (Table 2). Attempts will be made to increase the sugar concentration in the hemicellulose extract so as to improve ethanol yield in the ethanol fermentation broth. It is conceivable that higher xylose yields may be achieved with optimal combination of temperature, acid (enzyme) concentration, pH, and reaction times.

8. ACKNOWLEDGEMENT

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