Prehydrolysis of birch wood with sulfur dioxide

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The ever-increasing price of crude oil has prompted great interest in production of chemicals from biomass. Waste or low-value woods. especially the abundant low-grade hardwoods. could serve as a raw material for chemical production. Previous analyses have indicated that the best approach to chemical production is to separate the various wood components and to produce high-quality products from the separate fractions (*1*). However, the prospect of producing chemicals such as furfural and ethanol from hardwoods is not very promising with present technology (*2*). New approaches need study.

Prehydrolysis of hardwoods with sulfur dioxide at low water-to-wood ratios (about 1:1) is being studied in our laboratory. The intended approach is to hydrolyze a large portion of the xylan hemicellulose prior to using the lignocellulosic residue for fiber products. The cellulose in the residue might alternatively he hydrolyzed to glucose. Two new acid hydrolysis processes for converting cellulose to glucose are currently under development (*3, 4*). The xylose from prehydrolysis could be converted to furfural, xylitol. yeast, or a great variety of other chemical and biochemical products.

Recently Lee *et al.* (*5*) studied the prehydrolysis of southern red oak sawdust with aqueous solutions of sulfuric acid, sulfur dioxide, and acetic acid. Sulfuric acid was thought to be the most promising catalyst. Best reaction conditions for the prehydrolysis were thought to be: 0.1% sulfuric acid, 4:1 liquor to wood, 170°C. and a 2-hr reaction time. Rased on these conditions, the process economics for producing a 7% pentose solution were estimated. It was found that the total processing cost of sugar in the pentose solution (not including raw material cost) was 2.9¥/lb (6.4¥/kg) of sugar. The cost of steam for heating the reactor and evaporating the dilute neutralized solution to 7% was 64% of the total processing cost.

Work in progress on prehydrolysis of white birch (*Betula papyrifera*) wood with sulfur dioxide presents an alternative means for producing a relatively concentrated pentose solution with a very small requirement for steam or other forms of energy. The key ideas are to conduct the prehydrolysis reaction at a very low liquor-to-wood ratio (called vapor-phase cooking in the pulp industry) and to obtain a relatively concentrated solution by countercurrently extracting the xylose. xylose oligomers, and other solubilized material from the reacted chips.

Materials and methods

Vapor phase prehydrolysis of Wiley-milled white birch wood was carried out in 0.75-in. (1.9-cm)-diameter type 316 stainless steel tubes 8 in. (20.3 cm) long, fitted with end caps. One end cap on each reactor was fitted with a valve and the other cap contained a pressure transducer for determining reaction pressure. The reaction was carried out by immersing the tube in a constant-temperature oil bath. For each reaction, condition-fresh Wiley-milled birch wood particles that passed through a USS No. 12 screen but were held by a USS No. 20 screen were loaded into a tube, and a vacuum was drawn on the tube to remove the air. The tube was weighed before and after evacuation to determine the quantity of water lost. So that the precise weight of ovendry wood and of water in the tube would be known, the moisture content of a representative sample of the screened wood particles was accurately determined, Pure sulfur dioxide gas was introduced into the tube through the valve and the tube reweighed to accurately determine the quantity of SO_2 present. The tube was then plunged into an oil bath controlled at the reaction temperature; after the desired reaction time the tube was removed. Reaction pressure was observed with the pressure transducer.

Contents of the tube were removed after cooling and thoroughly washed with distilled water. These washings were made up to exactly 500.0 ml and analyzed for reducing sugars using paper chromatography (*6*). An aliquot of the wash liquor was subjected to a post hydrolysis (4.0% H_2SO_4, 120°C. 1 hr) to hydrolyze oligomers; reducing sugars again were determined. Both the original wood and the washed solid residue left after react ion were analyzed for lignin and anhydrosugar units using TAPPI Standard Method T-250-75 for analysis of wood and pulps (*6*). The amount of sulfur dioxide present in the liquid phase on the wood particles at the beginning of the reaction (at reaction temperature) was determined using the sulfur dioxide–water equilibrium data of Spall (*7*). For a given reaction temperature and pressure, Spall's data were used to obtain the vapor phase composition and density. The amount

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of unvaporized sulfur dioxide associated with the unvaporized water and wood could then be calculated from the weights of sulfur dioxide. water, and ovendry wood introduced into the tube and from the exact tube volume. This quantity of liquid phase sulfur dioxide is expressed as percent of sulfur dioxide in the total unvaporized water and unvaporized sulfur dioxide.

Results and discussion

Data for two reaction conditions are given in Table I. For both conditions, about 10% of the initial lignin was solubilized and about 5% of the initial glucan, but the principal component hydrolyzed and solubilized was the xylan. Thus, nearly 60% of the original xylan in the wood was solubilized for Condition 1 and nearly 90% for Condition 2. Most of the solubilized xylan was found as xylose and its oligomers in the solution. Xylose plus xylose oligomer concentration in the liquid on the wood particles was 17% for Condition 1 and 21% for Condition 2. Countercurrent extraction of these wood particles with water could yield solutions having xylose concentrations well over 10%. These solutions should not require further concentration before being used for furfural production (*8*). Production costs for xylose in this situation would be expected to be much lower than those estimated for the process proposed by Lee *et al.* (*5*).

I. Results of vapor phase prehydrolysis of white birch wood with sulfur dioxide

	Condition	
	1	*2*
Variable		
Temperature, °C	100	120
Reaction time, min	120	120
Water:wood	0.57:1	0.57:1
SO_2 in liquid, %	14	13
Beg inning pressure,[a] atm	6.5	8.7
Result		
Yield of solid, %	73	62
Potential xylose solubilized, %	55	88
Solubilized xylose and xylose oligomers found in solution, %	94	81
Xylose and xylose oligomers in the solution on the wood particles. %	17	21

[a]To convert to Pa, multiply by 1.013 × 10^6

Mammers and Grave (*9*) studied the vapor phase sulfur dioxide pulping of *Eucalyptus regnans*. They cooked their chips in a digester which contained a quantity of liquid SO_2 beneath but not contacting the chips. At a reaction temperature of 120°C their reactor pressure was over 36 atm (3.6×10^6 Pa). The reactor pressures observed here (Table I) never attained 10 atm (1.0×10^6 Pa). For an aqueous solution of 13% sulfur dioxide, the equilibrium vapor pressure at 120°C is 15.8 atm (1.6×10^6 Pa). With birch wood present in our reactor tube, the initial pressure exerted by the 13% sulfur dioxide in the unvaporized water and sulfur dioxide on the wood was only 8.7 atm (8.8×10^5 Pa) at a temperature of 120°C. This great reduction in pressure, which was also observed in Condition 1, is due to the interaction of the wood with the sulfur dioxide. Such wood–sulfur dioxide interactions have been previously reported. Dry white spruce wood has been found to absorb 13.6% SO_2 when placed in gaseous sulfur dioxide at 22°C and 1.0 atm (1.0×10^5 Pa) pressure (*10*). The reactor pressure for Condition 2 was just slightly higherthan that found in the prehydrolysis process evaluated by Lee *et al.* (0.1% H_2SO^4, 170°C), where reactor pressure was about 8 atm (8×10^6 Pa).

Based on the present data, vapor phase prehydrolysis of hardwoods with sulfur dioxide appears promising for removal of large fractions of the xylan hemicellulose and consequent production of xylose solutions with concentrations above 10%. The suitability of the prehydrolyzed residues for further processing to pulp, glucose, or other products needs to be carefully studied. Vapor phase prehydrolysis with mineral acids, although not studied, also could be promising when compared with liquid phase prehydrolysis.

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