Saccharification of Hardwood Hemicellulose by Solid Acid

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고체산에 의한 활엽수 헤미셀룰로오스의 당화

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ABSTRACT

The kinetics of secondary hydrolysis of hemicellulose prehydrolyzate by a solid superacid, Nafion, was investigated. The maximum attainable xylose yields determined from continuous column reactor operation were about 90%. Nafion was found to be a stable hydrolytic catalyst provided that the feed solution was free of cationic substances.

INTRODUCTION

Hemicellulose accounts for 10-40% of natural cellulosic biomass (1). Its utilization in the overall biomass processing is of vital importance especially from the economic standpoint. The fact that hemicellulose is considerably easier to hydrolyze than cellulose, makes it possible to selectively hydrolyze only the hemicellulose from the biomass. Conventional hemicellulose hydrolysis by dilute sulfuric acid produces sugar products containing considerable amounts of oligomers (primarily soluble xylans) (2). Thus it becomes necessary to conduct a secondary hydrolysis to convert the oligomers into monomers. The secondary hydrolysis is generally carried out by acid treatment in which a substantial amount of acid is consumed and an appreciable degree of sugar decomposition occurs (3). As a means of overcoming these problems, the use of solid superacid as the hydrolytic catalyst was explored in this study.

Superacids are defined in a broad sense as proton donors stronger than pure sulfuric acid. The solid form of superacid catalysts has been under extensive investigation in a number of reactions involving hydrocarbons (4-6) and cellulosic and other carbohydrate materials (7)

For this work, a commercially available perfluorinated sulfonic acid resin, Nafion, was chosen in consideration of its proven hydrolytic activity (7) and a thermal stability much higher than conventional nonfluoro-type resins. The overall process scheme projected in this study is a two-stage hydrolysis of hemicellulose : autohydrolysis (or water hydrolysis) of hardwood hemicellulose, followed by secondary hydrolysis using Nafion. The advantages sought in this scheme are that there is no catalyst consumption, very little sugar decomposition, and the reaction is carried out under an acid free, and thus a corrosion free reaction environment. The main purpose of this investigation was to evaluate Nafion as a process catalyst in the secondary hydrolysis of hemicellulose, and to determine the reaction kinetics associated with it.

MATERIALS AND METHODS

Feed preparation

Particles of hardwood (southern red oak) were used as the initial feed material. The prehydrolyzates used for secondary hydrolysis were prepared by autohydrolysis of wood particles in which only water was used without the addition of acid. In the procedure the water slurry of wood particles (20% solid) was heated in an autoclave

(Parr Instrument, Model 4552) for one hour at 160℃. The slurry was then filtered to remove the solids. The prehydrolyzates thus prepared were demineralized by treating with cationic exchange resin (Amberlite IR 120P) and subsequently with anion exchange resin (Amberlite IRA 68) to adjust the pH to 4.2. The anion treatment was done to suppress the reaction by free acid. The feed hydrolyzates were concentrated where applicable using a vacuum evaporator.

Reactor and Operation

A schematic diagram for the reactor set-up is shown in Fig. 1. Reactors of three different sizes(7.8, 15.2, and 57ml) were constructed out of SS-314 tubing (I.D. 1.1cm) and used in packed-bed form. The two smaller reactors were used as a differential reactor for which the reaction conversion per pass did not exceed 5%. The larger reactor (57ml) was used as a continuous integral reactor in which the reaction conversions were not limited in its operation. The reactor temperature was controlled by oil bath (Haake FS2) and monitored by ther-

mocouple thermometer (Omega 2175A). To prevent evaporation of reactant fluid, the reactor system was put under 60 psig of nitrogen back pressure in tank A of the diagram. Samples of continuous operation were taken after four times the reactor void volume of liquid had passed through the reactor, at which time a steady state was reached. The catalyst used in this study was perfluorinated sulfonic acid resin (Nafion 1200, C.G. Processing, Rockland, Delaware) with nominal particle size of 60-100 mesh.

Analytical Methods

The sugar and oligomer contents were determined by HPLC equipped with refractive index detector (Waters Associate). The column contained Bio-Rad Q-15S ion exchange resin in calcium form. The furfural and hydroxymethyl furfural (HMF) contents were measured by the same HPLC unit using a UV detector (Varian, Aerograph VUV 10) set at 254nm. The prehydrolyzates of hardwood hemicellulose are composed primarily of xylose and its oligomers (about 90% of total sugar content). Therefore, only the xylose component was accounted in calculations involving kinetics.

RESULTS AND DISCUSSION

Preliminary Study

A preliminary test was undertaken to confirm the catalytic activity of solid superacid in hydrolytic reactions. In this study, Nafion 1200EW, 60-100mesh was used to hydrolyze a model compound of cellobiose. Additionally, free sulfuric acid and Bio-Rad Aminex AG 50Wx4 ion exchange resin (less than 400mesh, hydrogen form) were tested for comparison purpose. The experiments were carried out in glass ampules, and the reaction temperature and initial cellobiose concentration were 130℃ and 2% W/V, respectively. The results are summarized in Fig. 2 and Table 1 showing reaction progress and reaction rate constants, respectively. The amount of each catalyst was preadjusted such that the overall hydrolytic reactivity is about the same for each case. The data therefore do not verify the specific activity. However, the point to be stressed here is there is very significant difference information of HMF, a decomposition product. Note the scale difference between HMF and sugar. Decomposition of sugar is always accompanied in acid catalyzed hydrolysis of di- or polysaccharides. The sugar
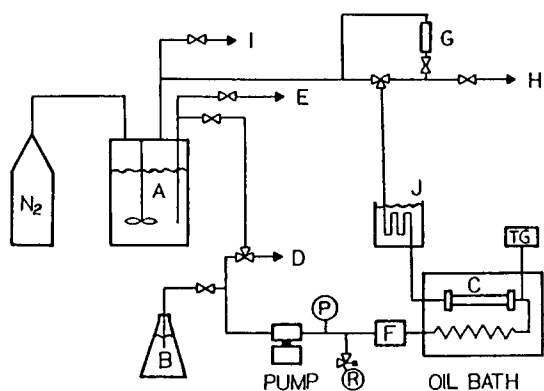
A : Feed reservoir for recirculation batch operation
B : Feed reservoir for continuous operation
C : Reactor
D : Sample outlet for recirculated batch operation
E : Waste
F : On-line filter
G : Sample holder for continuous operation
H : Sample outlet for continuous operation
I : Pressure release valve
J : Cooling tank
N_2 : Nitrogen back pressure tank
P : Pressure gauge
R : Relief valve
TG : Thermocouple gauge

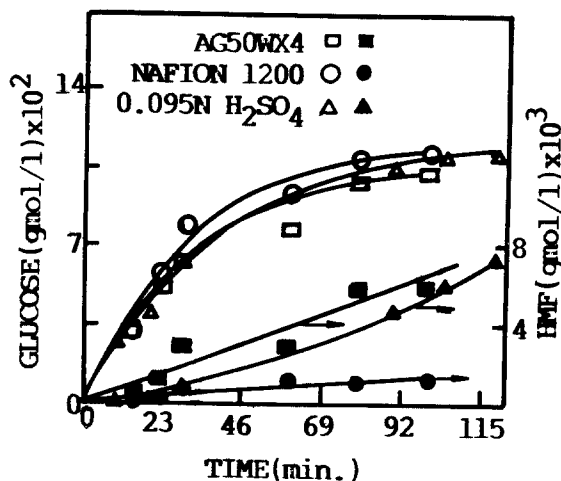**Fig. 1. Schematic Diagram for Reactor Set-Up.**

Fig. 2. Reaction progress in cellobiose hydrolysis by solid and free acids.

Table 1. Statistically Determined Rate Constants for Hydrolysis of Cellobiose Using Solid and Free Acids.

(Reaction: Cellobiose $\xrightarrow{k_1}$ 2 Glucose $\xrightarrow{k_2}$ 2 HMF)

	k_1 (min^{-1})	k_2 (min^{-1})	k_1/k_2
AG50WX4	0.0275	0.00138	20
Nafion 1200	0.0333	0.00018	185
0.0953N H$_2$SO$_4$	0.0326	0.00073	45

decomposition products such as furfural and HMF are potent inhibitors in fermentation process causing direct cell death even at a low level (8). From this standpoint, a clear advantage goes with Nafion over regular ion exchange resin or free sulfuric acid as seen in Fig. 2 and Table 1. The level of HMF formed with Nafion at the completion of hydrolysis is about 1 / 5 of that formed with either Aminex resin or free sulfuric acid. In quantitative terms, the ratio of the two kinetic constants(k_1 / k_2) represents an index for the selectivity of the catalyst. Such a ratio for the solid superacid is an order of magnitude higher than that of sulfuric acid or Aminex resin.

Kinetics

The kinetic investigation was focused on hydrolysis of oligomers in prehydrolyzate (A) into xylose monomer (B). For convenience, the molarity of the prehydrolyzate (reactant) was defined in terms of total moles of xylose units so that the stoichiometry could be expressed simply by A→B. To avoid the effect of xylose decomposition, which becomes significant only at high conversion, the kinetic experiments concerning rate constant determination were performed for the initial rate.

The initial rate data were obtained by operating the differential reactor in a continuous manner. The reaction rates were computed from the following differential reactor equation:

$$- r_A = \frac{v \cdot C_{Ao} \Delta X_A}{W_{cat}} \text{(g-mol / min·g-cat)} \qquad (1)$$

where v = flow rate (ℓ / min)

C_{AO} = initial oligomer concentration(g-mol/l)

$\Delta X_A = X_A - X_{A, \text{ initial}}$ = conversion

$X_{A, \text{ initial}}$ = conversion during prehydrolysis

W_{cat} = weight of catalyst in the reactor(g)

In Fig. 3 the initial rates at a fixed temperature of 110℃ are presents as a function of feed concentration. The linear relationship in the figure indicates that the reaction is of the first order. The initial rate data were obtained at various temperatures ranging from 100 to 140℃ and presented by the Arrhenius plot of Fig. 4. From the shape of the plot it is seen that the reaction is under the influence of diffusion at temperatures of 130℃
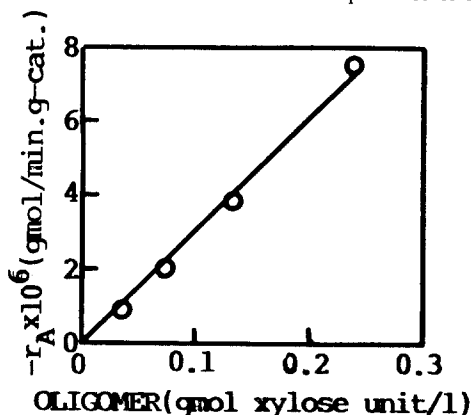

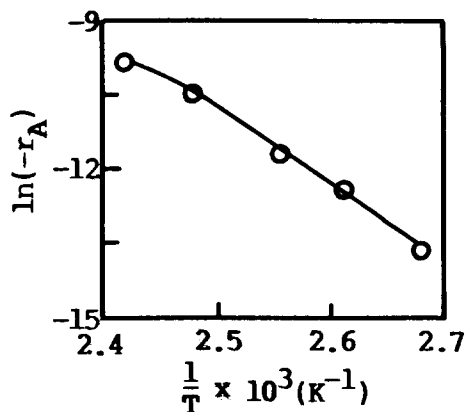Fig. 3. Initial rate versus feed concentration. (110°C & 10.42g catalyst loading)

Fig. 4. Arrhenius plot of initial rate data.

Fig. 5. Xylose production in continuous hydro-lysis using integral plug flow reactor. (catalyst loading, 42g/ml reactor volume).

and higher. The activation energy estimated from Fig. 4, excluding the data point at 140℃, was E = 30,200cal / g-mol. This value was somewhat lower than that of xylose oligomer hydrolysis by free sulfuric acid reported by Kamiyama et al. (9), E = 34,000cal / g-mol. For activation energies, a difference of this magnitude is often within the standard deviation, indicating that the reaction mechanism of solid acid catalyzed hydrolyis does not differ from that of homogeneous hydrolysis catalyzed by free acid. They also reported that hydrolysis of xylose oligomers in dilute sulfuric acid followed first order kinetics. The following Arrhenius equation can then be used to estimate the rate constants at temperatures below 130 :

$$k = 4.63 \times 10^{12} . \exp\frac{-30,200}{RT} \qquad (2)$$

where k is in units of ℓ / min·g-cat, a quantity proportional to catalyst loading, and T is in degrees Kelvin.

Performance

The solid superacid has also been tested as a process catalyst in experiments using an integral plug flow reactor. In these experiments the feed solution was continuously pumped through the reactor column, allowing sufficient residence time to achieve a high degree of conversion in a single pass. The conversion versus residence time (reactor void volume/flow rate) profiles are shown in Fig. 5 for reaction temperatures of 120℃ and 130℃. As shown in the figure, a maximum degree of conversion was achieved with residence times of 10 and
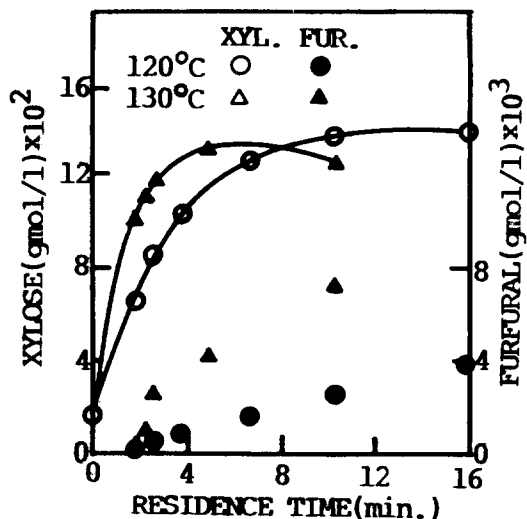
3 min at 120 and 130℃, respectively. A residence time above these limits promoted a rather significant decomposition of xylose as indicated by furfural data shown in the figure. The maximum attainable xylose yields as determined from Fig.5 were about 90%, the balance being unreacted oligomer and loss due to decomposition of sugar. A yield of this level would be quite satisfactory from a process viewpoint. As for the loss of xylose by decomposition, only a small fraction of it appeared as furfural. (Note that the furfural level is shown on a scale expanded 10 times). The rest is unaccounted for at this time since the analytical work performed in this study was limited to sugars and furfural only.

Stability of Nafion

During the ion exchange resin treatments, the color of the prehydrolyzate was changed from dark brown to light yellow. It is known that cation resins remove proteinaceous components, some color materials as well as metallic constituents of salts. Anion resins remove odiferous and flavoring components, and color materials (11). In spite of the ion exchange resin treatments of the prehydrolyzate, Nation had darkened with repeated use and deposition of foreign substances was observed on the surface of the catalyst particles. Nevertheless continuous use of Nafion for 160 hours did not cause any appreciable degree of deactivation (see Fig. 6). This test was conducted using deionized feed solution. The conductiv-
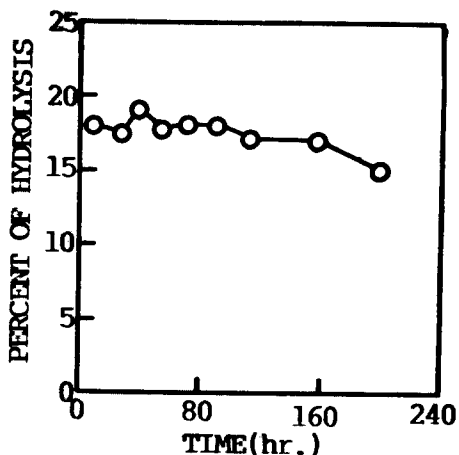
Fig. 6. Catalyst deactivation during continuous hydrolysis. (110°C & 6g catalyst loading)

ity of this feed was measured at 40 microhmos / cm^3.

The flow rate of the feed solution was set at 0.25ml / min. When the samples were taken at given time intervals, the flow rate was increased to 2.45ml / min to reduce conversion. This procedure was necessary to bring the converson into a linear region in relation with catalyst activity. Percent of hydrolysis shown on the ordinate of the figure is percent of conversion of xylose oligomers during hydrolysis. A small degree of deactivation occurred after 160 hours of continuous operation. The primary cause of this deactivation seemed to be the deposition of foreign substances. Deactivated catalysts. however, were easily regenerated by treating with 10-20% nitric acid. The catalyst was restored to its original color after the regeneration process.

요 약

활엽수의 헤미셀룰로오스를 autohydrolysis하여 얻은 용액을 초강 산고체, Nafion을 사용하여 2차 가수분해시키는 반응에 관한 kinetics를 고찰했다. 연속 column반응기를 사용해 얻을 수 있는 최대 xylose수율은 약 90%이었다. 양이온 물질이 제거된 feed를 사용하면 Nation은 안정된 가수분해 촉매를 사용될 수 있음이 판명되었다.

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