Optimization of Hydrolysis of Cellulosic Materials by a Solid Acid Catalyst

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ABSTRACT

The hydrolysis of lignocellulosic materials, specifically rice-straw, bagasse and Japanese cedar, with a highly active solid acid catalyst, a carbon material bearing SO₃H, COOH and OH groups, was investigated at 373 K through an artificial neural network (ANN) and a response surface methodology (RSM). The ANN models developed for experimental design accurately reflect the novel solid-solid interface catalysis. The ANN models revealed that the amount of water dominates the hydrolysis reaction. The correlations between the reaction properties and the properties of these lignocellulosic materials are discussed on the basis of the reaction mechanism.

Keywords: Response surface methodology, Artificial neural network, Carbon-based solid acid, Cellulose, Biomass and Glucose.

1. INTRODUCTION

Lignocellulosic material, especially cellulose, is linked by β-1,4 glycosidic bonds and is a promising raw material for producing important chemicals, including cellulosic-ethanol, hydrocarbons, and starting materials for the production of polymers [1,2], if it can be simply converted into reducing sugars. Sulfuric acid (H₂SO₄) is a standard catalyst for producing alcohols, esters, ethers, and various starting materials for polymers and resins. The hydrolysis of cellulose is also usually catalyzed by dilute or concentrated sulfuric acid, although substantial effort has been devoted to the development of appropriate hydrolysis schemes, including catalysis using mineral acids [3-5], enzyme-driven reactions [6], the use of subcritical and supercritical water [7-9], and solid catalysts for hydrogenolysis [10]. However, sulfuric acid requires special processing in the form of neutralization, which involves costly and inefficient catalyst separation from homogeneous reaction mixtures, and then results in an unrecyclable sulfate waste. The need for a “green” approach to chemical processing has stimulated the use of recyclable strong solid acids as replacements for unrecyclable liquid acid catalysts such as H₂SO₄ [11-18]. The solid acid particles can be readily separated from liquid products by decontamination or filtration, and the catalyst can be used repeatedly for the reaction without neutralization, minimizing energy consumption and waste.

Recently, we reported that an amorphous carbon material with SO₃H, COOH and OH groups can function as an efficient solid catalyst for the hydrolysis of cellulose at 343-373 K [10]. The carbon material can be readily prepared by sulfonation of partially carbonized cellulose, and is a novel solid Bronsted acid composed of SO₃H, COOH- and phenolic OH-bearing nanographene sheets in a random arrangement. The carbon catalyst can hydrolyze not only pure crystalline cellulose, but also natural lignocellulosic reactants, such as eucalyptus or straw tips, into water-soluble β-1,4 glucan, followed by the hydrolysis of water-soluble β-1,4 glucan into glucose, just as well as mineral acid catalysts. The high catalytic performance of the carbon material for the reaction is attributable to its adsorption capability for β-1,4 glucan, including cellulose [19]. The surface of the carbon material readily attaches to cellulose and water-soluble β-1,4 glucan, the hydrolytic product of cellulose, through hydrogen bonds between OH groups in the catalyst and cellulose or water-soluble β-1,4 glucan. Strongly acidic SO₃H groups bonded to the carbon material function as effective active sites for decomposing strong hydrogen bonds and hydrolyzing β-1,4 glycosidic bonds in cellulose or water-soluble β-1,4 glucan, resulting in the efficient conversion of cellulose into glucose. The reaction mechanism resembles enzymatic hydrolysis of cellulose; the amorphous carbon bearing SO₃H, COOH and OH groups is not so much a solid acid as an inorganic enzyme with highly active sites.

The optimum reaction conditions for the hydrolysis of crystalline-cellulose using this carbon-based solid acid catalyst have been investigated through an artificial neural network (ANN) and response surface methodology (RSM) [20]. While ANN is a powerful method that is expected to reveal functions representing phenomenon, it cannot clarify both interaction among variables and the significance of each variable. To clarify this, RSM has been applied to the study. RSM is an established method in statistics [21-26], revealing the significance of each variable and the interaction among variables. ANN and RSM analyses revealed that the catalytic hydrolysis of cellulose using amorphous carbon bearing SO₃H, OH and COOH groups proceeds in the same way as cellulose saccharification using conc. H₂SO₄: the reaction depends strongly on the amount of water. The glucose yield in the heterogeneous catalytic reaction reaches a maximum with an amount of water comparable to the solid catalyst weight. An amount of water that is less than the optimal amount is favorable for the decomposition of β-1,4 glycosidic bonds and strong hydrogen bonds in cellulose into water-soluble β-1,4 glucan, due to the strong acidity of the catalyst. However, it is not advantageous for the hydrolysis of water-soluble β-1,4 glucan into glucose, from the viewpoints of both kinetics and equilibrium.

In the present study, the hydrolysis of lignocellulosic materials (rice-straw, bagasse and Japanese cedar) using the carbon material bearing SO₃H, COOH and OH groups has been investigated through artificial neural network (ANN). The relationship between the rate of reaction and several parameters (the amounts of water, catalyst, and cellulosic reactant) in the hydrolysis reactions also has been studied with respect to the different structures of the lignocellulosic materials, and in comparison with hydrolysis by H₂SO₄.

2. Materials and Methods
Saccharification of lignocellulosic materials
Carbon material with SO\(_3\)H, COOH and OH groups was prepared by sulfonation of partially carbonized crystalline cellulose, and the details of the preparation of and structural information on the carbon material have been described elsewhere [10,27,28]. The hydrolysis of lignocellulosic materials (rice-straw, bagasse and Japanese cedar) in the presence of the carbon material was carried out in a polytetrafluoroethylene (PTFE) cylindrical reactor (90 cm\(^3\)) with a PTFE-coated stirring device, described previously [20]. The hydrolysis reaction was started by placing the reactor in an oil bath. After the reaction, a part of the supernatant solution readily obtained by centrifugation was analyzed using a high performance liquid chromatography (HPLC) equipped with a SUGAR SP0810 1EA column (operating temperature, 353 K; mobile phase, distilled water (0.5 ml min\(^{-1}\); Shodex).

In the case of the hydrolysis using sulfuric acid, after the removal of sulfuric acid from the reaction solution as BaSO\(_4\) precipitate by the addition of aqueous BaCO\(_3\), the remaining supernatant solution was analyzed by HPLC.

In both cases, the amount of water-soluble \(\beta\)-1,4 glucan (linear polysaccharides composed of glucose monomers linked by \(\beta\)-1,4 glycosidic bonds), produced by the hydrolysis of cellulose, was estimated by analyzing the glucose produced by the hydrolysis of water-soluble \(\beta\)-1,4 glucan using a dilute sulfuric acid solution [20]. A suitable amount of sulfuric acid solution was added to part of the supernatant solution collected after the hydrolysis reaction; the sulfuric acid concentration in the resulting solution was adjusted to 4 wt%, and was then warmed to 394 K for 1 h to hydrolyze the polysaccharides into glucose [20]. The amount of glucose in the solution after sulfuric acid-catalyzed hydrolysis of \(\beta\)-1,4 glucan was estimated using the HPLC.

Raw cellulosic materials (rice-straw, bagasse and Japanese cedar) were harvested in the Kanto region, Japan. The feedstocks were naturally dried. Moisture contents of rice-straw, bagasse and Japanese cedar were 7.6%, 7.8% and 9.1% by dry base, respectively. Components of the feedstocks were investigated by the 72 % sulfuric acid method (Klason Method) [29]. The monosaccharides (glucose; xylose; galactose; arabinose; mannose) were measured by HPLC as described above. The amounts of substrates (1.0–4.0 g), carbon material (1.0–3.0 g) and distilled water (1.0–5.0 g) on the basis of the Box-Behnken design arrangements for rice-straw, bagasse and Japanese cedar, responses and data for modeling by artificial neural networks.

### Table 1. Box-Behnken design arrangements for rice-straw, bagasse and Japanese cedar, responses and data for modeling by artificial neural networks.

<table>
<thead>
<tr>
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<th>Glucose / mg</th>
<th>Xylose / mg</th>
<th>Glucose / mg</th>
<th>Xylose / mg</th>
<th>Galactose / mg</th>
<th>Arabinose / mg</th>
<th>Mannose / mg</th>
<th>Forma tion rate of glucose (%)</th>
<th>Forma tion rate of xylose (%)</th>
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**Experimental design and performance estimation**

The hydrolysis of lignocellulosic materials by the carbon material was planned using the Box-Behnken design [23–26] feature of the JMP® package (SAS Institute Inc.) (Table 1). In the experimental design, the reaction temperature, reaction time and the stirring rate are 373 K, 2 h and 400 rpm, respectively, and are constant. The formation rates of monosaccharides (glucose and xylose) from lignocellulosic materials in the presence of the carbon material were measured by varying the amounts of substrates (1.0–4.0 g), carbon material (1.0–3.0 g) and distilled water (1.0–5.0 g) on the basis of the Box-Behnken design. Performance maps representing the relationships between the formation rates of monosaccharides, and the amounts of substrates and distilled water at each amounts of carbon material were estimated using the ANN models feature of the JMP software.

**Artificial neural network (ANN)**

The ANN architecture used in this study is illustrated in Figure 1. The input layer consists of the amounts of water, substrate and carbon material. The outputs in this study are the formation rates of monosaccharide (glucose and xylose).

In the present study, an unsupervised learning-type feed-forward neural network, with one-hidden layer first-stage-logistic and
second-stage-identity model, was adopted for ANN modeling [30]. A logistic sigmoid transfer-function expressed by Eq. (1), was used as the activating function and inputs and outputs were normalized within the range of (0, 1) [30].

\[
S(x) = \frac{1}{(1 + e^{-x})^2}
\]  

(1),

\[x: \text{variable. The hidden node (} H_i \text{) is defined as follows [30]:}
\]

\[
H_j = S_H \left( \sum_{i=1}^{N_H} k_{ij}X_i \right)
\]  

(2),

\[N_i: \text{number of variables.} S_H(x): \text{logistic function.} X_i: \text{normalized input variables. The output variables (} \hat{Y}_k \text{) are calculated by the following equation [30].}
\]

\[
\hat{Y}_k = S_Y \left( \sum_{i=1}^{N_H} \beta_{jk}H_j \right)
\]  

(3)

\[N_{HC}: \text{number of hidden nodes.} S_Y(x): \text{identity function.} \hat{Y}_i: \text{normalized output variables. Coefficients} a, b, c \text{ and} d \text{ are estimated values. In the model estimation step, the weight-decay-stabilized Gauss-Newton method [30] was used to prevent over-fitting, and three neurons were used in the hidden layer (Figure 1). Taking the results produced by the network, statistical methods were used to make comparisons. At the model estimating and testing stages, the sum squared error (SSE), the root mean squared error (RMSE) and the coefficient of determination (R^2) were calculated. These are defined as follows [30]:}
\]

\[
SSE = \sum_{i=1}^{N} (Y_i - \hat{Y}_i)^2
\]  

(4),

\[
RMSE = \sqrt{\frac{SSE}{DF_e}}
\]  

(5),

\[
R^2 = 1 - \frac{SSE}{\sum_{i=1}^{N} (Y_i - \bar{Y})^2}
\]  

(6),

\[Y_i: \text{experimental value.} \hat{Y}_i: \text{predicted value.} N: \text{number of experiments.} DF_e: \text{degrees of freedom of error.} \bar{Y}: \text{average of experimental values. These values represent the fit of the ANN model to the actual phenomenon. The minimum values of SSE and RMSE in the model were selected during model refinement using the JMP. In regression, } R^2 (0 \leq R^2 \leq 1) \text{ shows the fit between the regression line and actual data [30].}
\]

Electron microscope analysis
The microscopic shape of crushed lignocellulosic material was examined under a scanning electron microscope (SEM, Hitachi High-Technologies Corporation. S-4800) set at an accelerating voltage of 5 kV, and a working distance of 25-26 mm.

3. RESULTS AND DISCUSSION

Components of the feed-stocks
The components of rice-straw, bagasse and Japanese cedar as investigated by the 72 % sulfuric acid method (Klason Method) [29] are shown in Table 2. The proportion of cellulose detected as glucose was ca. 30% in each feed stock. Hemicellulose was defined as polymeric combinations of xylose, galactose, arabino and mannose. Its proportion was 26-43%, and was especially high in bagasse. The ratio of lignin detected as acid-insoluble lignin was especially high in Japanese cedar (34%). The ratio of ash was high in herbal materials (rice-straw, 17% and bagasse, 11%). Rice-straw and bagasse belong to the family ‘Poaceae’. Poaceae are well known silica (Si) accumulating plants [33]. Hydrated silica (Si(OH)4) absorbed into the plant becomes solid amorphous hydrous silica (SiO2·nH2O), which serves structural functions in the plant [34,35]. Consequently, the ash in herbal materials is mostly silica.

Conversion and yield
The results for the hydrolysis of lignocellulose materials, Japanese cedar, bagasse, and rice-straw, using the Box-Behnken design (temperature, 373 K) are summarized in Table 1. The main products from the hydrolysis of lignocellulosic materials that were observed in all experiments shown in Table 1 were glucose and xylose. Galactose, arabino and mannose were also observed in some conditions. Conversion of rice-straw into monosaccharides from cellulose and hemicelluloses by acid-catalyzed hydrolysis reached ca. 30 mol% at 2 h. Conversion of bagasse and Japanese cedar reached ca. 23 and 14 mol%, respectively. Glucose yield of rice-straw, bagasse, and Japanese cedar reached 5.7, 3.6, and 2.5 mol% at 2 h, respectively. Xylose yield of these substrates reached 40, 57, and 23 mol%, and galactose yield reached 46, 28, and 21 mol%, respectively. The Arabinose yield reached 62 mol% in the hydrolysis of rice-straw. Mannose was produced only in hydrolysis of Japanese cedar, and the yield reached 9 mol%.

Formation rate of glucose
The ANN models for the glucose formation rate of rice-straw, bagasse, and Japanese cedar were developed using the results in Table 1. The fidelity of the developed ANN models was checked in the same manner described previously [20]. The developed models correctly describe the actual reaction. The performance maps for every model at an amount of catalyst of 2 g are shown in Figures 2, 3, and 4. The glucose formation rate increases with an increasing amount of water, reaching a maximum at ca. 3–4 mL, and further addition of water beyond this value results in a decreased formation rate. This can be attributed to the essential nature of acid-catalyzed hydrolysis. A large amount of water is advantageous for the hydrolysis reaction, for both kinetics and equilibrium. On the other hand, the acidity and hydrolysis performance of acid catalysts markedly decreases with an increasing amount of water, due to hydration of the acid sites [20]. Therefore, the glucose formation rate reaches a maximum at a certain amount of water. On the other hand, the glucose formation rate increases linearly with an increasing amount of substrate at 3–4 mL of water.

<table>
<thead>
<tr>
<th>Component / wt%</th>
<th>Rice straw</th>
<th>Bagasse</th>
<th>Japanese cedar</th>
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<tr>
<td>Cellulose</td>
<td>27.0</td>
<td>30.5</td>
<td>28.8</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>25.8</td>
<td>42.7</td>
<td>32.5</td>
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<tr>
<td>Xylose</td>
<td>10.6</td>
<td>27.3</td>
<td>8.7</td>
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<tr>
<td>Galactose</td>
<td>2.4</td>
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<td>4.3</td>
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<tr>
<td>Arabinose</td>
<td>5.2</td>
<td>6.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Mannose</td>
<td>1.6</td>
<td>3.4</td>
<td>13.4</td>
</tr>
<tr>
<td>Lignin</td>
<td>26.5</td>
<td>22.1</td>
<td>34.4</td>
</tr>
<tr>
<td>Ash</td>
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</tr>
<tr>
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<td>106.0</td>
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<td>-6.0</td>
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</table>

Table 2. Components of rice-straw, bagasse and Japanese cedar.
The water required for hydrolysis of lignocellulosic materials was much more than for the hydrolysis of pure crystalline cellulose (ca. 2.5 mL) [20]. The formation rate of glucose from pure crystalline cellulose (25 mg h⁻¹) was also higher than that from lignocellulosic material in the same reaction conditions: temperature, 373 K; time, 2 h; catalyst, 2 g; stirring rate, 400 rpm (the experiments are not described here). This is attributed to water adsorption inside the lignocellulosic material and differences in the structure or components of the material. Chemically bonded water is adsorbed onto the hydrophilic hydroxyls which are part of amorphous cellulose, lignin, and other low-molecular-weight polysaccharides (hemicellulose), inside the cell wall [36]. Since water cannot adsorb on pure crystalline cellulose which does not contain amorphous cellulose, lignin, or other low-molecular-weight polysaccharides, the required water for the hydrolysis of pure crystalline cellulose was comparatively low and the formation rate was high. The existence of lignin also inhibits the action of the carbon material on cellulose, especially in Japanese cedar. Japanese cedar is 34% lignin. Consequently, the activity of the carbon material is decreased.

Figure 5 shows SEM images of bagasse and Japanese cedar, and diagrams of cell wall of wooden material [37].

Figure 5 shows SEM images of bagasse and Japanese cedar, and diagrams of cells and inside cell walls. Cellulose and hemicellulose, which are the targets of the catalytic hydrolysis reaction, are contained in the cell wall with lignin. The ratio of these contents is different depending on the lignocellulosic material as shown in Table 2. Wooden material has a thick-layered cell wall because of lignification. In this structure, lignin inhibits carbon material contact with cellulose and hemicellulose.
Figure 6 shows the interactions between the amount of water and carbon material in the hydrolysis of lignocellulosic materials. The reaction conditions were: reaction temperature, 373 K; reaction time, 2 h; substrate, 1 g; stirring rate, 400 rpm. The lines are the predictions by the developed ANN models of the glucose formation rates of lignocellulosic materials. The maximum glucose formation rates were increased by increasing the amounts of carbon material and water. Figures 2 to 4 and Figure 6 indicate that the interaction between the amount of water and the amount of carbon material is stronger than the interaction between the amount of water and the amount of substrate. This result also can be attributed to the essential nature of acid-catalyzed hydrolysis described above. The amount of water is adjusted to the amount of carbon material to achieve maximum activity for the hydrolysis reaction.

Formation rate of hemicellulose

The ANN models for the xylose formation rate of rice-straw, bagasse and Japanese cedar are shown in Figures 7, 8 and 9. Those Figures show models for 2 g of catalyst. The xylose formation rate increases with an increasing amount of water, reaching a maximum at ca. 3.5−4.5 mL, and further addition of water beyond this value results in a decreased formation rate. This can also be attributed to the essential nature of acid-catalyzed hydrolysis described above. In Figure 8, the formation rate of xylose for bagasse was very high at high water and substrate amounts. This is attributed to the proportion of xylose in bagasse.

Hemicelluloses consist of five-carbon sugars (xylose and arabinose) and six-carbon sugars (galactose, glucose, and mannose) [38]. Hemicellulose are embedded in the cell walls of plants, sometimes in chains, and they bind to cellulose through pectin to form a network of cross-linked fibres. Although cellulose and hemicelluloses are both polysaccharides, hemicellulose consists of shorter chains, 500-3000 sugar units as opposed to 7,000-15,000 glucose molecules per polymer seen in cellulose. In addition, hemicellulose is a branched polymer, while cellulose is unbranched. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. Compared to cellulose, hemicellulose is easy to hydrolyses, with dilute acids or any of many hemicellulose enzymes. However, conventional solid strong Bronsted acids, including inorganic oxide solid acids (Nb2O5•nH2O and H-mordenite (zeolite)) and SO3H-bearing polymer-based solid acids such as Nafion NR50 (perfluorosulfonated ionomer) and Amberlyst-15 (polyestrene-based cation-exchangeable resin with SO3H) do not react with lignocellulosic materials [10]. The carbon material is an efficient catalyst for hydrolysis of hemicellulose, including lignocellulosic materials.
In the hydrolysis of rice-straw, although sulfuric acid can produce more xylose compared with the carbon material, both catalysts were equally active in producing glucose. It is expected that the catalytic activity of the carbon material would be improved by pretreatment to remove lignin.

4. CONCLUSIONS

The catalytic hydrolysis of lignocellulosic materials (rice-straw, bagasse, and Japanese cedar) into glucose using the carbon-based solid acid catalyst proceeds as well as with sulfuric acid, even though lignocellulosic material has a very complex structure, the cell wall. The formation rates of glucose in the hydrolysis of lignocellulosic materials were lower than those in the hydrolysis of pure crystalline cellulose. This is attributed to the complex structure of the cell wall of lignocellulosic material, especially the presence of lignin. It is expected that the catalytic activity of the carbon material would be improved by pretreatment to remove lignin.

5. ACKNOWLEDGMENT

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6. REFERENCES