Hydrogen Peroxide and Carbon Dioxide Effect on Biomass Hydrothermal Treatment

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Hydrogen peroxide and CO₂ effects on the hydrothermal degradation of biomass are examined using a semibatch reactor. Woody biomass is acquired from Japanese cedar and Japanese zelkova. Cellobiose is also studied as a model biomass. The effects on the sugar yield and the fermentation inhibitor yield are discussed. Hydrogen peroxide decreases the cellulose and hemicellulose decomposition temperature, whereas CO₂ exhibits a limited effect on their decomposition.

Key Words

Biomass hydrothermal treatment, Hydrogen peroxide, Carbon dioxide

1. Introduction

Bioethanol is an alternative energy to fossil fuel. However, the use of biomass from food competes with the food demand; thus, many researchers have tried to develop bioethanol production from lignocellulosic materials. Lignocellulosic biomass exhibits a more rigid structure than food biomass. Therefore, before saccharification, it requires pretreatment by methods such as milling, steam explosion, ammonia-fiber explosion (AFEX), CO₂ explosion, ozonolysis, acid hydrolysis, alkaline hydrolysis, and oxidative delignification. Pretreatment must meet the following requirements: (1) improve the formation of sugars or the ability to subsequently form sugars by enzymatic hydrolysis, (2) prevent the degradation or loss of carbohydrate, (3) prevent the formation of byproducts inhibitory to the subsequent hydrolysis and fermentation processes, and (4) be cost effective.

There are several reports on biomass hydrothermal pretreatment. A basic hydrothermal experiment with cellobiose, glucose, or xylan/xylose revealed that glucose decomposes over 200 °C and xylose over 180 °C, producing triose, tetrose, or acid. Acid or base was further used as additives to improve the hydrothermal treatment. According to Mosier et al., the pH during this process should range between 4 and 7 to prevent the degradation of sugar. In addition, Lu et al. indicated that the pretreatment of rapeseed straw with sulfuric acid 1% and solid content 20% for 10 min at 180 °C is the optimal for ethanol production. Finally, Zhang et al. reported the improved hemicellulose and lignin removal by the addition of acid.

In the present study, the effect of using hydrogen peroxide or carbon dioxide as additives on the hydrothermal treatment temperature is investigated with a semibatch reactor, since hydrogen peroxide is well known for the delignification process and carbon dioxide will control the liquid pH condition. These additives also have benefit for the cost and the after-treatment compared to the other acid and base additives. Biomass from Japanese cedar and Japanese zelkova is studied, and cellobiose is used as the biomass model. The treatment temperature is set between 140 °C and 350 °C and the pressure is maintained at 25 MPa, which keeps the samples in liquid condition at any temperature.
2. Experimental

2.1 Materials

As the experimental biomass samples, 5-10 mm Japanese cedar and Japanese zelkova wood pieces were prepared (Fig. 1). The chemical composition of the biomass samples (Table 1) was determined by TORAY TECHNO CO., LTD. Cellobiose purchased from WAKO Chemical was selected as the model biomass.

2.2 Cellobiose hydrothermal experiment

The apparatus used for the hydrothermal experiment is presented in Fig. 2. It consists of a liquid pump, a syringe pump for CO₂, a preheating coil, a reaction cell (0.94 cm³), a backpressure regulator, and a cooling coil. The reaction column is made of HASTELLOY C-276, whereas the preheating and cooling lines are made of SUS316. The measuring procedure is described below. The cellobiose experiment was carried out using a tubular flow reactor. Cellobiose solution (0.5 wt%) and water was pumped through the flow line. When hydrogen peroxide was added to the process, the hydrogen peroxide solution replaced water. Alternatively, when CO₂ was added, it was pumped using the syringe and mixed with the water line before the preheating point (5 wt%). Then, the preheated water and the cellobiose solution were mixed and loaded onto the cell. The cell pressure was maintained at 25 MPa, which is higher than the vaporizing pressure at maximum temperature using a backpressure regulator. The temperature was set between 140 °C and 340 °C. The eluents were collected in sample vials. The cellobiose residence time was 4 s.

2.3 Woody biomass hydrothermal experiment

The same apparatus was used in this case, except for the semibatch system. Initially, the biomass sample was loaded onto the cell (1.0 g). The water-additive flow line was the same as in the cellobiose experiment. The temperature was gradually increased from 20 °C to 340 °C at a rate of 5 °C/min, and the eluents were collected at each temperature level. The cell volume was 15 cm³ and the residence time was 60 s.

2.4 Analysis

The collected samples were analyzed with regard to the sugar and the fermentation inhibitor yields (e.g., phenol derivatives). The sugar yield was analyzed by HPLC with post-column fluorescence derivatization (Column: Asahipak NH2P-50 4E 250 × 4.6 mm I.D., eluent: acetonitrile/water/phosphoric acid (0.5 vol%), reaction solvent: arginine/boric acid, column oven: 40 °C, reaction temperature: 150 °C). The sugar analysis results appear in Fig. 3. Several types of sugars, including monosaccharides and their oligomers, are distinguished by their corresponding sharp peaks. The phenol derivatives and the furfural were analyzed with HPLC-UV (column: ODS HYPERSIL 250 mm × 4.6 mm, oven temperature: 30 °C, eluent: water/methanol/tetrabutylammonium hydrogensulfate = 714/245/06 weight.

![Fig. 1 Woody biomass samples (a) Japanese cedar, (b) Japanese zelkova](image)

![Fig. 2 Hydrothermal apparatus](image)

![Fig. 3 Example of HPLC peaks corresponding to several sugars. 1: Xylose, 2: Fructose, 3: Glucose, 4: Maltose, 5: Cellotriose, 6: Cellotetraose, 7: Cellohexose](image)

|     | Cellulose | Hemi-Celulose | Lignin | Ash |
|-----|-----------|---------------|--------|-----|
| J Cedar | 43.6      | 29.7          | 32.3   | 0.72 |
| J Zelkova | 44.9      | 30.2          | 27.1   | 1.03 |
The organic acids were analyzed with ion-chromatography (column: IC SI-50 4E).

The sugar yield and the fermentation inhibitor (or organic acid) yields were defined as follows:

**Sugar yield [%]**

\[
\text{Sugar yield} = \left( \frac{\text{weight of sugar after hydrothermal and saccharization}}{\text{weight of holocellulose in biomass material}} \right) \times 100
\]

**Fermentation inhibitor (or organic acid) yield [%]**

\[
\text{Fermentation inhibitor yield} = \left( \frac{\text{weight of inhibitor}}{\text{feed weigh}} \right) \times 100
\]

3. Results and Discussion

3.1 Cellobiose

The sugar and the fermentation inhibitor yields obtained from cellobiose at different temperatures during the hydrothermal experiment with no additives appear in Fig. 4. Cellobiose begins to decompose at around 220 °C, yielding glucose and fructose. At 340 °C, all cellobiose and sugars are degraded. The furfural concentration increases with temperature, indicating that sugar hydrolysis is consistent with the cellobiose decomposition trend.

The effect of hydrogen peroxide and CO₂ on the glucose yield is presented in Fig. 5 a). Hydrogen peroxide (0.5 wt%) increases the glucose yield at 280 - 300 °C, whereas H₂O₂ (0.05 wt%) or CO₂ have a smaller effect. The effect of hydrogen peroxide and CO₂ on the furfural and 5-HMF yields appears in Fig. 5 b). H₂O₂ decreases the furfural yield, perhaps because of the oxidative decomposition of furfural during the experiment. The furfural yield also decreases, when CO₂ is used as an additive, but this effect is attributed instead to the altered pH conditions.

3.2 Woody biomass

The temperature dependence of sugar yields from Japanese cedar through the hydrothermal experiment with no additives and the semibatch process appears in Fig. 6 a). Sugar production begins at around 160 °C, mainly pentose (xylose and arabinose). Hexose (glucose, fructose, mannose, and galactose) is produced from 200 °C, and the maximum yield appears at 260 °C. No sugar is produced over 280°C.

The fermentation inhibitor yield of cedar through the same experiment appears in Fig. 6 b). The main component is syringaldehyde at low temperatures around 160-240 °C, which is a product of lignin decomposition, whereas the process begins to yield furfural around 200 °C. Fig. 6 c) shows organic acid yield of cedar. The main components
Fig. 6  Temperature dependence data of a) sugar yields, b) fermentation inhibitor yield and c) organic acid yield from Japanese cedar through the hydrothermal experiment with no additives.

are lactic acid and acetic acid which are products of sugar and lignin decomposition.

The effect of hydrogen peroxide and CO₂ additives on the pentose and hexose yields from cedar is presented in Figs. 7 a)-b). The temperature for maximum hexose yield is 200–220 °C, when hydrogen peroxide is added; thus, hydrogen peroxide increases the sugar yield at lower temperatures (below 200 °C). The maximum sugar yield is reached around 260-280 °C, when CO₂ is added; thus, CO₂ shows a smaller effect on the sugar yield. There are small differences for pentose. The effect of hydrogen peroxide and CO₂ additives on the pentose and the hexose yields from zelkova is presented in Figs. 7 c)-d). The results for zelkova show almost the same trend as observed in the case of cedar.

The effect of hydrogen peroxide and CO₂ additives on the furfural, the syringaldehyde, organic acid yields from cedar and zelkova appear in Fig. 8. In Fig. 8e, organic acid yields for CO₂ additives were missing because of our HPLC trouble. The use of hydrogen peroxide as an additive decreases the furfural and the syringaldehyde yields and increases the organic acid. On the contrary, CO₂ does not affect the furfural yield greatly, but the syringaldehyde yield is significantly smaller.

The colors of the collected samples are displayed in Fig. 9. Samples without additives are dark, especially at 260–280 °C, but the samples with hydrogen peroxide or CO₂ are colorless. This may be connected to the Maillard reaction, i.e., the reaction between a sugar and an amino acid, the product of which has a dark color. This reaction is controlled by pH (neutral ~ basic). Because hydrogen peroxide and CO₂ make the pH acidic, using them as additives inhibits the Maillard reaction.

4. Conclusion

In the present study, we examined the effect of using hydrogen peroxide and CO₂ as additives in the hydrothermal treatment of woody biomass, with respect to temperature. Hydrogen peroxide decreases the temperature of the glucose eluent, whereas CO₂ does not exhibit a significant effect. Comparing the colors of the collected samples suggests that the use of these additives inhibits the Maillard reaction.
Fig. 7  Hydrogen peroxide and CO$_2$ additives’ effect on pentose and hexose yields from cedar and zelkova.  a) Pentose yield from cedar, b) Hexose yield from cedar, c) Pentose yield from zelkova, d) Hexose yield from zelkova

Fig. 8  The effect of hydrogen peroxide and CO$_2$ additives on furfural and syringaldehyde yields from cedar and zelkova a) Furfural yield from cedar, b) Syringaldehyde yield from cedar, c) Furfural yield from zelkova, d) Syringaldehyde yield from zelkova
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