Development of Liquefaction Technique of Pulverized Ligneous Biomass Powder

Toyoyuki Sato, Nobusuke Kobayashi, Yoshinori Itaya,
Department of Chemical Engineering, Nagoya University
Shigekatsu Mori
Center for Cooperative Research in Advanced Science and Technology, Nagoya University

ABSTRACT

The wood biomass was liquefied by the pressurized hydrothermal method. The wood biomass powder in the different particle size, which was pulverized by a vibration mill, cutter mill and grinder, was used for the liquefaction. The liquefaction material was biomass slurry, which was prepared by mixing the wood biomass powder and water together (1:9). After filling the biomass slurry in a pressure vessel, the vessel was heated up around 423 to 573 K. The pressure of the vessel was as same as the water vapor pressure of that temperature. After the reaction, the vessel was cooled down to room temperature immediately to prevent secondary reaction. As the result, around 60 % of the wood biomass powder was soluble in water and around 40 % was remained in the bottom of the vessel as residual. The dissolved liquid was sugars that were decomposed components of cellulose, hemi-cellulose or lignin. Depend on the reaction temperature and particle size of the biomass powder, the ratio between dissolved liquid and residual changed dramatically.

INTRODUCTION

Of recent years, the utilization of unused ligneous biomass has been attracted attention as the environmental-friendly resource for the development of resource cycling society in Japan, because of the environmental issues, such as CO_2 emissions.

Although the wood biomass exists abundantly, those were not considered as rescues for the energy or chemical for a long time, they were used as the pulp material partially or dumped to a landfill. Recently, the biomass has been expected as alternative resource and the various technological research and developments on wood biomass utilization has been encouraged for the electric generation by the gasification [1] and bio-fuel production or chemical production by the liquefaction. However, there were still lots of issues for commercialization, because of low efficiency and productivity and bad economical efficiency.

The liquefaction was the one of methods to produce chemicals from wood biomass and this method was one of the component fractionation techniques of wood constituent called hydrothermal process. There were a lot of liquefaction methods, such as steam explosion method and supercritical water method, but the liquefaction in a hot compressed water was mild reaction condition and simple operation condition rather than the other liquefaction method. Therefore, it was possible to simplify the total system and cut down

energy consumption. For such reasons, liquefaction by a hot compressed water was considered as the effective method for the efficient ligneous biomass utilization [2].

For the effective liquefaction by a hot compressed water, pretreatment such as pulverization could be effective on operations and reactions. The liquefaction technique used pulverized fine powder as materials started developing, because reactivity of the materials may enhance [3]. However, there were few papers considering the effect of the particle size on the liquefaction efficiency.

In this study, in order to develop the efficient liquefaction technique of wood biomass, the wood biomass pulverized into micron order particle by a vibration mill was liquefied in a hot compressed water and measured the liquefaction productivity. In the experiment, the effects of reaction temperature, pulverizing method of wood biomass and size of wood particles on the yield of liquefied substance were discussed.

EXPERIMENTAL

Pretreatment of liquefaction material

The pulverized biomass was used for the liquefaction material. The liquefaction material was prepared by pulverizing the shaving dust of Oregon pine (conifer). The shaving dust size was distributed widely, and it was a few millimeters in thickness and a few centimeters in length. The moisture content of biomass was controlled around 10% dried in air for several days before pulverization. Three pulverization machine, vibration mill, cutter mill and grinder were used for the pulverization in this study. Cumulative particle size distribution was measured by laser diffraction / dispersion particle diameter distribution analyzer (Shimadzu Co. Ltd.). The particle size distributions in the different pulverization method were shown in **Figure 1**. The 50 % particle diameter pulverized by the vibration mill was about 35 μm and that of the cutter mill was around 200 μm, respectively. The 50 % particle diameter of grinder mill was around 500 μm, but the particle size distribution pulverized grinder mill was too broad to be shown in the figure. Over the 10 % of the particle pulverized by the vibration mill was less than 10 μm.

Specific surface area of the pulverized powder was also measured by an automated mercury porosimeter (Shimadzu Co. Ltd.). The specific surface area of wood powder in each pulverization method sieved between 212 μm and 500 μm was summarized in **Table 1**. The surface are was not include the nano-order pore area. Even the same particle size range, the powder pulverized by the vibration mill had the biggest surface area and it was around two times bigger than that of grinder mill.

The shape of wood particles was observed by the Scanning Electron Microscopy (SEM). The SEM micrographs of the particles pulverized by the different methods were shown in **Figure 2**. In the case of using the vibration mill, the structure of wood fiber was completely broken down, the shape of the particles was almost round and homogeneous in each particle, and the surface of the particle was smooth. On the other hand, the particle

shape pulverized by the cutter mill was rectangle and the wood fibers could be observed clearly. The particle shape pulverized by the grinder mill was irregular and the wood fibers were branch off at the end of each particle.

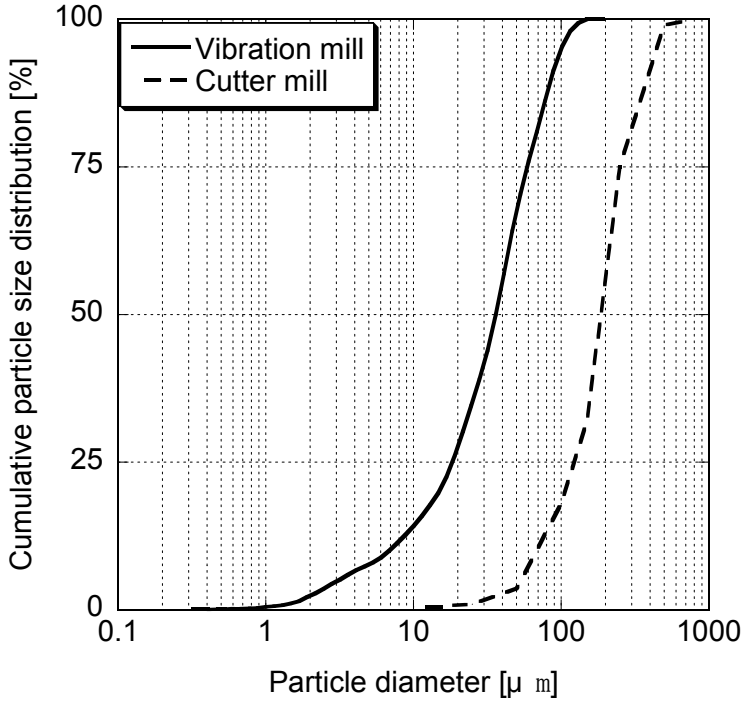

Figure 1. Cumulative particle size distribution of the pulverized particles

Table 1. Specific surface area of the wood particles

	Specific surface area [m^2/g]
Vibration	2.62
Cutter	1.85
Grinder	1.37

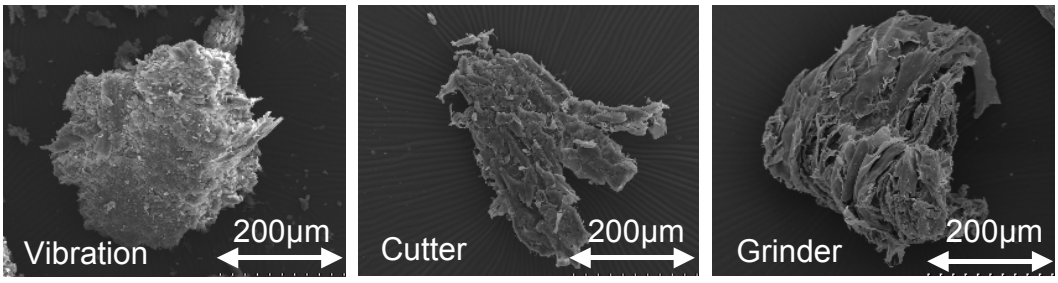

Figure 2. SEM micrographs of the wood particles

Preparation of biomass slurry for liquefaction

The wood biomass slurry was prepared by using the pulverized power. The wood powder was mixed with deionized water and it was agitated for several minutes by shaker

utile the pulverized power was dispersed uniformly. In the experiment, the biomass slurry of 80 g was made by mixing 8 g wood powder and 72 g deionized water together.

Batch reactor for liquefaction

Schematic diagram of liquefaction system was shown in **Figure 3**. This was the batch type reactor (autoclave). The apparatus was consists of a pressure vessel, heater, pressure gauge, agitator for mixing the biomass slurry, thermocouple, temperature controller and rpm controller. The pressure vessel was made of stainless and the volume was 120 cc. The pressure vessel was sealed by an insulator to reduce the heat release. The temperature biomass slurry inside of the pressure vessel was measured by the inserted thermocouple and was controlled by the PID temperature controller. The biomass slurry was agitated by the agitator during the reaction to prevent the deposition of biomass power. The number of rotation was set 500 rpm. The pressure of the vessel was the same as the water vapor pressure of that temperature.

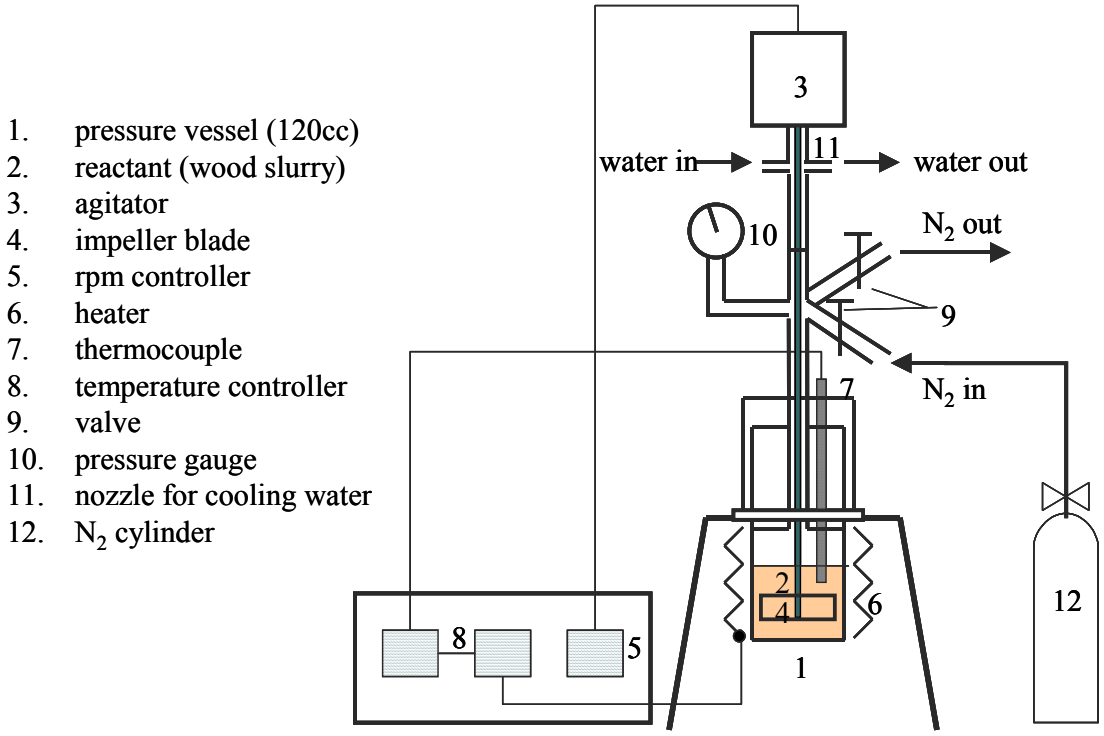

Figure 3. Schematic diagram of batch reactor for liquefaction

Experimental Procedure

Well-mixed biomass slurry of 80 g was fed in the pressure vessel. Nitrogen gas was purged for 15 minutes with agitating the biomass slurry to create an inert condition. After replacing the gas, the vessel was pressurized 2 MPa. Then the vessel was heated up at the temperature of 423 K to 573 K. After the temperature of the slurry reached the target

temperature, the heater was turned off and the temperature was kept for 1 minute. One minute was the reaction time at that temperature, however it took 15 to 20 minutes for heating up the target temperature. Then, the vessel was quenched to 298 K by water immediately to prevent the secondary reaction. The reaction product was taken from the pressure vessel and it was separated solid residue from liquefied product by a suction filtration. Solid residue was dried at 378 K for 24 hours in an oven and was measured the weight.

Calculation of water soluble product (WS) yield

In this study, water soluble product was defined as the liquid that the solid residue was removed from the whole liquefied product. Water soluble product and dried solid residue were designated as WS and S, respectively. Yield of the water soluble product was calculated by the following equation;

Yield of WS = (1 – amount of S / amount of charged dry biomass powder)$\times$100 [wt%]

Although the gas or oil soluble content was generated by the liquefaction process, the amount of those was so low that it was neglected.

RESULT AND DISCUSSION

Effect of the reaction temperature on the yield of WS

The effect of the reaction temperature on the yield of WS was measured. The pulverized powder that was sieved between 53 μm and 100 μm were used. The reaction temperature was set 423 K to 573 K by each 50 K. The yield of WS in the different reaction temperature was shown in **Figure 4**. As the reaction temperature rise, the yield of WS also increased gradually. The yield of WS was around 60 % at the temperature more than 523 K. The soluble water product were decomposed components that came from cellulose, hemi-cellulose and lignin. Those decomposed included disaccharide, monosaccharide, or phenolic compounds etc. According to the results of analysis, the component of the water soluble product was

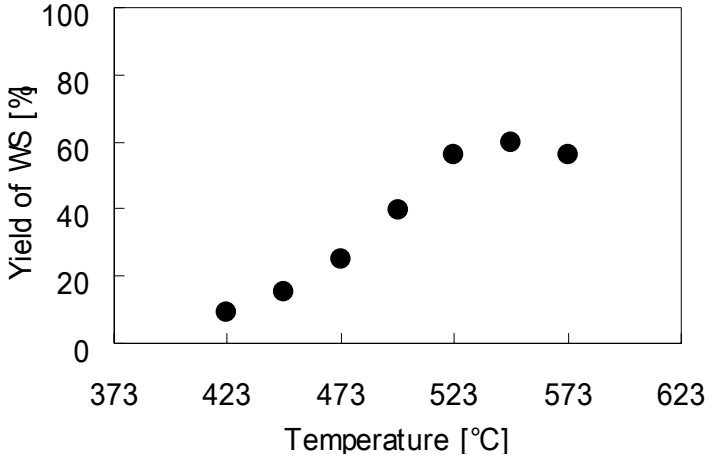

Figure 4. Effect of the reaction temperature on the yield of WS

considered to be different from the product formed in the different temperature.

The effect of the powder pulverized in different method on the yield of WS

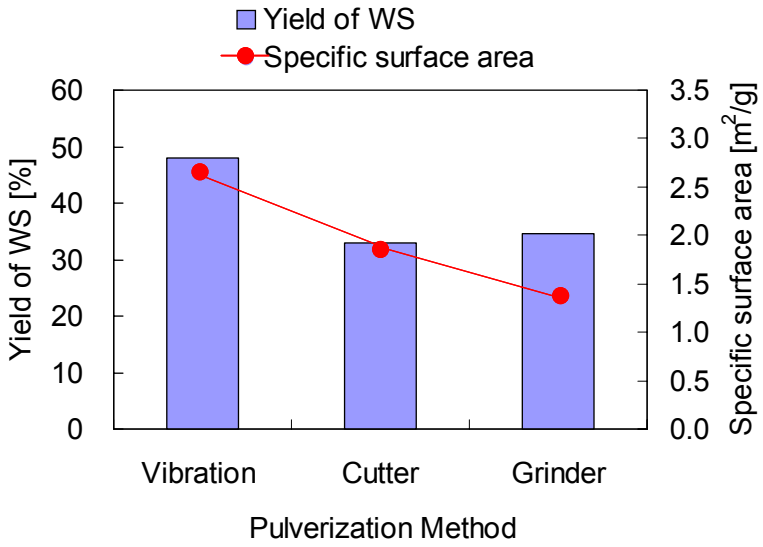

Figure 5. The effect of the particles pulverized in different method on the yield of WS

Wood powder pulverized by the vibration mill, cutter mill and grinder was used as liquefaction materials. The wood powder was sieved between 212 μm and 500 μm to minimize particle size effect. The reaction temperature was set 523 K in this case. **Figure 5** showed the experimental result of liquefaction. The left axis indicates the yield of WS and the right axis indicates the specific surface area of the wood particles. The yield of the wood particles pulverized by the vibration mill was higher than that of the cutter mill and grinder. The specific surface area of the wood powder pulverized by the vibration mill was bigger even in the same particle size range. The contact area of the reaction enlarged and it improved reactivity of the wood powder. However, the specific surface area of the wood particles pulverized by the grinder was lower than that of the cutter mill, the yield of both materials was almost same. It indicated that the shape of the wood powder also might affect the yield.

Effect of the particle diameter on the yield of WS

The wood powder pulverized by the vibration mill was used as liquefaction materials. The wood powder were sieved in the different range of –20 μm, +20 μm –53 μm, +53 μm –100 μm, +100 μm –212 μm and +212 μm –500 μm. The reaction temperature was also set 523 K in this case. **Figure 6** showed the experimental result of liquefaction. The left axis indicates the yield of WS and the right axis indicates the specific surface area of the wood particles. The 56 % of wood powder were dissolved in water with using under 20 μm particles. However, the only 48 % of the yield of WS obtained from the wood particles over 212 μm under 500 μm. It was appeared that the smaller wood powder was used, the higher yields of WS were obtained. As the particle diameter became smaller, the specific surface area of the wood particles also increased. The specific surface area was strongly related to the contact area of reaction. Therefore, when the particle diameter of less than 53 μm was

used for the liquefaction, the yield of WS was higher comparing with others. The particle size was the most important factor for the liquefaction, because the internal diffusion of liquefied components in the particle was improved. Aggregation was also an important factor to be considered in the case of using very fine powder. When the particle diameter of more than 53 μm was used, there was less difference in the yield of WS. Because the big particle was composed of tens of fine particles by the aggregation, when the biomass slurry was agitated in the pressure vessel, the big particles were separated off the small particles. Consequently there could be less difference among the yields.

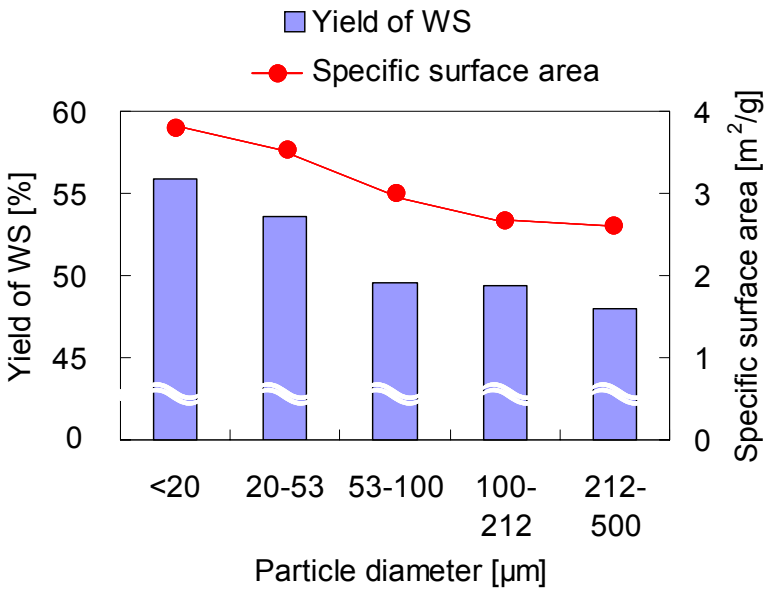

Figure 6. Effect of the particle diameter of the materials to the yield of WS

CONCLUSION

To develop the efficient liquefaction technique of wood biomass, the wood biomass pulverized by the vibration mill was liquefied in hot compressed water. The wood biomass pulverized in different pulverization method such as the cutter mill and grinder was also conducted. The effects of reaction temperature, pulverizing method and size of wood particles on the yield of liquefied substance were measured. The results were summarized as following.

1. As the reaction temperature rise, the yield of WS also increased gradually. The yield of WS was around 60 % at the temperature more than 523 K.
2. The wood particles pulverized by the vibration mill were obtained the highest yield of WS that has the biggest specific surface area. Although the surface area was important factor for the liquefaction, the particle shape might affect the yield of WS as well as the specific surface area.
3. When the particle diameter was less than 53 μm, the yield of WS was higher than that of +53 μm –100 μm, +100 μm –212 μm and +212 μm –500 μm. Especially when the wood powder of less than 20 μm was used for the liquefaction, the yield showed the

highest value, 56 %. As the particle diameter became smaller, the specific surface area of the wood particles became bigger in the same particle shape.

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