Liquefaction of pulverized ligneous biomass powder in hot compressed water by using microwave heating

Nobuhiko Okada, Nobusuke Kobayashi, Shigenobu Hatano Yoshinori Itaya
Department of Chemical Engineering, Nagoya University
Guilin Piao
Nagoya Urban Industries Promotion Corporation
Shigekatsu Mori
Center for Cooperative Research in Advance Science and Technology, Nagoya University

ABSTRACT

The liquefaction of ligneous biomass by a hot compressed water method was studied for the utilization of useful biomass components. The pulverized ligneous biomass powder, which diameter was around 10 to 20 micrometers, was used as the raw material for the liquefaction process. In previous paper, it was found that the reactivity and extractability of biomass components were dramatically increased with decreasing the particle diameter. In this study, microwave was used for the heating wood slurry instead of heater. The microwave heating system can be controlled the heating period and reaction period easily and can be expected the decomposition or extraction reaction by microwave itself. In this experiment, the effect of microwave on the generated component was compared with the generated component at various temperature and reaction period. As the results, total yield of the liquefaction material was not different, but the produced components of the liquefaction material were different between those heating system.

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. 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 remained for commercialization, because of low 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 hot compressed water was conducted in 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 hot compressed water was considered as the effective method for the efficient ligneous biomass utilization [2].

For the effective liquefaction by 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].

Conventional external heating system by a heater was used for heating wood biomass slurry, but in this study, microwave was used for heating up wood biomass slurry because microwave was expected to have some abilities without heater. First merit was that microwave itself could foster the decomposition, because microwave affected molecular in wood biomass slurry directly. Secondly rapid heating could be possible. Finally microwave heating system could be controlled the heating period and reaction period easily.

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 hot compressed water and measured the liquefaction productivity. In the experiment, the effects of reaction temperature, microwave, and reaction time on the yield of water soluble product and the amount of monosaccharide in water soluble product, especially glucose or xylose were discussed.

Experimental

Pretreatment of liquefaction material

The pulverized ligneous biomass powder was used for the liquefaction. Shavings of zelkova were pulverized by a vibration mill. The particle size distributions of this powder were shown in Figure 1 and the 50% particle diameter was about 23.2μm. The shape of wood particles was observed by Scanning Electron Microscopy (SEM). The SEM micrograph of the particles pulverized was shown in **Figure 2**. 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.

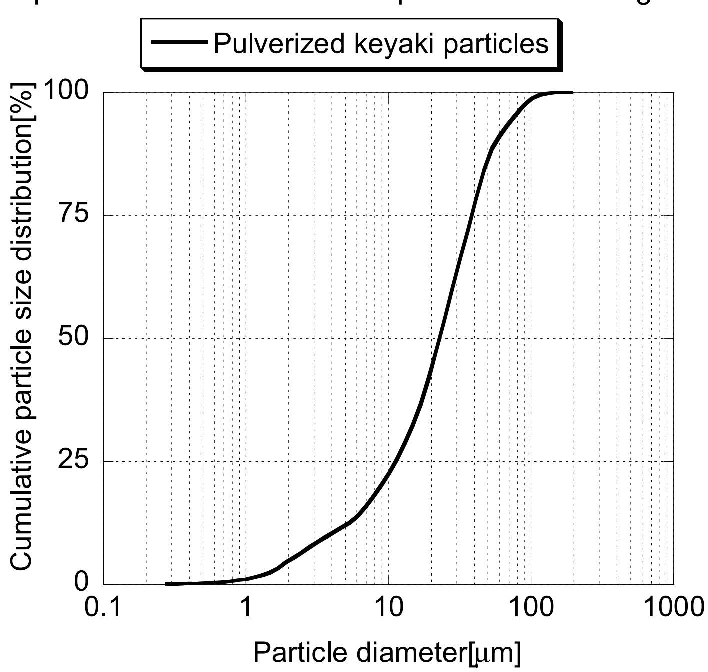

Figure 1 Cumulative particle size distribution of the pulverized particles

The wood biomass slurry was prepared by using the pulverized powder. The wood powder was mixed with deionized water and it was agitated for several minutes by shaker until the pulverized power was dispersed uniformly. In the experiment, the biomass slurry of 60 g was made by mixing 6 g wood powder and 54 g deionized water together.

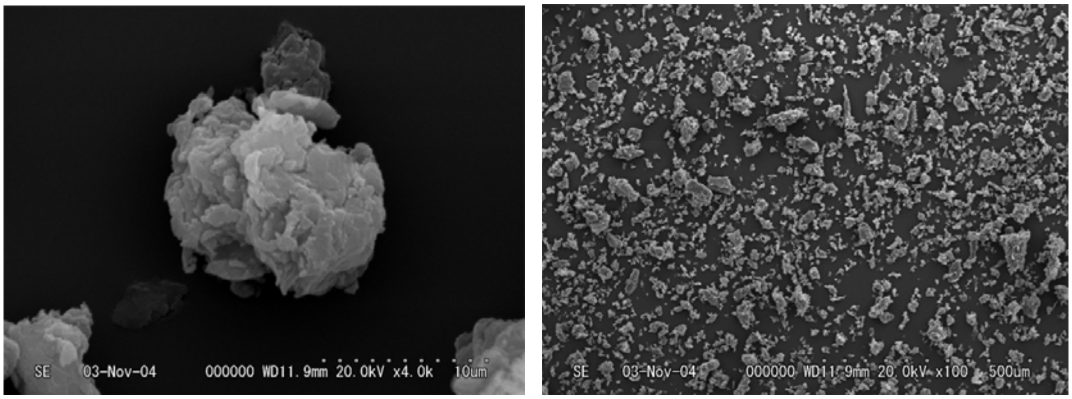

Figure 2 SEM micrographs of the wood particles

Batch reactor for liquefaction

Schematic diagram of autoclave was shown in **Figure 3**. 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.

Schematic diagram of microwave heating system was shown in **Figure 4**. This system enabled to irradiate microwave from the upper part and heat up the biomass slurry rapidly in compared with autoclave. This system has two magnetrons of 800W, but the maximum power was 1000W. The reaction temperature and time was decided by the controller. The reactor was made of TFM and the volume was 100cc. It was fit in protection shield made of HTC plastic to endure inner pressure and insulate inner temperature.

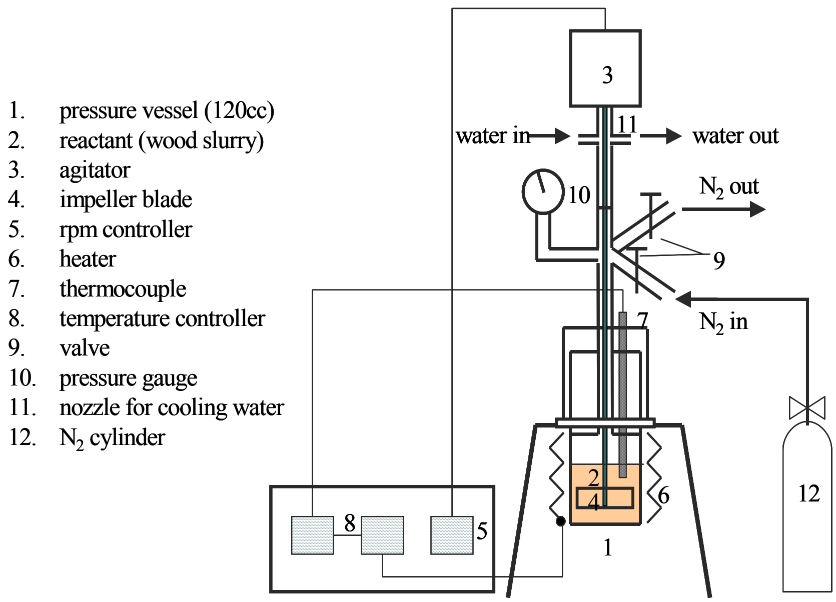

Figure 3 Schematic diagram of autoclave

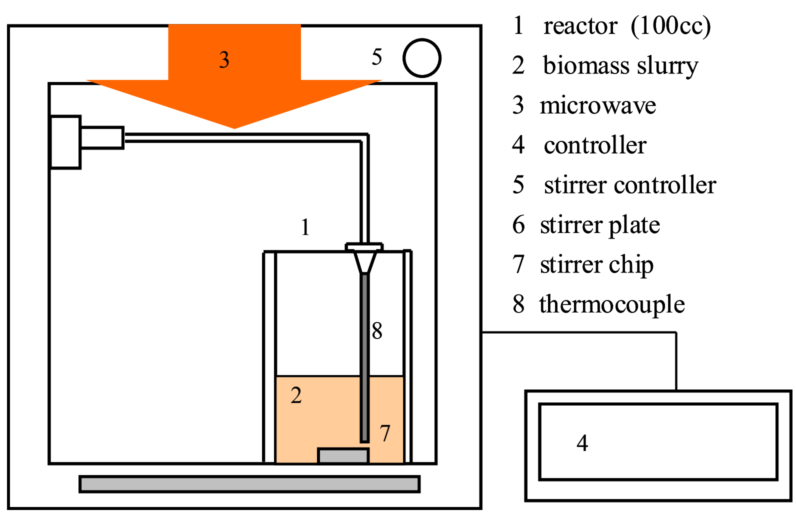

Figure 4 Schematic diagram of microwave heating system

Experimental Procedure

Well-mixed biomass slurry of 60 g was used. For the experiments using autoclave, 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 523 K. After the temperature of the slurry reached the target temperature, the temperature was kept for several minutes. Then, the vessel was quenched to 298 K by water immediately. Reaction temperature was defined from the time to start heating to the time to quench. 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.

For the microwave heating system experiment, wood biomass slurry was just put into the reactor. Then the vessel was also heated up at the temperature of 423 K to 523 K. After the temperature of the slurry reached the target temperature, the temperature was kept for several minutes. Then, the vessel was quenched to 298 K by water mildly. Following operation was the same as for autoclave.

Calculation of water soluble product (WS) yield and analysis of the components in WS

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;

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

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

And HPLC was used for analysis of the components in WS. In this study, the amount of saccharide, especially monosaccharide like glucose or xylose was measured by HPLC.

RESULT AND DISCUSSION

Effect of microwave and reaction temperature on the yield of WS and the components in WS

The effect of microwave and reaction temperature on the yield of WS and the amount of monosaccharide was measured. The reaction temperature was set 423K, 473K, and 523K. And both autoclave and microwave heating system were used for liquefaction. To examine the effect of microwave itself, the reaction conditions such as heating speed and reaction time except for reaction temperature were constant. The heating speed was about 20K/min and the reaction time was always 21.5min. **Figure 5** showed that the yield of WS in the different reaction temperature and different heating method. **Figure 6** and **Figure 7** showed that the amount of glucose or xylose respectively.

As the reaction temperature rose, the yield of WS also increased. The decomposition of hemi-cellulose was started under 473K, and the decomposition of cellulose was started under 523K. And the yield of WS did not change between those heating system, however the components in WS changed. When the reaction temperature was 473K, the amount of xylose was increased by using microwave, and the amount of glucose was decreased when the reaction temperature was 523K.

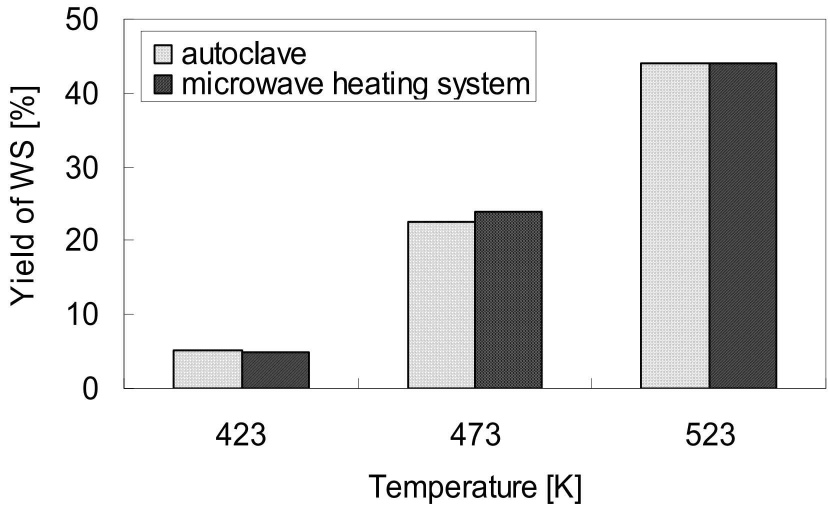

Figure 5 Effect of the reaction temperature and microwave itself on the yield of WS

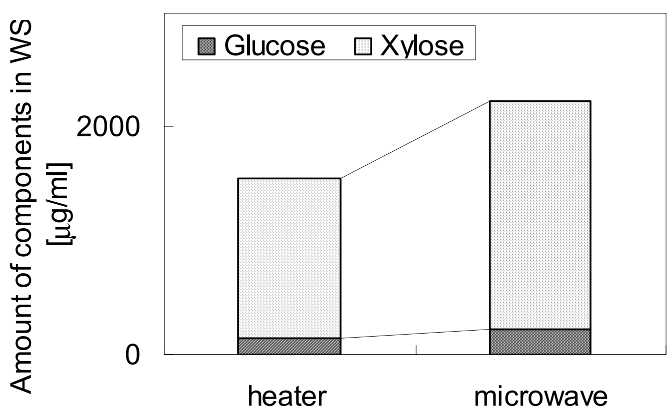

Figure 6 Effect of microwave on the components in WS at 473K

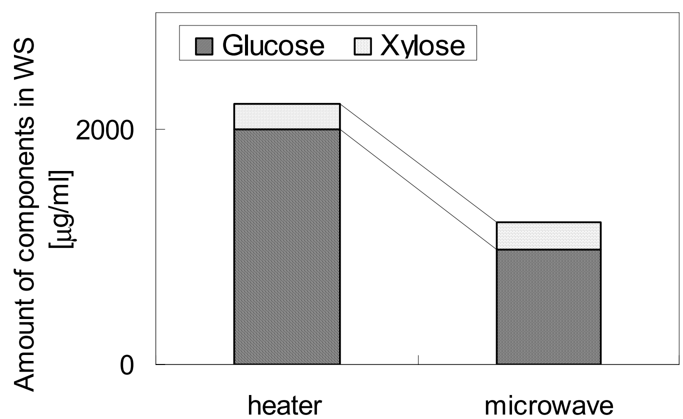

Figure 7 Effect of microwave on the components in WS at 523K

Effect of reaction time on the yield of WS and the components in WS

The effect of reaction time on the yield of WS and the amount of monosaccharide was measured at 473K, 523K. The microwave heating system was used for liquefaction. To examine the only effect of reaction temperature, the other reaction conditions were constant. The heating speed was about 100K/min and 473K and 523K were taken as the reaction temperature. **Figure 8** showed the yield of WS in the different reaction time. (Figure8 was the data at 523K.) And **Figure 9** and **Figure 10** showed the amount of glucose or xylose at various reaction time. (**Figure 9** and **Figure 10** were the data at 473K and 523K respectively.)

The yield of WS was changed by reaction time. The longer reaction time was, the more the yield was increased until it reached about 55%. After reaching about 55%, it was not increased more if reaction time was taken longer. It became obvious that the amount of xylose was increased and glucose was decreased when reaction time was taken longer.

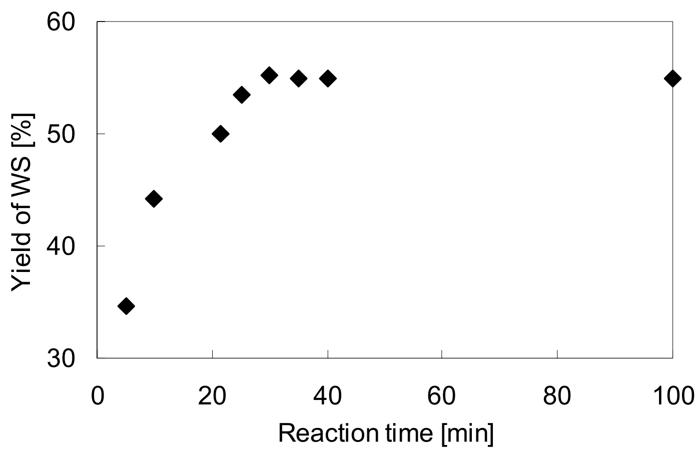

Figure 8 Effect of the reaction time on the yield of WS at 523K

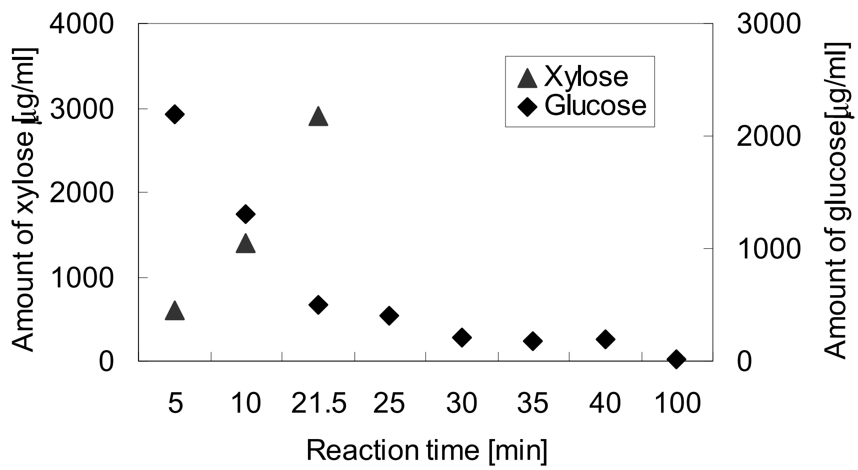

Figure 9 Effect of the reaction time on the amount of xylose or glucose in WS

Two-step liquefaction reaction

To utilize the components of biomass efficiently two-step liquefaction was examined. First liquefaction was conducted at 473K and the WS was sampled. Secondly the remained residue was mixed by deionized water and biomass slurry was made again, and liquefaction reaction was conducted at 523K. **Figure 10** showed the components in WS at each temperature when two-step reaction was conducted. **Figure 11** showed the effect of two-step liquefaction on the final components in WS at 523K.

When the liquefaction was conducted by two-step, xylose could be obtained at low temperature around 473K and glucose could be obtained at high temperature around

523K.The components in WS of two-step liquefaction at 523K were the almost same as those of one-step liquefaction, which meant the liquefaction that wood biomass slurry was heated up by 523K directly. So by two-step liquefaction, the components of biomass were utilized more efficiently than one-step liquefaction.

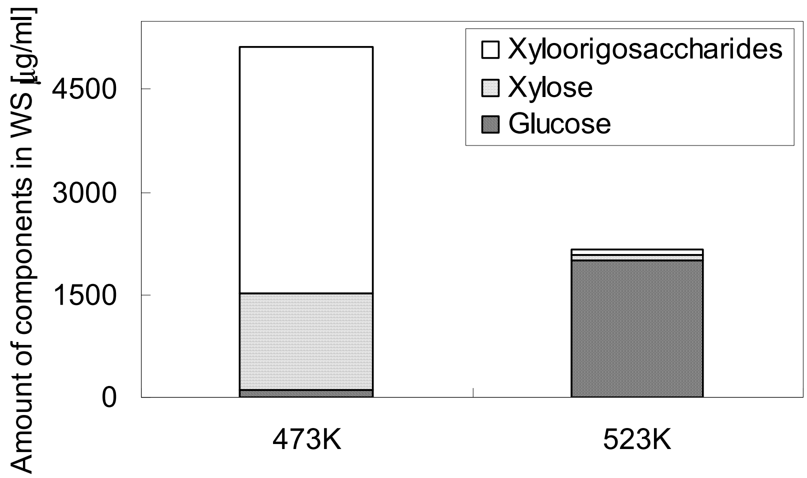

Figure10 Components at each temperature, 473K and 523K in two-step reaction

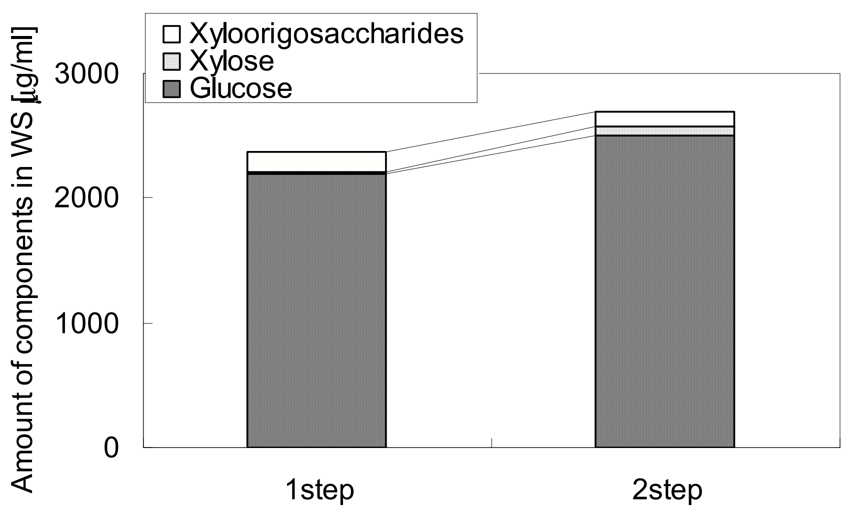

Figure11 Effect of two-step liquefaction on the components in WS at 523K

CONCLUSION

To develop the efficient liquefaction technique of wood biomass, the wood biomass pulverized by the vibration mill was liquefied in hot compressed water. Microwave was used to heat up the wood biomass slurry. The effects of microwave itself, reaction temperature, and reaction time on the yield of WS and the amount of saccharides in WS were measured. The results were summarized as following.

1. As the reaction temperature rose, the yield of WS also increased. By the difference of the reaction temperature, the components in WS were different.
2. The yield of WS was not changed by microwave itself, however, the components in WS was changed. The amount of xylose was increased at 473K, and the amount of glucose was decreased by using microwave for heating.
3. The final amount of saccharides as one-step liquefaction was the almost same as two-step liquefaction. So two-step liquefaction was more effective to obtain saccharides from the wood biomass efficiently.

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