

The Study on the liquefaction residues of wood biomass

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Introduction

Liquefaction process of wood biomass was the one of the promising technologies to produce clean and environmentally friendly energy and material resource. Wood biomass was the carbon neutral and renewable resource, and it was distributed all over the world. Producing ethanol from wood biomass was the most attracted attention of recent years, since the environmental issues by green house gas and exhaustion problems of fissile fuel has been came to front.

There were several technologies to produce monosaccharide from wood biomass, and the acid hydrolysis method, supercritical water method, enzyme saccharization method and blasting method had been studied. The acid, usually dilute sulfuric acid, hydrolysis method was in a verification test level in North American country, European country and Japan for the production of ethanol, but lots of economical issues were still remained for the commercialization, because the deacidification process, acid recovery process and water treatment facility was necessary. Recently, new hydrolysis method of wood biomass by using hot compressed water, called hot-compressed-water method (HCW), was proposed [1, 2, 3]. This method was able to hydrolyze the wood biomass without any acid. Because only the water was used for hydrolysis in HCW process, this process was the clean, simple and low cost, but the hydrolysis efficiency was usually low.

In these hydrolysis processes, solid residue was also produced as well as the liquid saccharine product as in **Figure 1**. Solid residue was considered to be used as energy recycle source for the hydrolysis process, but the solid residue from the acid hydrolysis method contained sulfur, and it could not be used as the fuel without desulphurization facility in Japan. On the other hand, the solid residue from HCW process, the solid residue contained no sulfur at all, and it could be used as the high quality solid fuel. The hydrolysis efficiency of HCW process was lower than that of the acid hydrolysis process, but considering the liquid product and clean solid product together, the total energy conversion efficiency of wood biomass was better than that of the acid hydrolysis process. Therefore, it was very important to understand the properties of solid residue and utilization method for the development of HCW process indeed. However, there were a few papers reporting the solid residue characteristics in the HCW process so far.

In this paper, the characteristics of solid residue on HCW process was discuss and two different utilization processes of the residue were proposed. For the evaluation of solid residue, composition analysis, particle size and shape were measured. As the utilization process, the solid residue was evaluated as the clean solid fuel and biodegradable material.

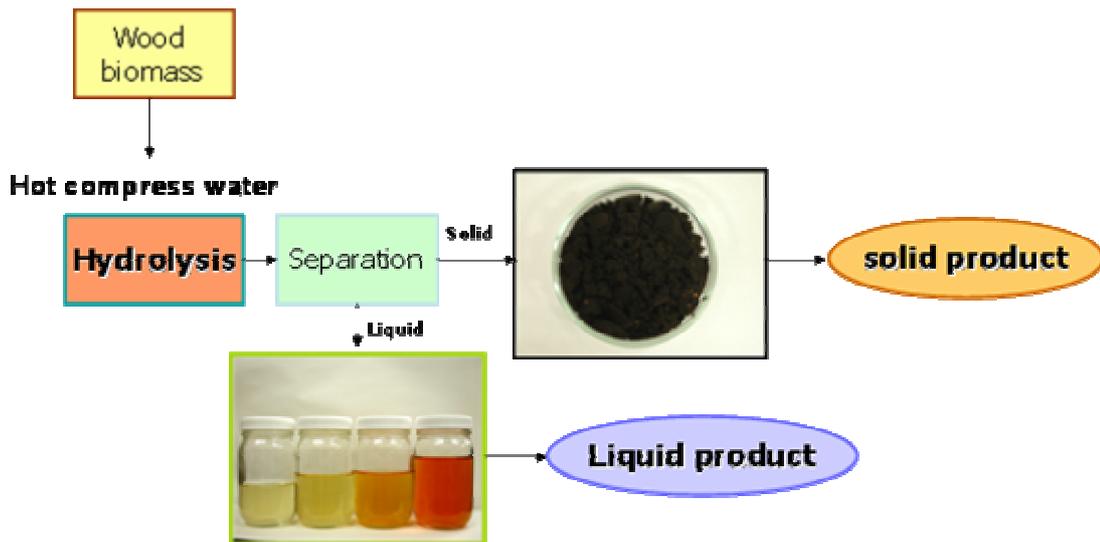


Figure 1. Products from HCW process of wood biomass

Experimental

Liquefaction experiment of wood biomass was conducted in the HWC method. Schematic diagram of liquefaction system was shown in **Figure 2**. This equipment was the batch type reactor (autoclave). The experimental system consists of a pressure vessel, heater, pressure gauge, agitator for mixing the wood biomass slurry, thermocouple, temperature controller and rpm controller. The pressure vessel was made of stainless steel and the volume was 120 cc. The pressure vessel was sealed by an insulator to reduce the heat release. The temperature of the 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 wood biomass powder. The number of rotations was set 500 rpm. The pressure of the vessel was the same as the water vapor pressure of that temperature.

Before the liquefaction experiment, wood biomass was pulverized into the powder. The wood biomass slurry was prepared by using the pulverized powder. The 50 % particle diameter was around 30 μm , and the surface area was 2.62 m^2/g . The wood powder was mixed with deionized water, and it was agitated for several minutes by shaker until the pulverized powder was dispersed uniformly. In the experiment, the wood biomass slurry of 80 g was made by mixing 8 g wood powder and 72 g deionized water together. 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 to the target 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 to the target temperature. Then, the vessel was quenched to 298 K by ice water immediately to prevent the secondary reaction. The reaction product was taken from the pressure vessel and it was separated solid residue from liquid product by the suction filtration. Solid residue was dried at 378 K for 24 hours in an oven and its weight was measured. To evaluate the characteristics of wood biomass in the liquefaction

process, several analyses from the different aspect was conducted. Firstly, ultimate and industrial analysis of solid product was conducted. Particle size distribution and particle density of products was measured to evaluate physical property of solid product. Particle shape was observed by SEM. Composition of solid was also analyzed by FT-IR.

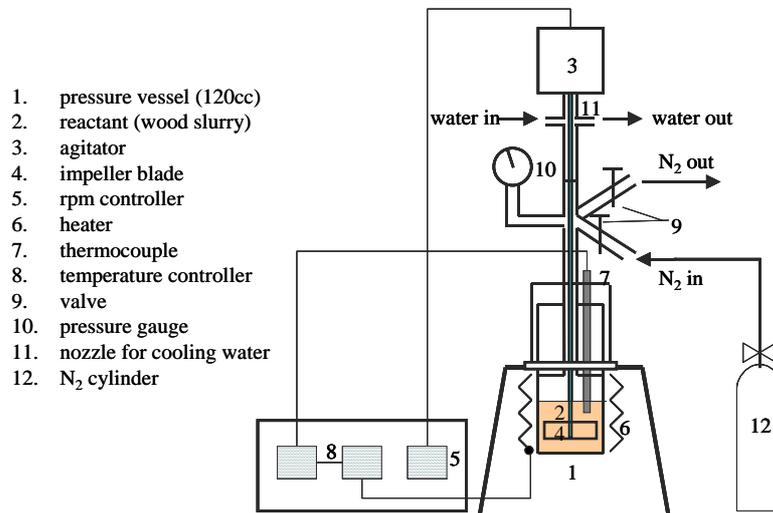


Figure 2. Experimental apparatus of HCW liquefaction process of wood biomass

Result and discussion

Chemical and physical properties of solid product

Before discussing the solid product property, the yield of solid product from the HCW process in the different operation temperature was shown in **Figure 3**. The yield of solid product was calculated by Eq.1.

$$\text{Yield of solid product} = \left\{ \frac{\text{(solid residue weigh after liquefaction (dry))}}{\text{Initial wood biomass weight (dry)}} \right\} \quad (\text{Eq.1})$$

The yield of solid product was decreasing with increasing the operation temperature dramatically. This was meaning that the yield of liquid product was increasing with increasing the operation temperature. The yield of solid product was less than 50 % of initial wood biomass weight at the temperature of 513 K. To understand the chemical composition change, **Table 1** shows the ultimate and industrial analysis of solid product produced at different temperature. Carbon content was increased with increasing operation temperature, and oxygen content was decreased with increasing operation temperature on the contrast. Hydrogen content was slightly decreased with increasing operation temperature. Along with the element composition change, volatile matter and fix carbon ratio was also changed with the operation temperature. Fix carbon content was increased with increasing the operation temperature, and volatile matter was decreased with increasing the operation temperature. Ash content was apparently increased with increasing the operation temperature.

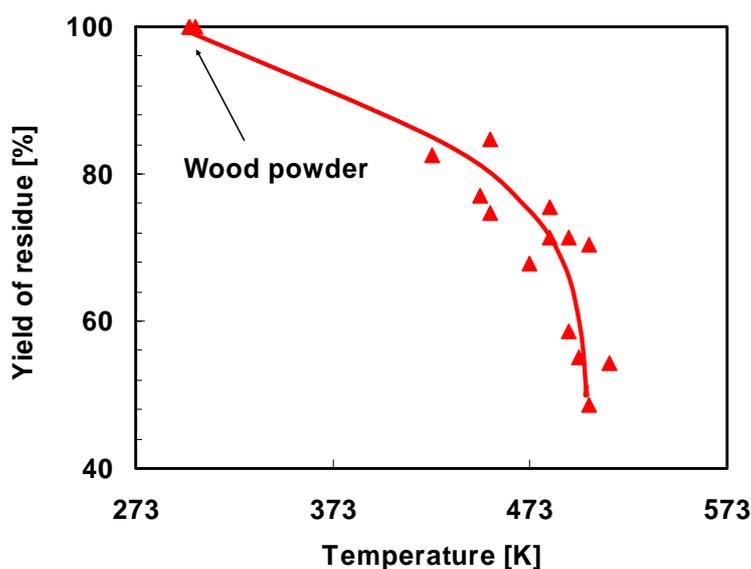


Figure 3. Yield of solid product at different liquefaction operation temperature

Table 1. Ultimate and industrial analysis of solid products at the different operation temperature

	Unit	Wood	423 K	473 K	523 K	573 K
C	%	49.9	47.2	49.1	58.0	67.3
H	%	6.3	6.2	6.1	5.6	5.0
N	%	0.19	<0.01	0.05	0.03	0.05
O	%	42.76	46.3	44.6	36.1	27.3
H/C	-		1.58	1.49	1.16	0.89
O/C	-		0.74	0.68	0.47	0.30

	Unit	Wood	423 K	473 K	523 K	573 K
Ash	%	0.77	0.3	0.18	0.25	0.34
Volatile	%	81.22	86.85	85.7	72.48	55.83
Fix carbon	%	18.01	12.85	14.12	27.27	43.83

To better understanding these changes in the liquefaction process, H/C and O/C values of solid product was plotted in **Figure 4** with coal band together. Both H/C and O/C value was decreased with increasing the operation temperature. Solid product produced at the temperature of 573K, the composition was similar with the lignite. Actually, the change of composition by the liquefaction was following the dehydration and decarbonation. When the chemical composition of wood biomass was hydrolyzed, the solid residues lose the H₂O apparently. Not only the explaining the solid product from the chemical element difference, but also the clearing the solid product composition from the chemical functionality by using FT-IR. **Figure 5** shows the chemical functionality change of solid product produced at different operation temperature. It was very difficult to break off those complicate peaks, but 1700 cm⁻¹, 1600 cm⁻¹ and 1100 cm⁻¹ peak was paid attention in this experiment. Both 1700 cm⁻¹ and 1600 cm⁻¹ peaks identified the benzene skeleton, and 1100 cm⁻¹ peak identified stretching of the glucose ring. Benzene skeleton peak intensity was sharper with increasing the operation

temperature, but the stretching of the glucose ring peak became smaller with increasing the operation temperature.

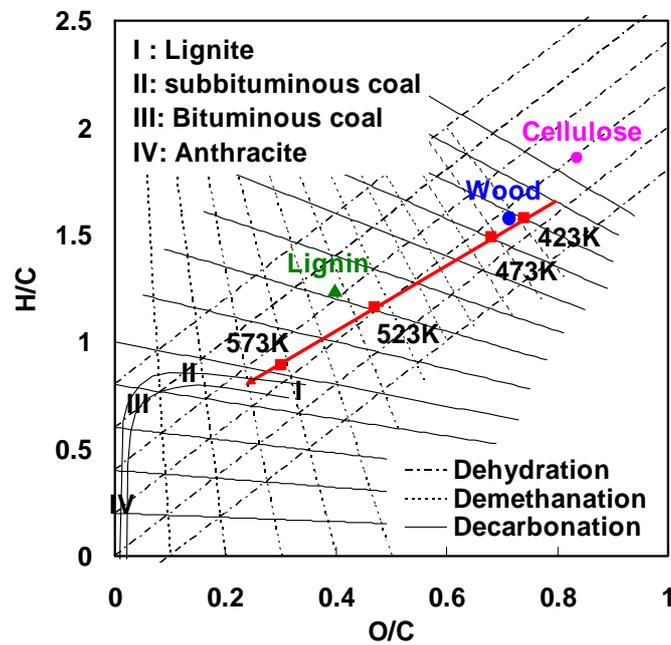


Figure 4. H/C and O/C plot of solid product produced at the different operation temperature

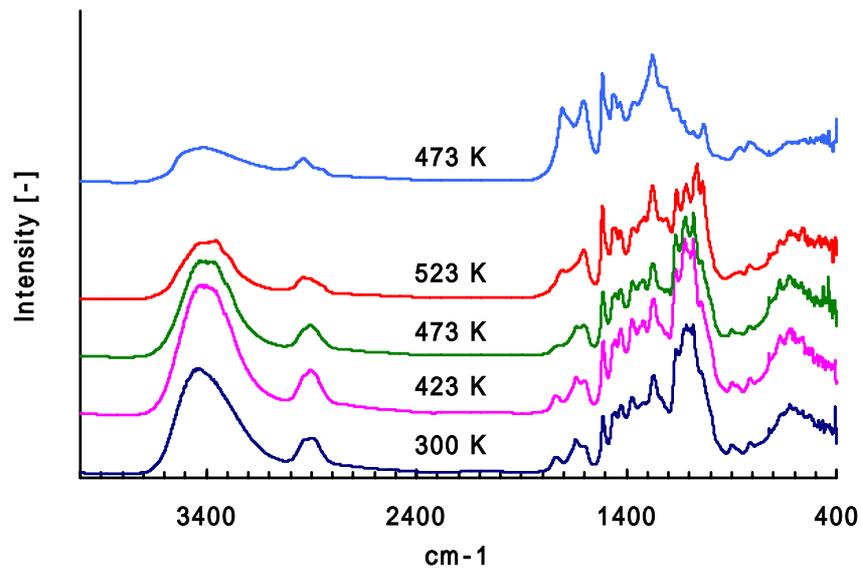


Figure 5. FT-IR curve of solid product produced at the different operation temperature

Usually, hemicellulose starts decomposing around 453 K, cellulose start decomposing around 503 K. Therefore, composition of solid product produced at the temperature of 423 K was similar with wood biomass composition. But, increasing the operation temperature, the composition change, because, those hemicellulose and cellulose was start hydrolyzing over 473 K. Considering the table 1, figure 4 and figure 5 together, part of cellulose component was

hydrolyzed to water soluble saccharine, insoluble lignin, which was consisted of benzene skeleton initially, was remained mostly as the solid residue. But, the increasing temperature, dehydration of solid residue was promoted more and more.

After discussing the effect of the operation temperature on the chemical property of solid product, physical property of solid product was examined by measuring particle diameter, particle shape and crystallinity. **Figure 6** shows the particle diameter distribution of solid products produced the different operation temperature. The average particle diameter was decreased with increasing the operation temperature. The diameter became 1/7 of initial particle diameter at the temperature of 523 K.

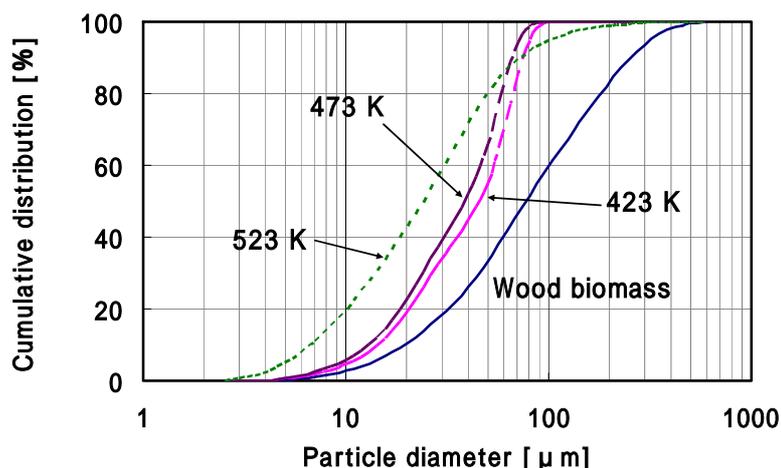


Figure 6. The particle diameter distribution of solid product produced at the different operation

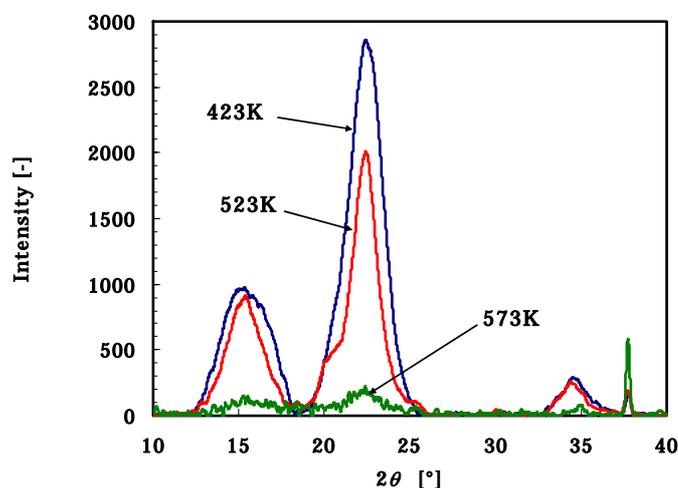


Figure 7. XRD curve of solid product produced at the different operation temperature

Figure 7 shows the XRD curve of solid products produced at the different operation temperature. The peaks observed at $2\theta = 16$ and 23 became smaller with increasing the operation temperature. Increasing the temperature, the cellulose crystal structure was changed

amorphous structure. Actually, the cellulose crystal peak was not observed at all over 573 K. This was meaning that the cellulose structure was decomposed into soluble product by HCW.

Utilization of solid product

In the HCW liquefaction process, the solid product utilization was the most important challenge for the commercialization. From the chemical and physical analysis of solid product, it was the very fine carbonaceous amorphous powder. It meant that the solid product had high reactivity. Carbon content was very high, but the volatile matter was also high comparing with the coal. It meant that the solid product has high combustibility. Since the solid product produced at high temperature had such characteristics, two different utilizations were considered and some analysis was conducted. One was for the solid fuel, and the other was for the bio-plastic. To evaluate the solid product as fuel, the heating value was calculated as shown in **Figure 8**. The heating value of solid product was increased with increasing the operation temperature. The heating value was similar with the coal produced over 573 K. However, there were several advantages comparing with coal.

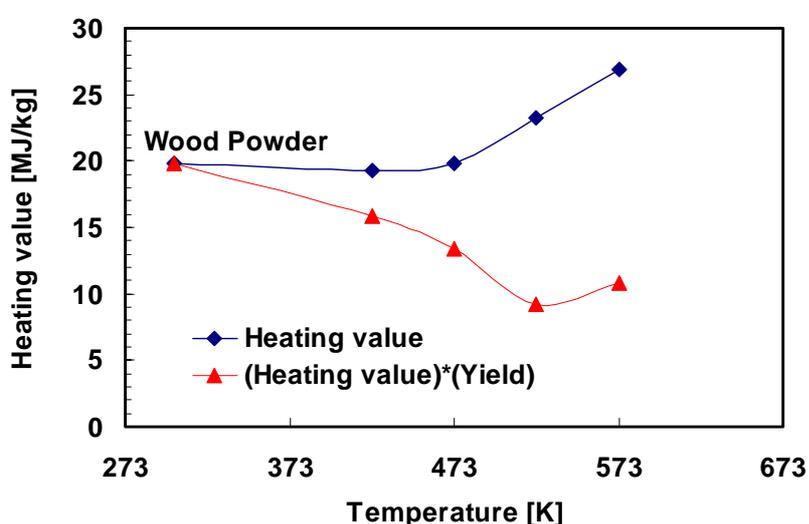


Figure 8. Heating value of solid product produced at the different operation temperature. The solid product contained low ash, low sulfur and low nitrogen, which lead environmental problems, such as SO_x and NO_x . More over, wood biomass was the carbon neutral and renewable. For such reasons, the solid product was recognized as the high quality and value-added solid fuel instead of fossil fuel.

To evaluate the bio-plastic ability as the one of the material utilization method, several experiments was conducted. The experiment result was summarized in **Table 2**. Photograph of bio-plastics was shown in **Figure 9**. Density, bend strength, water adsorption coefficient and water adsorption expansion coefficient was measured. MDF properties were in Table for comparison. The quality of bio-plastics was above that of MDF. This result indicated the possibility of bio-plastic use of solid product.

Table 1. Properties of bio-plastic made by solid product

		Density	Bend Strength	Water adsorption coefficient	Water adsorption expansion coefficient
		g/cm ³	MPa	%	%
Solid product	523 K	1.4	39.9	1.4	0.7
MDF	-	0.8	30	20>	12>



Figure 9. Photograph of bio-plastics make by solid product

Conclusions

Chemical and physical properties of solid product produced from HCW process was analyzed in this paper. The solid product characteristics were very different on the different operation condition. Especially, the operation temperature was most effective parameter on the solid product characteristic. The solid product was fine carbonaceous amorphous powder with high carbon content and high volatile matter. This meant that the solid product had high reactivity and high combustibility. Therefore, the solid product could be used high quality solid fuel and high quality bio-plastic.

References

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