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The influence of fast pyrolysis condition on biocrude-oil yield and homogeneity

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Abstract−The characteristics of biocrude-oil yield and quality have been investigated by changing fast pyrolysis condition for woody biomass. For the fast pyrolysis of woody biomass, a bubbling fluidized bed reactor having cylindrical shape was devised and a commonly used spiral quenching system was applied to the condensation of volatile gases from the reactor. Biomass feeding rate, nitrogen flow rate, pyrolysis temperature and particle size of woody biomass were changed to study the characteristics of volatile generation, its condensation and the homogeneity of the condensed biocrude-oil. In particular, the microscopic visualization of the collected biocrude-oil and its evaluation method by image processing technique were made for quantifying the homogeneity of the oil. From the results, the effects of heating and fluidization condition on the biocrude-oil yield and the homogeneity were fully scrutinized in a bubbling fluidized bed reactor. Also, the physical and chemical characteristics of the collected biocrude-oil were determined through various analysis techniques.

Key words: Biocrude-oil, Biomass, Fast Pyrolysis, Fluidized Bed, Heat Transfer

INTRODUCTION

Recently, international attention on environmental problems has been more and more increased, especially on global warming of the earth. Global warming is caused by greenhouse gases like carbon dioxide (CO_2) that is mostly generated by using fossil fuels. For one of the methods to reduce such greenhouse gas, recently CCS (carbon capture and storage) technique has intensively been investigated in many countries. As one example, the CCS process in a power plant is to capture CO_2 generated by using fossil fuels and to store the captured CO_2 underground or in aquifers in the ocean. However, this technique means the disposal of CO_2 which has already been generated; hence the suppression or reduction of CO_2 production is far from this one. On the other hand, energy techniques have widely been developed that obtain energy from nature such as sun, wind, tide etc. However, this is discontinuous energy and the start-up cost to construct their power plants is large. Also, their efficiencies are lower compared with a general power plant using fossil fuels. For the commercial use of natural power, these weaknesses should be overcome, but they are difficult to solve with the present technique. However, the energy from waste or biomass can be continuously provided and is more economical compared with the previous natural approaches. In particular, bio-energy from a cellulose biomass has little effect on the generation of greenhouse gas, even if the present combustion technique is directly applied because a cellulose biomass is carbon neutral by its photosynthesis process. Hence, researches on the conversion of raw biomass into bio-energy have been conducted in many countries, especially in Europe and North America [1-4].

The methods to make heat and energy directly from the combustion of a biomass have been developed and furthermore the decomposition methods of solid biomass into liquid or gas state also have actively been investigated. Among them, thermal conversion for a biomass is illustrated in Table 1 [5-7]. This method can be categorized into four sub-groups according to the target production ratio of gas, oil and char, and the production ratio is mainly affected by heating temperature and residence time. Among them, fast pyrolysis is known as an effective method for making the maximum yield of liquid oil. In this method, sufficient heat should be supplied to biomass within two seconds maintaining the pyrolysis temperature

Table 1. Thermal conversion methods for biomass

Thermal conversion methods	Operating temperature	Vapor residence time	Production ratio (weight, %)		
			Oil	Gas	Char
Fast pyrolysis	Around 500 °C	2 sec	75	12	13
Intermediate pyrolysis	Around 500 °C	10-20 sec	50	25	25
Slow pyrolysis (Carbonization)	350 °C-450 °C	Several hrs	30	35	35
Gasification	800 °C-1,300 °C	10 sec-30 min	5	10	85

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around 500 °C [7]. Then, the biomass is mainly decomposed into volatile, non-condensable gas and char. The volatile can be condensed into biocrude-oil. In the present study, the fast pyrolysis experiment for woody biomass is carried out to obtain biocrude-oil. For the fast pyrolysis of woody biomass, a bubbling fluidized bed reactor is used and the effects of the fast pyrolysis conditions on biocrude-oil yield and quality are studied by changing biomass feeding rate, nitrogen flow rate, pyrolysis temperature and particle size of biomass. Especially, their effects on the homogeneity of the collected biocrude-oil are investigated with the visualization of the collected biocrude-oil by using a microscope and image processing technique.

EXPERIMENTAL METHOD

Fig. 1 shows the experimental apparatus for the present fast pyrolysis experiment. A bubbling fluidized bed reactor is used for the fast pyrolysis of woody biomass, which uses an electrical furnace to control pyrolysis temperature. As shown in Fig. 1, woody biomass is supplied to the bubbling fluidized bed reactor by two-stage screw feeder. After that, the biomass is heated and then the heated biomass is mainly decomposed into volatile, non-condensable gas and char inside the reactor. In the reactor, sand particles are used for fluidization material and nitrogen gas is provided for the fluidization of the sand. The pyrolysis gas from the reactor is entered into the quencher for the condensation of the volatile, and finally the condensed biocrude-oil is collected. Also, an electrostatic precipitator is applied for the condensation of fine oil mist which is hardly collected in the quencher. The sample woody biomass used in the present study is bald cypress, and the physical characteristics of the sample woody biomass are shown in Table 2. Table 2 also shows the elemental analysis results for the sample woody biomass, and the carbon and oxygen contents are higher than other chemical elements.

Table 2. Physical characteristics and elemental analysis of woody biomass

Moisture (weight, %)[a]		20.9
Ash (weight, %)[a]		0.12
Higher heating value (kcal/kg)[a]		4187
Element (weight, %)[b]	C	47.12
	H	6.00
	N	0.11
	O	46.77
	S	0.00

[a]Dry basis
[b]Dry and ash free basis

Table 3. Experimental condition

Experimental Parameter	Case	Value
Biomass feeding rate (g/min)	1	2.2
	2	3.33
	3	6.25
	4	8.33
N_2 flow rate (liter/min)	5	10
	6	15
	7	20
	8	25
Pyrolysis temperature (°C)	9	450
	10	500
	11	550
	12	600
Particle size (mm)	13	0.5-1
	14	1-2
	15	2-3.3

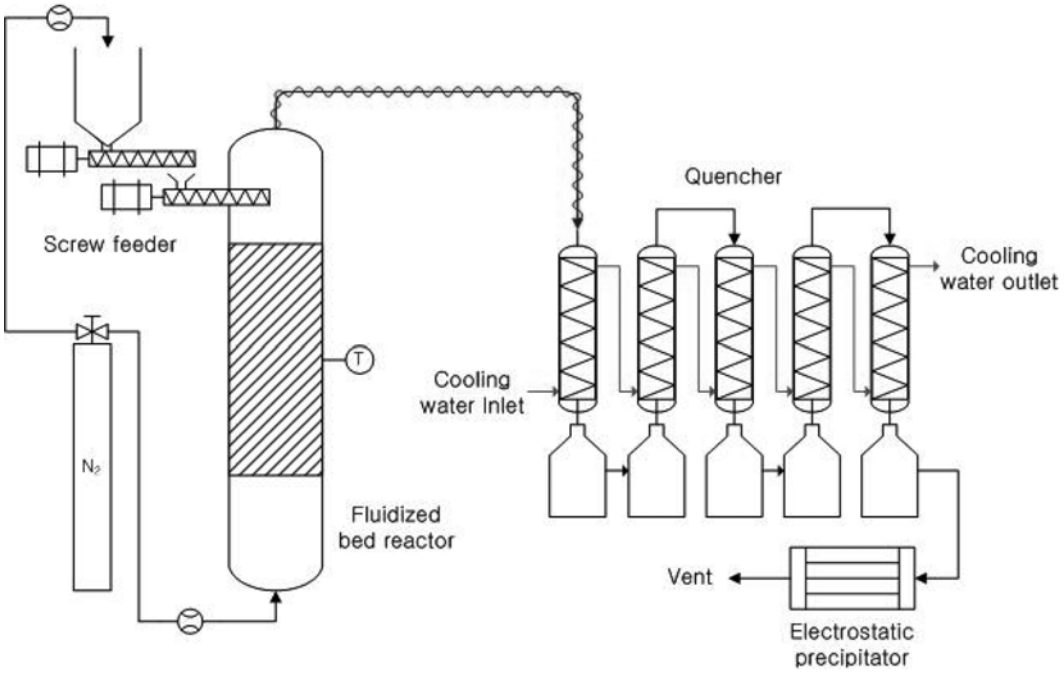

Fig. 1. Experimental apparatus for fast pyrolysis of woody biomass.

In the present study, the experimental parameters and conditions are selected as shown in Table 3 in order to determine the effects of biomass feeding rate, nitrogen flow rate, pyrolysis temperature and particle size of biomass on the biocrude-oil yield and quality. It is noted that for all the cases, only one parameter of Table 3 is different from the standard experimental case. For reference, the standard experimental case is as follows. N_2 flow rate of 15 liter/min, pyrolysis temperature of 480 °C, biomass feeding rate of 3.33 g/min and particle size of 1-2 mm are applied for the standard case. The weights of the biocrude-oil yield and raw biomass are measured by digital balance having 1/100 g accuracy and the measured data are processed by the following equation.

$$\text{Biocrude-oil yield}=(\text{weight of collected biocrude-oil})/(\text{weight of totally supplied woody biomass})\times 100 \quad (1)$$

To find the quality of the collected biocrude-oil, Oasmaa and Meier's method [8] is applied. The homogeneity of the collected biocrude-oil is qualitatively visualized by a 1/100 scale microscope. Fig. 2 shows the biocrude-oil pictures visualized by the microscope. According to each experimental condition, the low quality biocrude-oil may be obtained having impurities like water droplets, and solid materials as shown in Fig. 2(a), or the high quality biocrude-oil of Fig. 2(b) without impurities is collected. For the quantitative analysis of the visualized image, image processing [9] is applied to the photos, and the area occupied by impurities such as water droplets, and solid materials is calculated. As shown in Fig. 3(a), firstly, the territory occupied by impurities is defined at stage 1 and then the area is calculated at stage 2. The calculated area of the impurities is processed in the following equation to quantify the homogeneity of the collected biocrude-oil.

$$\text{Homogeneity}=(\text{total area}-\text{calculated area of impurities})/(\text{total area})\times 100 \quad (2)$$

Also, the physical characteristics and chemical compounds of the collected biocrude-oil are investigated by the following measurement techniques. To measure its moisture content, the Karl Fisher titration method is applied and LECO AC-350 instrument is used for the measurement of heating value. For measuring the solid weight contained in the collected biocrude-oil, a filter of pore size 0.1 μm is adopted and for ash measurement, moisture and volatile gases

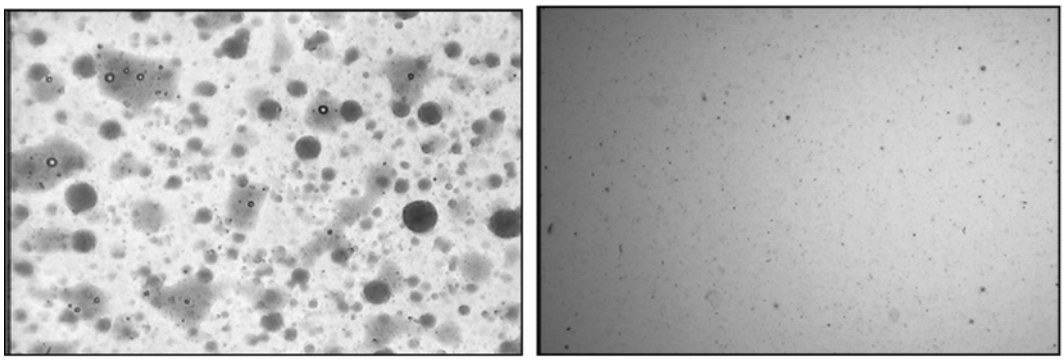

Fig. 2. Microscopic view of biocrude-oil.

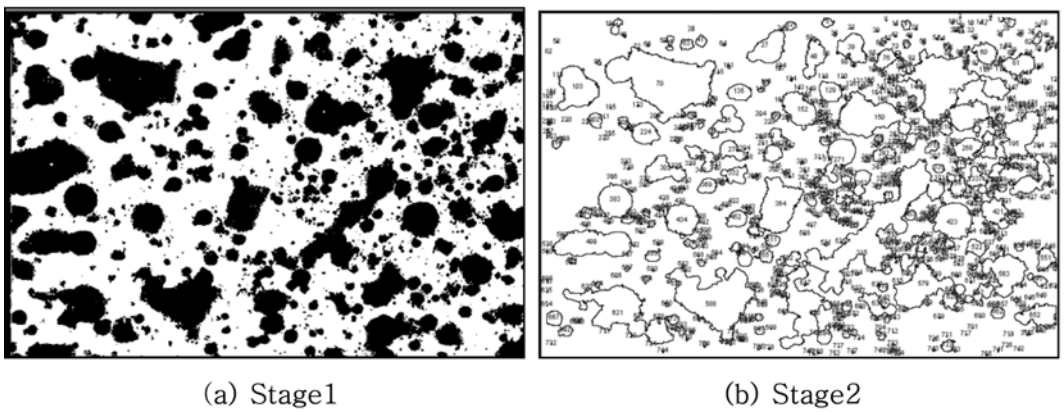

Fig. 3. Image processing of biocrude-oil photos.

Table 4. Physical characteristics of collected biocrude-oil at standard condition

Moisture (weight, %)	Density (kg/m^3)	pH (at 20 °C)	Low heating value (kcal/kg)	Solids (≤0.1 μm, weight, %)	Ash (weight, %)
26.96	1.22	2.40	3625	0.068	0.015

having low boiling point are evaporated to prevent the splashing of the sample, and then the weight of remnant is evaluated after its combustion at 770 °C. The chemical elements for C, H, N, O and S are measured by the thermo elementary analyzer, FLASH EA1112, and the chemical compounds of the biocrude-oil are found by gas chromatography with the mass selective detector.

RESULTS AND DISCUSSION

1. The Characteristics of the Collected Biocrude-oil

Table 4 shows the physical characteristics of the collected biocrude-oil under the standard experimental condition. Additionally, the biocrude-oil is dark brown and has a pungent odor. In particular, the low heating value of the biocrude-oil is 3625 kcal/kg, which is about one-third of heavy oil. For the solid particle contained in the biocrude-oil is measured as discussed in the previous section and Table 4 shows that the weight percentage of solid particles (≤0.1 μm in size) is less than 0.015% in the collected biocrude-oil. This represents that the solid particles like char do not exist in the biocrude-oil under the standard experimental condition. Table 5 and Fig. 4 show the elemental analysis results and chemical compounds for the collected biocrude-oil, respectively. In Table 5, the biocrude-oil still has higher oxygen content as in the sample biomass. However, nitrogen and sulfur do not exist in the biocrude-oil, which may become toxic materials when they burn. As shown in Fig. 4, the biocrude-oil is composed of various chemical compounds comparable to those of fossil crude-oil, and similarly the biocrude-oil can directly be used for boilers, gas turbines and engines. Furthermore, this can be reformed into transportation fuel, or high value-added chemicals can be extracted from it through a bio-refinery [2]. Hence, it is very valuable to investigate the yield and quality of the biocrude-oil under different experimental conditions for future industrial application. This will be discussed in the next chapter.

2. The Yield and Quality of the Collected Biocrude-oil

Fig. 5 shows the yield and quality of the biocrude-oil with increasing the sample biomass feeding rate. Here, the biocrude-oil yield is obtained by Eq. (1). The biocrude-oil yield is increased as the sample feeding rate grows. This can be explained as follows. The pyrolysis gas flow rate is increased as the sample biomass feeding rate rises. However, if the biomass feeding rate exceeds the pyrolysis capacity of the reactor, the quality of the biocrude-oil is decreased and this can be confirmed by the homogeneity in Fig. 5. For reference, the homogeneity is calculated by Eq. (2) after image processing of the biocrude-oil picture taken by a microscope. In the figure, the larger the homogeneity becomes, the better the quality of the biocrude-oil is.

Fig. 6 shows the effect of the nitrogen flow rate on the biocrude-

Table 5. Elemental analysis of collected biocrude-oil at standard condition

Element (weight, %)	C	43.30
	H	7.56
	N	0
	O	49.14
	S	0

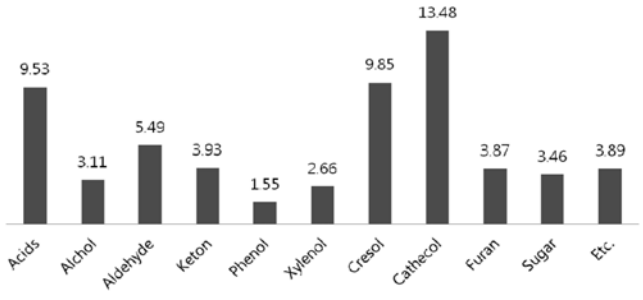

Fig. 4. Chemical compounds of collected biocrude-oil at standard condition.

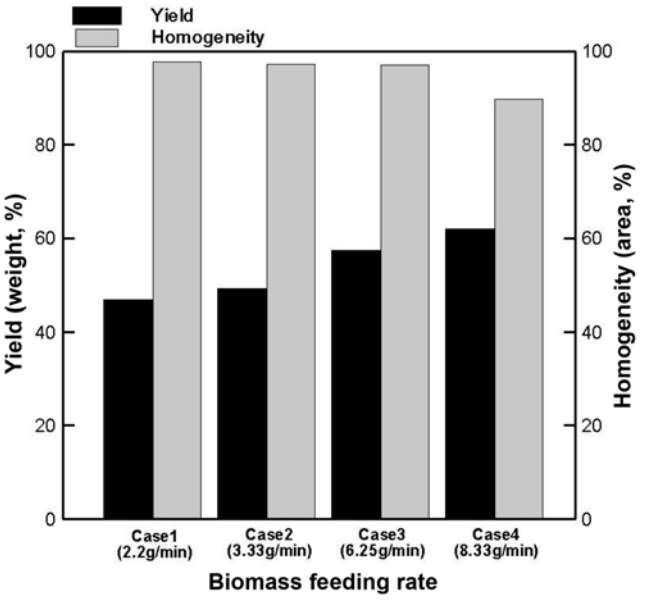

Fig. 5. Biocrude-oil yield and homogeneity with varying biomass feeding rate.

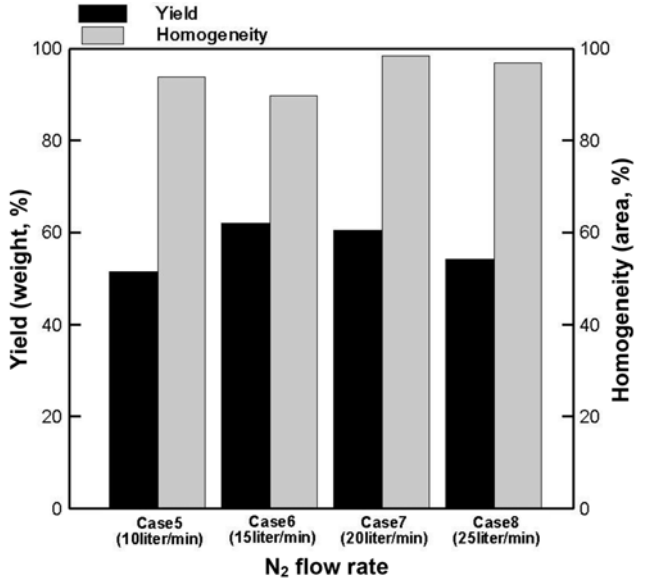

Fig. 6. Biocrude-oil yield and homogeneity with varying N_2 flow rate.

oil yield and quality. The change of the nitrogen flow rate affects the fluidizing pattern of the sand particles. The yield is increased as the nitrogen flow rate grows from 10 liter/min to 15 liter/min and then it is decreased as the flow rate is increased from 15 liter/min to 25 liter/min. If the nitrogen flow rate gets bigger from 10 liter/min to 15 liter/min, the fluidization condition of the reactor becomes steady bubbling fluidization state. Here, the steady bubbling fluidization state represents that the bubbles are distributed randomly for space and time [10,11]. In the present study, this condition is confirmed by a cold flow test considering gas volume expansion occurred under hot gas condition. In this fluidization condition, mixing between the sand and the sample biomass particle is enhanced by the stochastic flow patterns of the bubbles, and the consequent heat transfer from the sand to the biomass is also increased. Then, the fast pyrolysis of the biomass actively progresses, and the biocrude-oil yield is increased as shown in Fig. 6. On the other hand, if the flow rate surpasses 15 liter/min, the size of the bubble is increased and the fluidization condition is changed from the steady bubbling fluidization to slugging fluidization resulting in the decrease of the biocrude-oil. However, the homogeneity of the biocrude-oil is in inverse proportion to the yield because the generation of char and impurities may be raised together with the increase of the volatile production. It is noted that the change of the fluidization condition can have a great effect on the yield and quality in the bubbling fluidized bed reactor.

Fig. 7 shows the result when the pyrolysis temperature is increased in the reactor. If the pyrolysis temperature is increased from 450 °C to 600 °C, the biocrude-oil yield is first increased and then decreased. This may be due to the secondary reaction, which becomes dominant when the pyrolysis temperature exceeds 500 °C. By the secondary reaction, the tar generated by the primary reaction is decomposed into the char and non-condensable gas [12,13]. Hence, the optimal temperature of the fast pyrolysis for the sample biomass is around 500 °C. In Fig. 7, the homogeneity is somewhat decreased

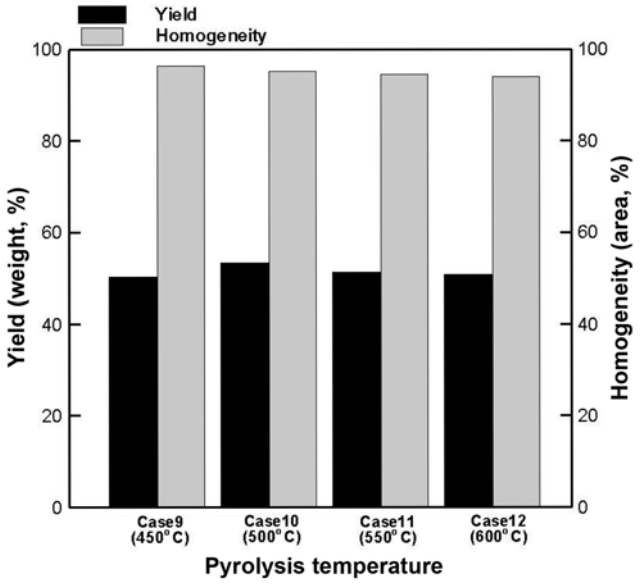

Fig. 7. Biocrude-oil yield and homogeneity with varying pyrolysis temperature.

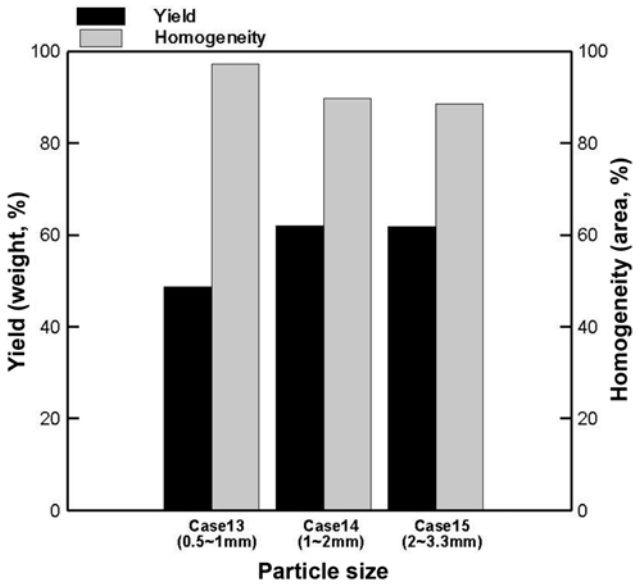

Fig. 8. Biocrude-oil yield and homogeneity with varying particle size.

as the pyrolysis temperature increases because the char and non-condensable gas are increased by the secondary reaction at higher pyrolysis temperature.

Fig. 8 shows the effect of the biomass particle size on the biocrude-oil yield and quality. In this case, a uniform biomass size is obtained by filtering the biomass through a mesh. With increasing the particle size, the biocrude-oil yield is increased but the yield is slightly decreased for the larger particles (size ≥2 mm). For the small size particle (size ≤1 mm), it is expected that the decrease of the yield arises from its pyrolysis position. That is, in case of the small particle, a pyrolysis reaction may occur between the outlet of the reactor and the fluidization bed in the pyrolysis system. However, the quality becomes better with decreasing the particle size.

CONCLUDING REMARKS

The effects of the biomass feeding rate, nitrogen flow rate, pyrolysis temperature and sample size on the biocrude-oil yield and quality were investigated by a fast pyrolysis experiment of the woody biomass. The results are as follows. In particular, in order to determine the quality of the collected biocrude-oil, the homogeneity of biocrude-oil was calculated by the image processing of the biocrude-oil picture captured by a microscope.

1. As the biomass feeding rate grows, the biocrude-oil yield is increased because of the increased pyrolysis gas flow rate. However, if the feeding rate exceeds the pyrolysis capacity of the reactor, the homogeneity is decreased about 10% compared with its maximum value.
2. If the nitrogen gas flow rate is changed, the fluidization condition of the bubbling bed reactor is affected, and this has a great effect on the biocrude-oil yield. Namely, in the steady bubbling case, the yield increases by 20% compared with its minimum value but the homogeneity is decreased by 9%.
3. When the pyrolysis temperature exceeds 500 °C, the tar gener-

ated by the primary reaction is additionally decomposed into the char and non-condensable gas by the secondary reaction. Then, the biocrude-oil yield is decreased by 6% compared with its maximum value, and the homogeneity is reduced as the char and non-condensable gas increase.

4. In the case of small particles, a pyrolysis reaction may occur between the outlet of the reactor and the fluidization bed, and the biocrude-oil yield is decreased by 20% compared with its maximum value. However, the quality becomes better with decreasing the particle size by 10 %.

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