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AGGLOMERATION MECHANISM DURING BIOMASS CARBONIZATION IN FLUIDIZED BED

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ABSTRACT

Among the various energy conversion technologies of the biomass, the fluidized bed is one of the devices used for its gasification. However, we pointed out the agglomerates of the bed materials surrounding char particles are observed in the bed. In the present study we carried out pyrolysis of Japanese cypress in a small fluidized bed reactor device with nitrogen flow. After cooling down, we sieved the solid in the bed and only recovered agglomerates. Afterwards we extracted solvent-soluble organic matter with chloroform/methanol solvent from agglomerates, and its yield was determined. The residual of the extraction was again sieved, and agglomerates yield after extraction and reduction in the agglomeration yield were determined. Agglomerates after extraction were incinerated in an electric furnace and determined solvent-insoluble organic matter yield. Finally, the relation between solvent-soluble organic matter yield and reduction in agglomerates yield, and that between solvent-insoluble organic matter yield and agglomerates yield after extraction were examined. From their correlations, it was suggested that agglomerates were brought by each organic matter.

Keywords: biomass; fluidized bed reactor; pyrolysis; char; agglomeration.

1. INTRODUCTION

Energy demands are increasing with population growth, especially in Asia. On the other hand, the depletion of fossil fuel resources is a worldwide problem and effective use of resources is required. Hence the use of renewable energy is recommended. Biomass as a renewable source of energy attracts attention because it is only storable chemical energy among various renewable energies. Hence, the present authors paid attention to integrated gasification combined cycle where biomass is firstly gasified under high temperature. In the gasifier, the introduced biomass is rapidly heated and the produced char is gasified. Therefore, the carbonization condition might affect the char gasification.

In the previous study, we pyrolyzed biomass, and char, carbon and ash yields were examined using an experimental fluidized bed reactor, FBR, where biomass pyrolysis under the rapid heating rate is possible (Kojima, Iwasaki, Kurosawa, Suganuma, Kato & Satokawa, 2010). In the later study, woody biomass samples were pyrolyzed at different temperatures and heating

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rates in a fluidized bed reactor (FBR). Only under the conditions of rapid pyrolysis between 600 and 1000 °C, porous alumina particles as the bed material adhered on the surface of the obtained char. The amount of particles adhering on the char derived from softwood was larger than that derived from hardwood (Iwasaki, Satokawa & Kojima, 2013a). In another paper, we conducted biomass pyrolysis in an experimental fluidized bed reactor (FBR) between 300°C and 1200°C at heating rate of fast (100-1000°C/s) or slow (10°C/min) and char yield was measured. The employed biomass samples were eleven different characteristic ones as follows; three kinds of softwoods, three kinds of hardwoods, two kinds of herbaceous plants and three kinds of agricultural residues. In case of fast pyrolysis char yields were much lower than those in case of slow pyrolysis for Eucalyptus camaldulensis (hardwood), Japanese cypress (softwood), switchgrass (herbaceous plant) and bagasse (agricultural residue). Furthermore, in the case of fast pyrolysis, char-bed particles (alumina particles) agglomerates were observed for most of the biomass samples which was hardly observed in the case of slow pyrolysis and char yields from softwood species were lower than those from other biomass species. The produced agglomerates were separated from bed particles and then the surface of the produced char was observed by SEM (Iwasaki, Suzuki & Kojima, 2013b).

One of the causes of the raising engineering problems under the operation of fluidized beds is the phenomenon of agglomeration of char and bed particles. Hence, the elucidation of the phenomenon and examination of measures are necessary. Burton & Wu (2012a) demonstrated that during the pyrolysis of mallee leaf (355–500 μm) in a fluidized-bed reactor (bed materials: silica sand, 125–355 μm) at 300−700 °C, bed agglomeration took place due to the formation of char−char and/or char−sand agglomerates connected by carbon-enriched necks. They reported that there were two types of bed agglomeration: one formed due to solvent-soluble organic matter which dissembled upon solvent washing and the other due to solvent-insoluble organic matter produced from biomass pyrolysis. The yield of each type of bed agglomeration was broadly proportional to the yield of the corresponding type of organic matter in the bed samples. The total yield of bed agglomeration decreased with increasing pyrolysis temperature, from 16.5% at 300 °C to 9.5% at 500 °C and 1.8% at 700 °C. The distribution of the two types of bed agglomeration was also strongly temperature dependent. At low temperatures (e.g., 300 °C), bed agglomeration was dominantly contributed by those formed by solvent-insoluble organic matter. As pyrolysis temperature increased, bed agglomeration due to solvent-soluble organic matter became increasingly important and reached a maximum at 500 °C. At pyrolysis temperatures above 600 °C, there was a drastic reduction in the bed agglomeration formed by solvent-soluble organic matter due to thermal cracking so that bed agglomeration was again dominantly formed by solvent-insoluble organic matter. Overall, bed agglomeration during biomass pyrolysis in a fluidized-bed reactor was due to the production of sticky agents, including both partially molten pyrolyzing biomass particles and the organic matter (both solvent- soluble and -insoluble) produced from biomass pyrolysis reactions (Burton & Wu, 2012a). The scientific reports on this type of agglomerates formation are very limited; de Wild, Huijgen and Heeres (2012b) also reported the observation of molten lignin at the tip of the feed-screw and formation of char-sand agglomerates in the reactor tube.

So many studies have been reported on the high temperature gasification and combustion, not only for the case of coal, but also biomass. The cause of the agglomeration are reported to be alkaline metal or alkaline-earth metal (Scala, Chirone & Salatino, 2003; Chaivatamaset, Sricharoon & Tia, 2011). However, the paper reporting that the cause of pyrolysis is organic matter such as the tar are very rare excepting the above papers (Burton & Wu, 2012a; de Wild et al., 2012b). Hence, in the present research, considering the agglomeration phenomena are more prominent for softwood than those for hardwood (Iwasaki et al, 2013b), the validity of the conclusion by Burton and Wu (2012a) that cause of the agglomeration by FBR pyrolysis is the organic matter is examined using the Japanese cypress sample, a kind of softwood.

2. MATERIALS AND METHODS

2.1 Reactor and Setup

The experimental fluidized bed reactor (FBR) is made of alumina, with the inner diameter of 35 mm and the height of 600 mm, is schematically shown in Fig. 1. Distributor was also made of alumina. In the FBR, silica particles were fluidized with nitrogen gas at 6 Umf (six times of minimum fluidization velocity of bed material [m/s]) and it was externally heated by siliconit® electric heaters between 300°C and 1200°C with a thermocouple ("TC" in Fig. 1) and a programmable temperature record controller ("TRC" in Fig. 1).

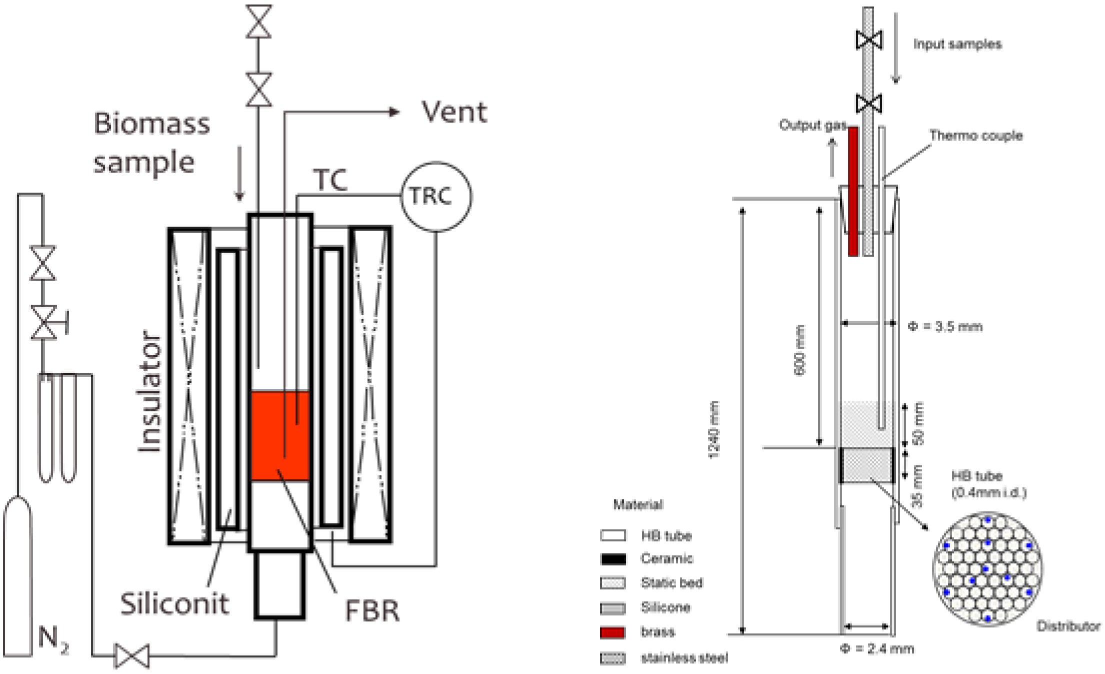

Figure 1: Schematic diagram of experimental set up and inside of FBR.

2.2 Samples

Japanese cypress sample (VM: 84.75 FC: 15.08 Ash: 0.17) with particle diameter of 355-500 µm was employed for this experiment. Bed particles used were 65 g of silica sand with particle diameter of 255-350 µm (Catalog value. Actually particles with some smaller diamater are included).

2.3 Experimental Procedures and Calculation

Small fluidized bed reactor with silica sand bed particle layer of 5cm high was heated in the nitrogen flow. After the bed temperature reached the pyrolysis temperature (300-900°C), the biomass sample was put from the upper reactor. The introduced sample is rapidly heated by the bed particles with high heat capacity (fast pyrolysis, ≲1000°C/s). After the sample biomass particles were kept for ten minutes at the pyrolysis temperature, the reactor was cooled down in the nitrogen flow. After leaving for one night, bed particles containing bed-char agglomerates were collected. Particle diameter distribution of the collected bed particles with agglomerates was measured with sieves. The particles upper the sieve with 355 μm opening were regarded as agglomerates and recovered as agglomerates to get agglomeration yield before extraction (based on total mass of bed particles and char including agglomerates). This is because the diameter of pyrolized biomass is reduced less than 355 μm and all of bed particles without agglomeration are less than 355μm.

The solvent-soluble organic matter in the recovered agglomerates was extracted with a solvent of methanol-20%-chloroform-80% by a Soxhlet apparatus. After the extraction, the recovered liquid was placed and solvent was removed by a rotary evaporator. The weight of the residual condensed liquid (almost solid form) was measured and yield (dry biomass weight basis) was calculated. The residual agglomerates with loose bed particles separated from agglomerates were again sieved and their particle diameter distribution was measured. The particles upper the sieve with 355 μm opening were again regarded as agglomerates and weighed as agglomerates to get agglomeration yield after extraction (based on total mass of bed particles and char including agglomerates before extraction). The difference between agglomeration yields before and after extraction is defined as “reduction in agglomeration yield” by solvent extraction.

The char-bed particles agglomerates after extraction was incinerated in an electric furnace and the decrease in the weight by the combustion is given as solvent-insoluble organic matter (yield is also given as dry biomass weight basis). Based on the above, the agglomerates yields before and after solvent extraction, reduction in agglomerates yield, solvent-soluble organic matter yield, and solvent-insoluble organic matter yield were determined.

3. RESULTS AND DISCUSSION

3.1 Agglomerates Yields and Reduction in Agglomerates Yields

Fig. 2 shows a microscope photograph of typical char-bed particles agglomerates formed at 700 °C fast pyrolysis of Japanese cypress in the experimental fluidized bed. No agglomerates were found below 500°C in the present experiment.

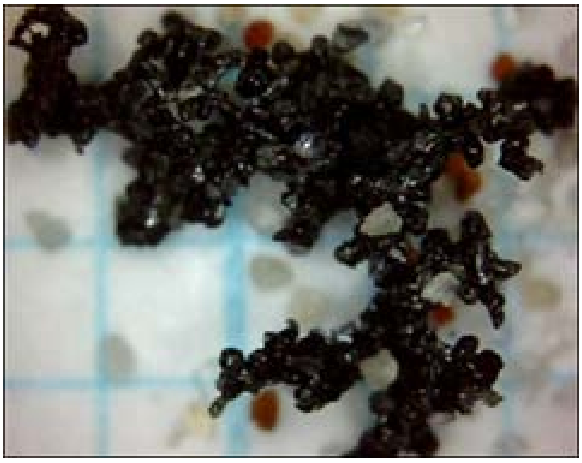

Figure 2: Microscope photograph of typical char-bed particles agglomerates.

Fig. 3 shows the results of agglomerates yields for Japanese cypress by fast pyrolysis at various temperatures in the bed. Agglomerates yields are given as the mass of char-bed particles agglomerates divided by total mass of char and bed particles including agglomerates (total bed weight basis). Pyrolysis experiments were repeated for two times at the same pyrolysis temperature between 550 and 800°C and the data of agglomerates yields are shown in closed circle or triangle. It was found that the reproducibility of the agglomerates yield for each temperature was poor, which is explained by the experiences that the agglomeration phenomena or clogging formation are catastrophic one (Kojima et al., 1992) and very small change in various factors such as mal-distribution of fluidizing gas in the bed might affect the agglomeration formation. Once small agglomerate is formed, the gas flow will change. Hence, the mal-reproducibility of the agglomerates is natural. In the present figure, the series of data of larger values are shown by closed circles and the series of data of smaller values by closed triangles. The data of agglomerates yields after solvent extraction are also shown in Fig. 3 using open cycle for data corresponding to the data of larger values and open triangle corresponding to the data of smaller values before extraction, respectively.

The difference in the agglomerates yields before and after the solvent extraction is calculated respectively for the two series of data of larger and smaller values and the results are shown in Fig. 4 as reduction in agglomerates yields. Irrespective of the mal-reproducibility in Fig. 3, the difference looks to have a tendency of decrease with increased temperature, though the difference in the data between the two series still exists.

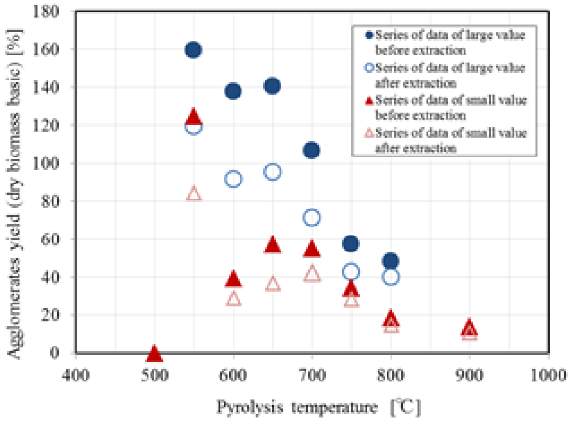

Figure 3: Agglomerates yields (total bed weight basis).

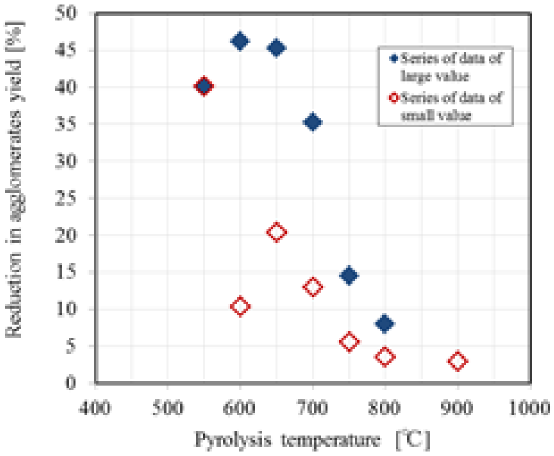

Figure 4: Reduction in agglomeration yield by solvent extraction (total bed weight basis).

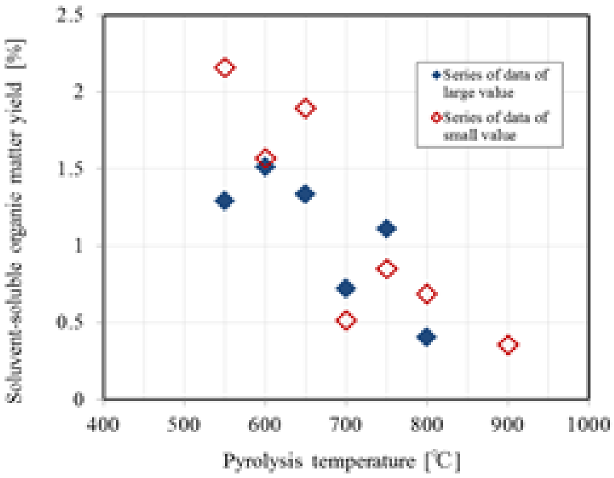

Figure 5: Solvent-soluble organic matter yield (dry biomass basis) by solvent extraction.

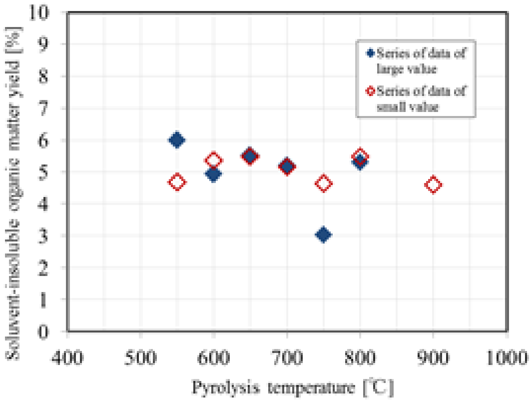

Figure 6: Solvent-insoluble organic matter yield (dry biomass basis) after solvent extraction.

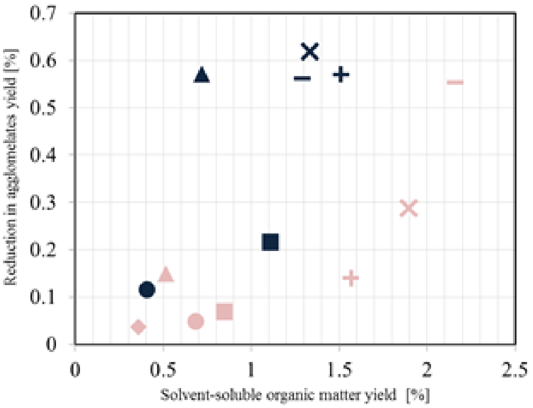

Figure 7: Correlation between reduction in agglomerates yield (total bed weight basis) and solvent-soluble organic matter yield (dry biomass basis).

Temperature [°C]	550	600	650	700	750	800	900
Larger values	—	+	×	▲	■	●	
Smaller values	—	+	×	▲	■	●	◆

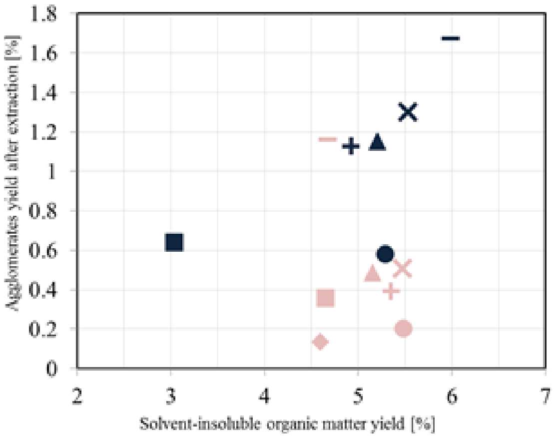

Figure 8: Correlation between agglomerates yield after extraction (total bed weight basis) and solvent-insoluble organic matter yield (dry biomass basis).

3.2 Organic Matter Yields

In addition, the solvent-soluble organic matter yield by solvent extraction is given on the basis of dry biomass weight which is shown in Fig. 5. As shown in Fig. 5, same tendency of decrease with increased temperature as reduction in agglomerates yields in Fig. 4. The solvent soluble organic matter showed maximum at the middle temperature of 550-650°C, while the organic matter or the agglomerates were hardly removed at the temperature higher than 700°C.

Fig. 6 shows the measured results of solvent-insoluble organic matter, which was determined by the weight loss by incineration of agglomerates after solvent extraction. The value looks almost unchanged with fast pyrolysis temperature, which is reasonable result by considering this value involves the weight loss of “fixed carbon” in char. However small decrease may be observed in solvent-insoluble organic matter, as the decrease in agglomerates yield in Fig. 3, with increased pyrolysis temperature.

3.3 Correlation between Agglomerates Yield and Organic Matter

Based on the above results and discussion, correlation between reduction in agglomerates yield (by extraction) and solvent-soluble organic matters is shown in Fig. 7. Though some variability of the data is found and the data for the series of larger values gives relatively higher values of reduction in agglomerates yield, some positive correlation is found between reduction in agglomerates yield (by extraction) and solvent-soluble organic matters, which indicates that exclude the part of agglomerates are formed by the binding effects of solvent-soluble organic matters and the agglomerates are broken down by the removing of the solvent-soluble organic matters. Namely, some agglomerates for Japanese cypress is suggested to be caused by organic matter which can be extracted.

Also based on the above results and discussion, the correlation between agglomerates yield after extraction and solvent-insoluble organic matters is shown in Fig. 8. Though some variability of the data is found and the data for the series of larger values gives relatively higher values of agglomerates yield after extraction, some positive correlation is also found between agglomerates yield after extraction and solvent-insoluble organic matters, which indicates that the part of agglomerates are formed by the binding effects of solvent-insoluble organic matters. However different from Fig. 7, the correlation line does not pass through the point of origin. Though the present results mean most of the solvent-insoluble organic matters comes from fixed carbon, some agglomerates for Japanese cypress is suggested to be caused by organic matter which can not be extracted.

4. CONCLUSION

The relation between solvent-soluble organic matter yield and reduction in agglomerates yield, and that between solvent-insoluble organic matter yield and agglomerates yield after extraction were examined. By their correlations, it was suggested that agglomerates were brought by both of the organic matter.

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