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Inhibition of char deposition using a particle bed in heating section of supercritical water gasification

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Abstract−Supercritical water gasification (SCWG) has attracted attention as a technology for utilizing wet biomass. We used a fluidized bed of alumina particles to prevent blockage of a SCWG reactor. A glucose solution was heated in the reactor with and without fluidized alumina particles. In the absence of alumina particles, char particles formed homogeneously in the reactor, but the use of a fluidized bed resulted in accumulation of char particles at the reactor's exit rather than inside the reactor. Therefore, the fluidized bed was effective at preventing blockage of the reactor. However, the alumina particles did not remove deposits from the reactor's walls. Instead, the fluidized bed caused larger char particles to form, preventing their adhesion to the reactor's wall.

Keywords: Supercritical Water Gasification, Char, Blockage, Particle Bed

INTRODUCTION

"Biomass" was originally defined as the amount of plant bodies that create energy by photosynthesis, but it now also refers to organic matter from plants and animals that can be used as renewable energy resources. The organic carbon in biomass can be converted into carbon-rich products like charcoal, useful gases like methane, and liquid fuels like methanol. Thus, biomass conversion has attracted attention as a measure to prevent global warming, because it uses renewable biomass as an alternative resource in place of fossil fuel consumption.

Among the various uses of biomass, supercritical water gasification (SCWG) is a promising technology for obtaining useful gases such as hydrogen and methane from wet biomass. SCWG uses water at high pressure (above 22.1 MPa) and high temperature (above 647 K). In this hot compressed water, organic matter is decomposed and converted into useful gaseous products [1]. Because half of the available biomass in Japan is wet biomass such as sewage sludge, cattle manure, and food waste, its effective use is highly desirable. To produce methane from wet biomass, conventional biomethanation takes almost 2-4 weeks using a large methane fermenter. To obtain charcoal from wet biomass, time- and energy-intensive drying is needed. However, wet biomass can be treated without a drying process in a short reaction time using SCWG, because the reaction proceeds in water. Biomass is rapidly decomposed into small molecules with a negligible amount of residue being formed [2-5].

Although SCWG is a prospective processing method for obtaining gas from wet biomass as discussed above, char generation in the subcritical region of the SCWG plant has prohibited its commercialization by reducing the gasification efficiency and/or blocking the reactor with the char. The detailed reaction mechanism of char production was studied by Chuntanapum et al. [6]. They reported that char production from glucose was observed only under subcritical conditions, indicating that char is produced not in the SCWG reactor itself but in the preheating section. The reaction mechanisms of cellulose, amino acids, and 5-hydroxymethylfurfural have also been studied as model compounds by several researchers [7-14]. In addition, technologies to prevent reactor blockage were studied. One approach was to use a catalyst such as activated carbon, metals (nickel and ruthenium), and alkalis (KOH, K_2CO_3, Na_2CO_3) to suppress char generation [15-27]. However, these countermeasures suffer from the high cost of the catalysts used. In another approach, proposed by Munetsuna et al., the reactor was cleaned by regularly rinsing the reactor with flowing water. They found that the staging of the reaction in intervals effectively prevented reactor blockage, but this approach resulted in a short residence time because of the longer water supply time, and in low gasification efficiency because gas formation was not performed during the rinsing step [28].

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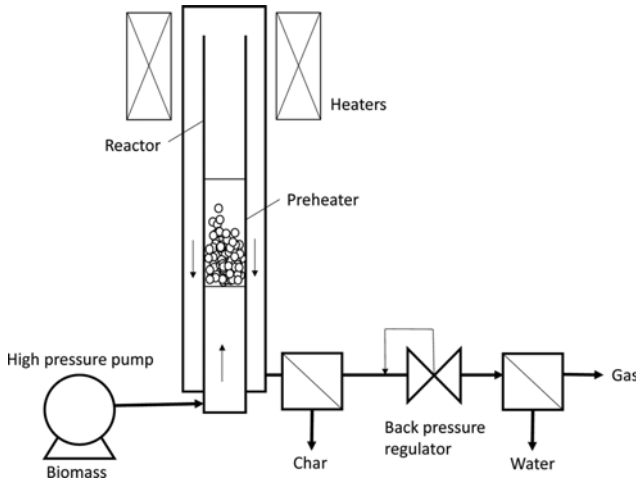

Fig. 1. Novel SCWG reactor with preheater employing fluidized bed.

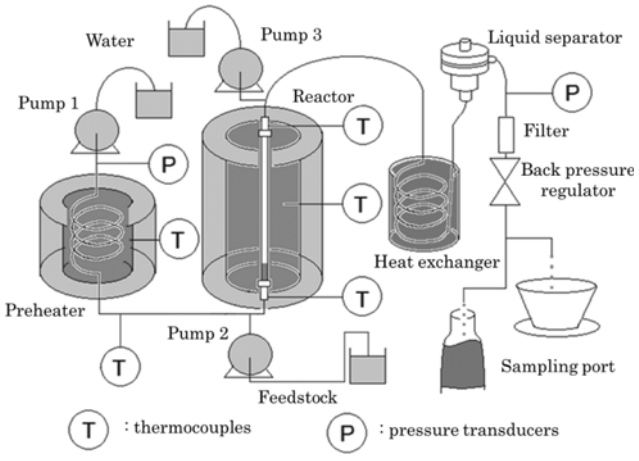

Fig. 2. Experimental apparatus.

To circumvent the problem of reactor blockage, a novel reactor is presented in this work in which fluidized particles remove deposits from the reactor's inner wall. Fig. 1 shows how to remove char from the reactor system. Generally, reactor blockage by char particles takes place in the subcritical region where char particles are produced and the flow rate is low. This subcritical region corresponds to the preheater. Thus, a fluidized bed is employed in the preheater to prevent reactor blockage, and the char particles are directly delivered into the reactor, then to an outside jacket for heat recovery, and then to the solid-liquid separator, where char particles are collected. The use of a fluidized bed to prevent reactor blockage was proposed in the previous study [29]. Alumina particles were chosen for the fluidized particles, because of their suitable thermal stability and low-cost. Alumina is known for its stability at high pressure and temperature. Also, some forms of alumina are known to have catalytic effects [30]. However, because catalytic alumina particles have increased in cost, non-catalytic alumina particles should be sufficient for prevention of reactor blockage. Fluidized alumina particles should prevent the accumulation of particles on the reactor, and so that any char that is produced in the reactor is removed. In previous studies, a fluidized bed reactor, which provides the good heat transfer efficiency and homogeneity needed for effective reaction, was investigated as a novel SCWG reactor [29,31], but the effect of char removal was not clearly demonstrated. If a fluidized particle bed can be used for char removal in an SCWG reactor and reactor blockage can be prevented, commercialization of SCWG technology should become possible. Accordingly, the purpose of this study was to build a fluidized particle bed to prevent reactor blockages in the preheater operated under the subcritical condition, where char particles are produced and the flow rate is low. We also examined its effectiveness by comparing its operation in the absence and presence of alumina particles.

EXPERIMENT

Fig. 2 shows the experimental apparatus used. The reactor was constructed of SS316 steel tubing. The outer and inner diameters of the reactor were 12.7 mm and 9.4 mm, respectively, and the reactor height was 0.63 m. A 1 mm diameter orifice was at the reactor's entrance. A 40 wt% glucose solution was delivered by pump 2 to the reactor after being mixed with preheated water at the reactor's inlet. This mixture passed through the orifice at an average speed of 0.54 m/s. Note that the minimum fluidization velocity of this particle bed was 0.02 m/s, and therefore, the particles were fluidized by jet flow at the entrance. The char generation reaction proceeded in the reactor. After the reactor was run for a desired time, the glucose solution was switched to water, and the reactor temperature was lowered. The reactor was then depressur-

Table 1. Experimental conditions

Pump	Pump 1	Pump 2	Pump 3
Delivered liquid	Water	Glucose solution	Water
Concentration	-	40 wt%	-
Concentration after mixed		10 wt%	-
Temperature		300 °C	
Pressure		25 MPa	
Flow rate	15 mL/min	5 mL/min	20 mL/min
Total flow rate in the reactor		20 mL/min	-
Operation time		200-733 s	
Residence time		88.1 (with Al_2O_3), 97.4 (without Al_2O_3) s	
Bed material		Alumina (Shinto V-cerax VB-0.5, 15 g)	

Table 2. Physical properties of alumina particle

Average particle size	0.5 mm
Density	3600 kg/m^3
Hardness	1200 HV
Purity	92% over
Catalytic	Non-catalytic

ized and disconnected. Since complete blockage was inconvenient in terms of operation efficiency, operation was stopped when the pressure drop reached 3 MPa. Char was recovered from the reactor and dried in an oven at 90 °C for weight measurement and SEM observation. For investigating particle size distribution, we also used a laser diffraction particle size analyzer. When needed, alumina particles were added to the reactor. Temperature was measured with five thermocouples and the pressure loss was determined by two pressure transducers attached to the reactor. See Table 1 for the experimental conditions. The temperature of the mixed flow was 300 °C, and this temperature was maintained in the reactor by using an electric furnace. The pressure of all experimental apparatuses was set to 25 MPa using a back pressure regulator. The concentration of glucose in the mixed flow was 10 wt%. The operation time was varied in the range of 200-733 s. Also, 15 g of alumina particles, which were obtained from SINTO V-CERAX, LTD., were added to the reactor when needed. The diameter of the alumina particles was 0.5 mm, and their density was 3,600 kg/m^3. Detailed properties of the alumina particles are shown in Table 2.

RESULTS AND DISCUSSION

1. Pressure Drop

The experimental apparatus was operated until the pressure drop reached 3 MPa in both the absence and presence of alumina particles to determine their effect on the removal of char deposits. Table 3 shows the comparison of reactor blockage times, or the times required for the pressure drop to reach 3 MPa, for operation with and without alumina particles. Surprisingly, the reactor blockage time without alumina particles was almost two-times longer than that with the particle bed. Fig. 3 shows the change of pressure drop over time. The pressure drop with the particle bed increased much faster than with the empty bed. To determine the cause of this unexpected result, the reactor was disconnected, and reactor blockages were observed. Blockages were found under both conditions at the cooling section near the exit of the reactor. These blockages were most likely caused by char particles washed out of the reactor, because char particles could not be produced at this position that was at a low temperature. More char was washed out earlier in the reactor with alumina particles than the one without alumina particles.

Table 3. Comparison of reactor blocking time

	With alumina particle	Without alumina particle
Blocking time [s]	420	733

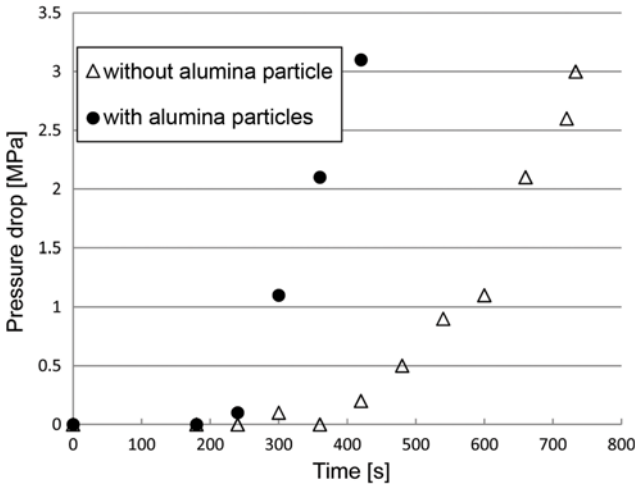

Fig. 3. Comparison of pressure drop (white triangle: with alumina particles, Black dot: without alumina particle).

2. Position of Char Deposition in the Reactor

After each experiment, the state of char deposition in the reactor was carefully confirmed. When char was recovered from the reactor, it was homogeneously packed throughout the whole reactor in the absence of alumina particles, while char existed only in the top 2 cm of the reactor when alumina particles were present, as shown in Fig. 4. These findings indicate that the fluidized bed of alumina particles was effective at removing char downstream.

3. Collected Char Weight

Fig. 5 shows the char weight in the reactor as a function of operating time. The weight of the collected char increased linearly with time. Without alumina particles, char production began 100 s after supplying glucose solution. This 100 s was the time needed for the glucose solution to reach the reactor, or the time it took it to flow through the dead volume between the pump and the reactor. When alumina particles were present in the reactor, a further delay of 100 s was observed before the char weight in the reactor

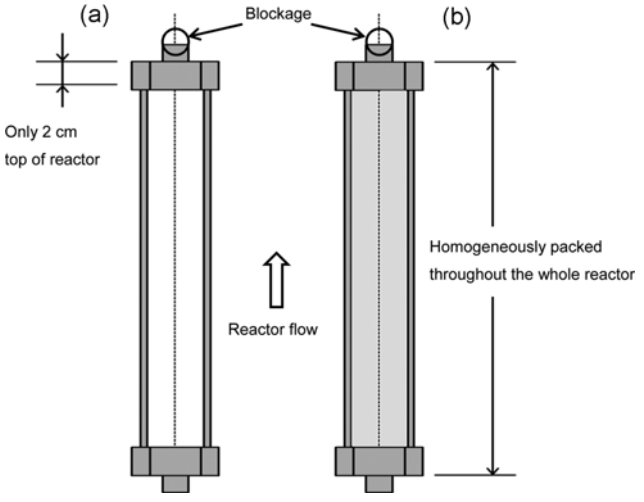

Fig. 4. Position of char deposition. (a) With alumina particle (b) Without alumina particle.

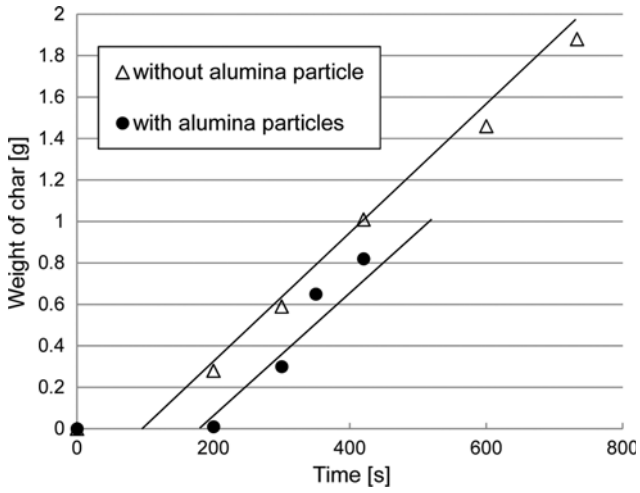

Fig. 5. Char weight against time (white triangle: with alumina particles, Black dot: without alumina particle).

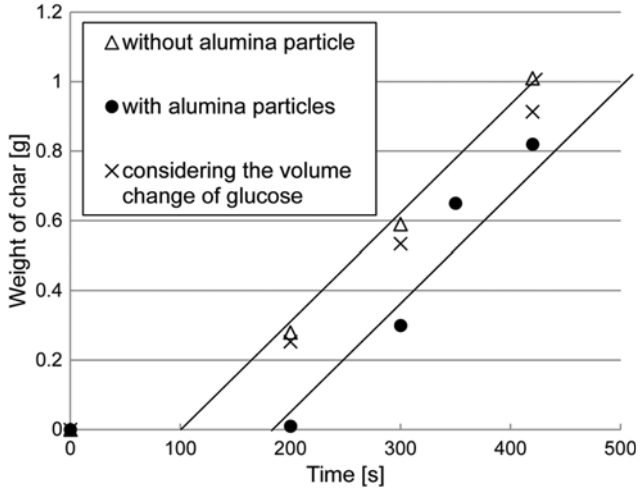

Fig. 6. Char weight as a function of operation time.

started to increase.

The linear increase in the weight of char in the reactor confirms the constant generation of char in the reactor. The delay in char accumulation in the reactor observed in the presence of alumina particles agrees with the idea that alumina particles were effective at washing char out of the reactor. Char should have been produced whether alumina particles were present in the reactor or not, because glucose is thermally decomposed and the presence of alumina particles does not affect the temperature.

The presence of alumina particles should have prevented the char weight from increasing because the effective reactor volume decreased. To evaluate this effective volume effect, the change in volume was calculated for char production. The volume of alumina particles was 4.167 cm^3 and the reactor volume was 43.721 cm^3. Since the alumina particles occupied 9.53% of the reactor volume, the amount of glucose in the reactor with alumina particles present decreased to 90.47% of the original amount. The char weight calculated in this manner is compared with char accumulation in the presence of alumina particles in Fig. 6. The actual char recovery is clearly much lower than the calculated amount, considering only the decrease in the glucose solution volume in the reactor. Therefore, the ability of the alumina particle bed to remove char particles was verified.

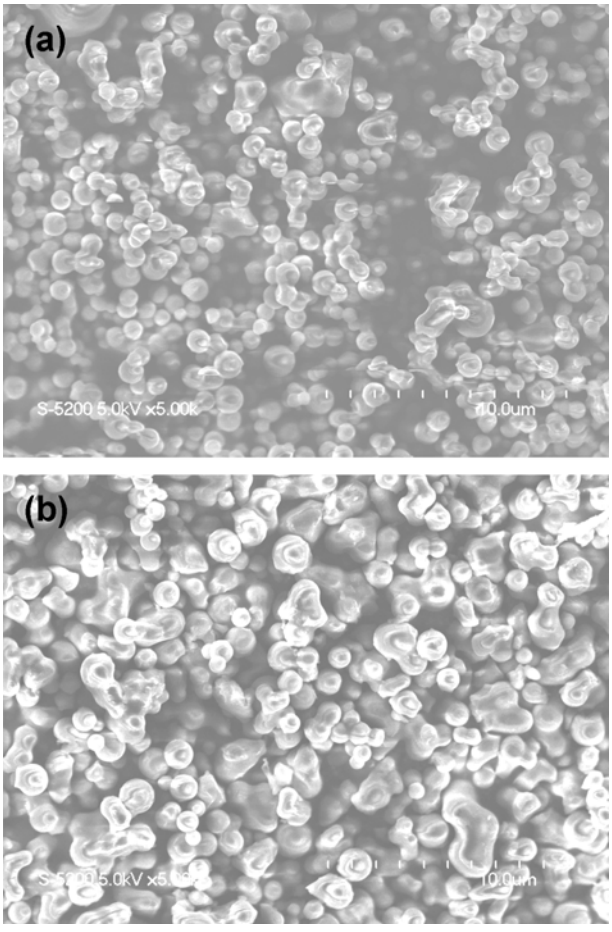

Fig. 7. (a) Char particles (without alumina particle, S5200 5.0 kV ×5.00 k). (b) Char particles (with alumina particles, S5200 5.0 kV×5.00 k).

4. Size of the Char Particles Produced

Figs. 7(a) and 7(b) show SEM images of the char recovered from the reactor without and with alumina particles, respectively. Char particles were approximately 1 μm in diameter for both cases. The particles generated in the reactor with alumina particles were slightly larger than those generated without alumina particles. Note that adjacent char particles tended to attach to each other and agglomerate in the presence of alumina particles. These results were also confirmed by particle size analysis, which is shown in Fig. 8. Larger mean particle sizes and broader particle size distributions were observed for char produced with alumina particles in the reactor.

This phenomenon of larger particles forming in the presence of alumina particles was unexpected but interesting. Apparently, char particles agglomerated much more easily with alumina particles present than when no alumina particles were present.

This difference in char particle size for the cases with and with-

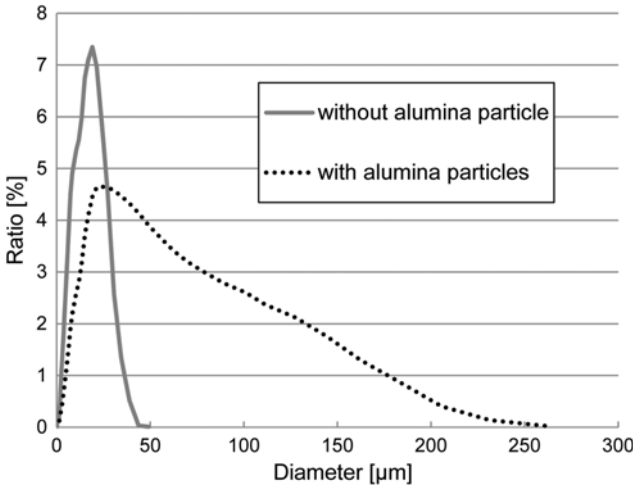

Fig. 8. Particle size distribution (straight line: without alumina particle, dotted line: with alumina particles).

out alumina particles might explain the distributions of char in the reactors. Without alumina particles, char was distributed homogeneously in the reactor, but char was only observed in the top 2 cm of the reactor containing alumina particles. As is well known, smaller diameter particles tend to develop into loose particle networks, because their surface forces are much larger than gravimetric forces. The char particles could easily interact with the wall material and develop a loose char particle network homogeneously inside the reactor. However, when particle size was larger in the presence of alumina particles, char particles did not stick to the wall or to each other. Therefore, the larger char particles reached the reactor's exit where they eventually adhered to each other and to the wall, because of the narrowed path and stagnant flow near the narrow outlet. Once a particle network developed at the reactor's exit, it functioned as a filter, trapping oncoming particles and causing all char particles to collect at the exit. A 100 s delay in char particle accumulation was observed in the presence of alumina particles. This delay time was most likely the time needed for the particles to develop into a network at the exit of the reactor. This delay time for the onset of char accumulation was in agreement with the time at which the pressure drop increased, supporting the hypothesis that this time was related to the development of a particle network at the reactor's exit. This particle network at the reactor's exit most likely increased the pressure drop, trapping oncoming char particles and accumulating them in the reactor.

The results of this study were unexpected. Placing a fluidized particle bed at the heating section of a reactor, the region in which char particles are generated, effectively prevented reactor blockage. However, blockage was not prevented by the deposits on the inner wall of the reactor being removed by the fluidized bed particles. Instead, the fluidized bed caused larger char particles to form and prevented them from adhering to the reactor. A detailed mechanism of the increased char particle size has not yet been determined, but this method of preventing reactor blockage should be applicable to other particle production systems, including chemical vapor deposition, gaseous reaction for solid particle production, etc.

CONCLUSION

Experiments were performed to explore the prevention of reactor blockages caused by char particles that are generated in the preheating section of SCWG plants. A fluidized bed was used for this purpose. A laboratory-scale, continuous reactor was employed, and the pressure drop, char weight, char deposition position, and char particle diameter were measured. When a particle bed was used, pressure drop increased more rapidly, because of the accumulation of char particles at the reactor's exit, indicating that char was effectively washed out of the reactor. Char weight in the reactor increased linearly with time. When alumina particles were present, a delay in the onset of char accumulation was observed. Char was homogeneously packed in the whole reactor without alumina particles, but char was present only in the top 2 cm of the reactor containing alumina particles. The diameter of the original char particles was around 1 μm. Agglomeration of char particles was observed when the fluidized bed was used. The particles in the fluidized bed did not remove deposits. Instead, the fluidized bed caused larger char particles to form and prevented them from adhering to the reactor's wall.

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