

Partial Oxidative and Catalytic Biomass Gasification in Supercritical Water: A Promising Flow Reactor System

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We have developed a flow reactor system that smoothly gasifies glucose and glucose–lignin mixture solution at 673 K, 25.7 MPa. The reactor system consists of three continuous reactors, which are a pyrolysis reactor, an oxidation reactor, and a catalytic reactor. We have investigated the reactions that occurred in each reactor and evaluated favorable residence time. We have succeeded in achieving high gasification efficiency based on carbon up to 96% at 673 K, 25.7 MPa with total residence time of about 1 min. The main gaseous products were H₂ and CO₂. The results indicated that this three-reactor system is promising for low-temperature (i.e., around 673 K) biomass gasification in supercritical water.

Introduction

Supercritical water gasification is a promising technology for gasifying biomass with high moisture content. One of the advantages of this technology is that it can omit the drying process of biomass. There exist many kinds of biomass with high moisture content up to 90%, which are difficult to gasify using conventional processes. Gasification using supercritical water could allow for the utilization of various kinds of biomass as an energy source. Another advantage is that water as a reaction medium results in a much faster reaction rate in supercritical water condition. Thus, there have been many investigations about supercritical water gasification.

Antal et al.^{1–5} conducted gasification of various biomass materials mainly with carbon catalyst and succeeded in getting good gasification efficiency in the temperature condition of 773–1073 K. Kruse et al.^{6–9} conducted gasification on the condition of moderate low temperature around 673–773 K with CSTR. They employed alkali or alkali salt catalyst and achieved smooth gasification without plugging caused by char/coke. A research group in Tohoku University, Japan, also investigated gasification biomass model compounds with a batch reactor at temperature around 673–713 K and examined the effect of several kinds of catalyst.^{10–13} However, to achieve high gasification efficiency over 95% in supercritical water environment, gasification should be conducted above 873 K.² Furthermore, there are some problems caused by ungasified products (i.e., char and tar) such as reactor plugging⁵ and catalytic deactivation.¹⁷ However, a detailed description of the formation of these ungasified products in supercritical water gasification of biomass hardly exists.

Nevertheless, we can refer to research on steam gasification^{18–21} or pyrolysis^{22–25} of biomass. It is widely known that gasification rate is high in the initial pyrolysis step.²¹ Hence, many researchers reported that rapid heating resulted in high yield of gases.^{8,25} Sjöström et al.²² suggested that significant chemical transformations producing tar and char took place in the initial treatment period of 0.5–1 s. Because this tar formation causes some troubles in the gasification process, there are some works investigating tar cracking with and without catalyst. Nickel catalyst is one of catalysts that are expected to crack tar.^{20,26}

Nickel catalyst is also known to promote water–gas shift reaction, methanation, and hydrogenation reaction. Therefore, some works investigated gasification of biomass in sub- and supercritical water using nickel catalyst.^{16,17,27–30} High water density is favorable for water–gas shift reaction,³² and several investigations have been conducted on the application in water–gas shift reaction to supercritical water.³³ Increasing the amount of catalyst loading is expected to enhance the water–gas shift reaction, hydrogenation, and methanation, thus resulting in higher yield of gas product, especially hydrogen and methane.

From the viewpoint of energy conversion efficiency, low-temperature condition and high gasification efficiency with much production of H₂ or CH₄ are favorable. There are some research studies focusing on the enhancement of biomass conversion in supercritical water through oxidation^{14,15} or partial oxidation¹¹ at temperature around 673 K. However, the product gas composition revealed less H₂ ratio than non-oxidized reactions.¹¹

In our previous reports of biomass gasification in supercritical water,^{16,17} it was indicated that some tarry products have caused catalytic deactivation. And in our preliminary experiments using a catalytic reactor, catalyst deactivation and plugging with char products were observed. In this work, we aim to propose a new type of flow reactor system for biomass gasification in

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Table 1. CHN Data of Lignin

element	wt %
C	47.0
H	5.2
N	0.2

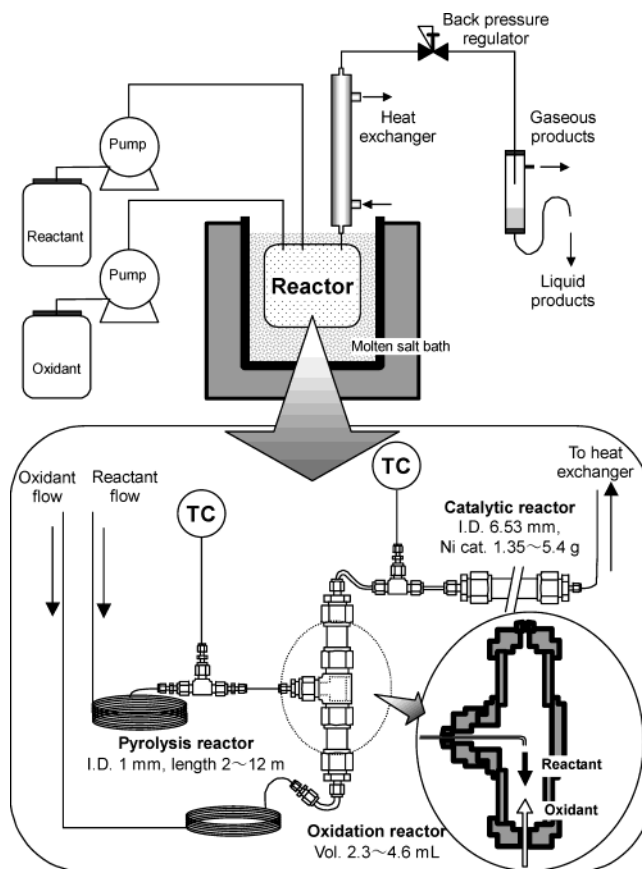
supercritical water around 673 K and 25 MPa. At low-temperature range supercritical water condition, it is thought that ionic reaction mainly proceeds. Biomass components would be decomposed through ionic reaction, but cleavages of aromatic ring hardly occur in supercritical water around 673 K. Moreover, some parts of aromatic compounds, such as lignin, are eventually polymerized to tar and char materials. To decompose an aromatic ring, radical reaction led by radical derivatives such as hydrogen peroxide will help.³¹

The first part of our reactor system is a pyrolysis reactor where biomass components are decomposed mainly via ionic reaction, and polymerization of fragment products follows. To decompose biomass components effectively, we employed an oxidation reactor after the pyrolysis reactor. Because oxidant will work as radical derivative, aromatic compounds are decomposed smoothly via radical reaction and tar/char materials are also decomposed in this reactor. In the following catalytic reactor, which is the last part of the three-reactor system, low-molecular-weight materials are gasified by catalytic reaction. In this paper, we have demonstrated how our reactor system works and have proved that the system with oxidation reactor is suitable for low-temperature supercritical condition because the fragments and tar/char materials are decomposed smoothly. The evaluation of each reactor and pressure dependency has been performed.

Experimental Section

D-Glucose (Kanto Kagaku) and lignin sulfonate (Kanto Kagaku) derived from softwood were used as model materials of biomass in this work. A 34.5 wt % solution of hydrogen peroxide (Kanto Kagaku) was used as oxidant, and it was diluted to the desired concentration assuming that a molecule of hydrogen peroxide provides half a molecule of oxygen. The values of O₂ equivalent were calculated by the chemical formula for glucose and by CHN analysis (shown in Table 1) for lignin, respectively. The reactants and oxidant were prepared by solving each reagent into degassed water.

Figure 1 shows the three-reactor system employed in this work. The reactors consisted of tubing and tube connections both made of 316 stainless. The pyrolysis reactor was a tube with o.d. of 1.58 mm and i.d. of 1 mm. Because char products occasionally accumulated in this pyrolysis reactor, we changed it for a new one at every experiment so that we could avoid the char effect that had formed in the former experiments. The oxidation reactor was a tube with o.d. of 9.53 mm and i.d. of 6.53 mm or with o.d. of 6.35 mm and i.d. of 4.35 mm. At the middle of the oxidation reactor, a tube that introduces reactant from the pyrolysis reactor was inserted. And the tip of the inserted tube was bent down so that a better mixing of the reactant with oxidant from the bottom of the reactor could be achieved, as shown in Figure 1. The catalytic reactor was a tube with o.d. of 9.53 mm and i.d. of 6.53 mm. A nickel catalyst (Ni-5256E, Engelhard) was employed, with fresh catalyst

**Figure 1.** Experimental apparatus and three-reactor system.

being introduced for each experiment. Type-K thermocouples were equipped between the pyrolysis reactor and the oxidation reactor, and between the oxidation reactor and the catalytic reactor.

To exclude the effect of H₂ preadsorbed on the nickel catalyst, pure water was flowed through the reactors at reaction temperature and pressure for 2 h before the experiment to release H₂ from the catalyst surface. The solution of biomass was fed into the pyrolysis reactor by HPLC pump (PU980, Jasco) and subsequently introduced into the oxidation reactor. The oxidant was delivered to the preheat line then led to the bottom of the oxidation reactor by a syringe pump (260D, ISCO). The ratio of flow rate (reactant/oxidant) was always set at 3.3. In the oxidation reactor, char products that were heavier than water were designed to remain until they were decomposed by the oxidant, whereas the rest of the products went out of the oxidation reactor from the top, which led to the catalytic reactor. The products from the catalytic reactor were cooled at the external heat exchanger, and depressurized by the backpressure regulator. Then the products were separated into gaseous products and liquid products (as water solvents) at the gas-liquid separator. The amount of gas product was calculated by the pressure difference of gas sampling system described in our previous research.¹⁶ Gaseous products were analyzed by GC-TCD (GC-14A and GC-8A, Shimadzu). Analyses of the liquid products were conducted by TOC (TOC5000, Shimadzu).

In this paper we use the terms "hydrogen gasification ratio", "carbon gasification ratio", "carbon yield of liquid

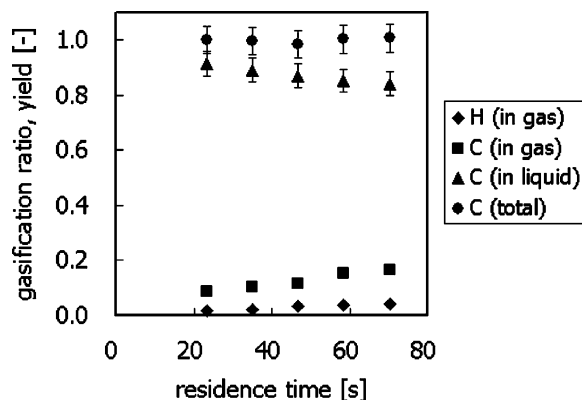


Figure 2. Pyrolysis of glucose solution in supercritical water (4000 ppm, 673 K, 25.7 MPa).

product”, and “carbon balance”, which are defined as follows:

$$\text{Hydrogen gasification ratio, } H(\text{in gas}) = \frac{\text{Hydrogen amount in the gas product}}{\text{Hydrogen amount in the material}}$$

$$\text{Carbon gasification ratio, } C(\text{in gas}) = \frac{\text{Carbon amount in the gas product}}{\text{Carbon amount in the material}}$$

$$\text{Carbon yield of liquid product, } C(\text{in liquid}) = \frac{\text{Carbon amount in the liquid product}}{\text{Carbon amount in the material}}$$

$$\text{Carbon balance, } C(\text{total}) = \text{Carbon gasification ratio} + \text{Carbon yield of liquid product}$$

Results and Discussion

Experiment with Glucose Solution. First we conducted the experiment of glucose gasification in the pyrolysis reactor. Details of glucose pyrolysis in supercritical water were investigated by Kabyemela et al.³⁴ They showed that glucose was decomposed to smaller molecules such as aldehydes and acids at the early stage of reaction in supercritical water. However, data of gaseous products in the early stage of the reaction were hardly available. Thus, we have examined the glucose pyrolysis in the time range of up to 72 s (Figure 2). The yields of gas are very low. Especially, the hydrogen yield is less than 5% at residence time of 72 s. Although little gas is produced in the pyrolysis reactor, the extent of degradation in the pyrolysis reactor has significant effects on gasification in our reactor system.

Figure 3 shows results of glucose gasification using the three-reactor system with different residence times in the pyrolysis reactor (13.3, 26.5, and 39.8 s). Main gaseous products are CO₂ and H₂. Although CH₄ is one of the major products in the equilibrium state of this experiment's condition, very little was obtained. Carbon gasification ratio increases with increasing residence time in the pyrolysis reactor. H₂ product amount is optimum at residence time of 26.5 s, and the CO product showed maximum amount at the residence time of 39.8 s. This phenomenon can be explained by catalytic deactivation. In our previous report,¹⁷ it was indicated that tarry products from cellulose and lignin caused carbonaceous deposition on catalyst and they prevented catalytic reactions. In this experiment, it is possible that

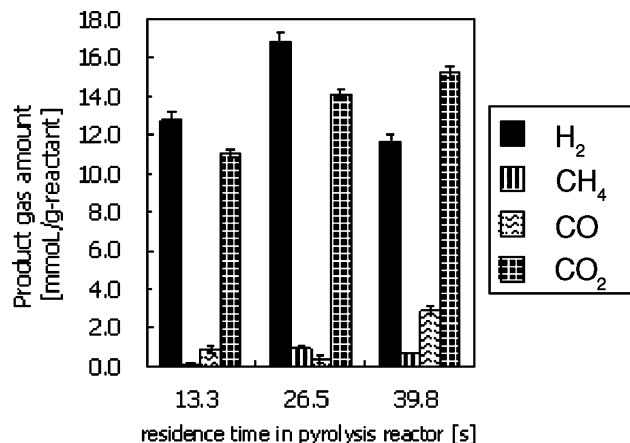


Figure 3. Effect of pyrolysis reactor length on product gas amount in glucose gasification using three-reactor system (4000 ppm, 673 K, 25.7 MPa, residence time in the oxidation reactor 22.0 s, O₂ equivalent 0.36, catalyst amount 1.35 g).

tarry products have formed in the pyrolysis reactor, and that a trace left undecomposed in the oxidation reactor deactivated the Ni catalyst. As for the production mechanism of tar, Sricharoenchaikul et al.³⁵ showed that it was a secondary product in their experiments of black liquor pyrolysis. Taking into consideration that tarry products in our experiments are also secondary products, the variation of H₂ and CO production in our experiments can be explained by catalytic deactivation caused by tarry products. Figure 4 a provides the gaseous products amount along time-on-stream in the experiment employing 39.8 s residence time in the pyrolysis reactor, which is the same experiment as in Figure 3. The CO product amount increases along the time-on-stream. And this increase of CO is not observed in the other two experiments in Figure 3. This increase means that the water–gas shift reaction is diminished along the time-on-stream because of catalytic deactivation caused by tarry products. Consequently, this deactivation is the reason for the optimum H₂ product at pyrolysis reactor residence time of 26.5 s. Therefore, a moderate residence time around 26.5 s is good for pyrolysis and hydrolysis of glucose without producing tarry products, especially in this condition.

To evaluate the role of Ni catalyst, we conducted an experiment with different catalyst loading. Figure 4b shows the result of a glucose gasification experiment with the same condition as that in Figure 4a but a 2 times larger amount of catalyst loading. H₂ production improves by 25%. CO production shows a gentler slope than that with the smaller amount of catalyst loading, this means that the water–gas shift reaction proceeded by increasing catalyst amount. This may be one of the reasons for the enhancement of H₂ production. Minowa et al. also reported the effect of catalyst loading in their experiments of cellulose gasification in subcritical water.²⁸ Though their conditions were different from those of our experiments, they got the same tendencies as our experiments; the increase of catalyst loading improved the H₂ and CO₂ yields, and depressed the yields of byproducts. They mentioned that steam reforming, water–gas shift reaction, methanation, and the liquefaction of biomass proceed on the catalyst. And these considerations are coincident with our results.

Experiments with Glucose–Lignin Mixtures. We have also conducted experiments using glucose–lignin mixtures. We employed lignin sulfonate derived from

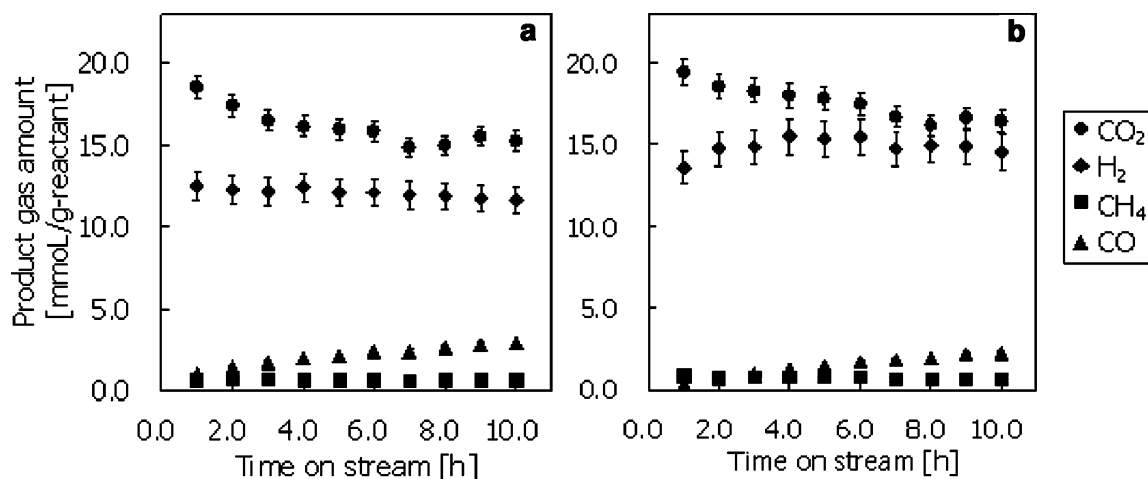


Figure 4. Effect of catalyst loading amount on product gas amount in glucose gasification (4000 ppm, 673 K, 25.7 MPa, residence time in the pyrolysis reactor 39.8 s, residence time in the oxidation reactor 22.0 s, O_2 equivalent 0.36, catalyst amount (a) 1.35 g and (b) 2.7 g).

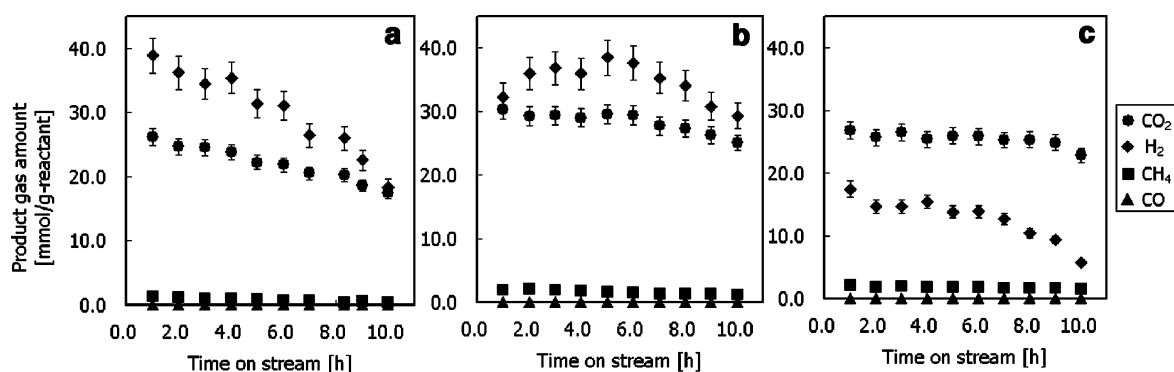


Figure 5. Effect of residence time in the pyrolysis reactor on time profile of product gas amount in glucose-lignin mixture gasification (3000 and 1000 ppm, respectively, 673 K, 25.7 MPa, residence time in pyrolysis reactor (a) 15 s, (b) 30 s, and (c) 45 s, residence time in the oxidation reactor 14.7 s, O_2 equivalent 0.55, catalyst amount 5.4 g).

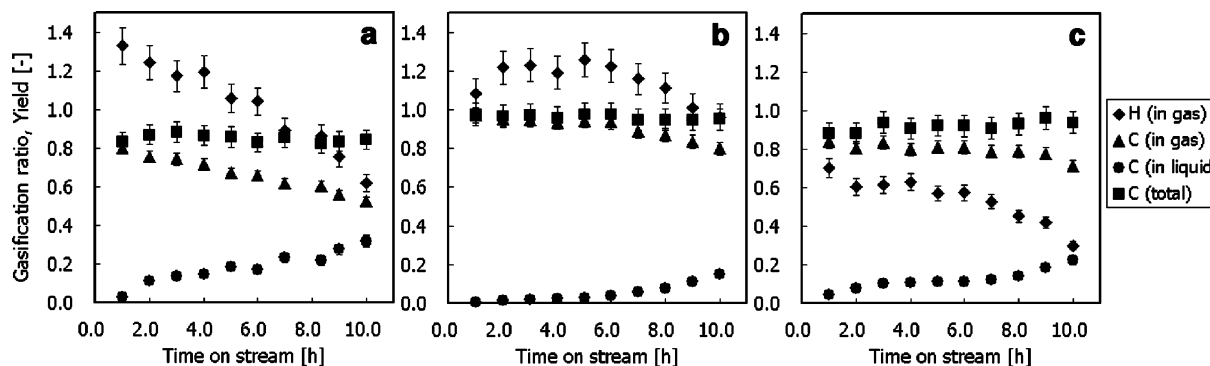


Figure 6. Effect of residence time in the pyrolysis reactor on time profile of carbon and hydrogen basis yields in glucose-lignin mixture gasification (3000 and 1000 ppm, respectively, 673 K, 25.7 MPa, residence time in pyrolysis reactor (a) 15 s, (b) 30 s, and (c) 45 s, residence time in the oxidation reactor 14.7 s, O_2 equivalent 0.55, catalyst amount 5.4 g).

softwood as lignin reagent, which is easily solved in water but is hardly decomposed to gas. As mentioned in the Introduction, char plugging prevented smooth gasification when we used only the catalytic reactor. This is the reason we added the oxidation reactor between the pyrolysis and catalytic reactors.

Figures 5 and 6 show the effect of pyrolysis reactor residence time in our reactor system. When the residence time in the pyrolysis reactor is 15 s (Figures 5a and 6a), CO_2 as well as H_2 production amount decreased along the time-on-stream. The reason for this reduction is that the fragments of lignin are not decomposed effectively before the catalytic reactor gradually sticks on, and consequently deactivates, the catalyst. More-

over, carbon balances are always at around 0.85. The missing carbon is accumulated in the reactor.

The result of the residence time of 30 s (Figures 5b and 6b) shows stable and effective gasification. Especially up to 5 h operation, the carbon gasification ratio is sustained at a high value (equal to 96%) with about 55 vol % of H_2 in the product gas. And the carbon balances are always around 0.96, which are better values than those obtained from the shorter residence time experiment.

When we set the residence time at 45 s (Figures 5c and 6c), the production of H_2 is diminished compared with that at the shorter residence time. We got the same effect in the glucose experiments (Figure 3). And this



Figure 7. SEM images of new Ni catalyst (a) and deactivated catalyst (b).

phenomenon can be explained by tarry products in the same way as the glucose experiments. Long residence time in the pyrolysis reactor causes polymerization of the fragment of glucose–lignin mixtures producing tar and char materials. In the catalytic reactor, these materials stick on the catalyst and prevent catalytic reaction. Considering that carbon balances are constant all through the experiments, char or tarry products remains in the reactor and would not be easily decomposed.

Taking into account the discussion above, we can understand that there are two dominating reactions in the pyrolysis reactor: the decomposition of biomass materials and polymerization of the fragments from the reactant. Long residence time in the pyrolysis reactor leads to undesirable polymerization of fragments. On the other hand, short residence time causes insufficient decomposition of biomass materials. As a result, moderate residence time in the pyrolysis reactor led to good gasification in our reactor system.

Figure 7 shows the SEM images of new Ni catalyst and the deactivated catalyst. We can observe macropores (shown in black) and secondary particles (shown in white) in the image of the new catalyst. In the deactivated catalyst, however, some materials, which are catalytic coke, cover the secondary particles and fill up the macropore structure. Catalytic coke is the heavy molecular weight product from polymerization of aromatic compounds. From these observations, we can understand that it is important to decompose aromatics before the catalytic reactor to avoid catalytic deactivation caused by catalytic coke.

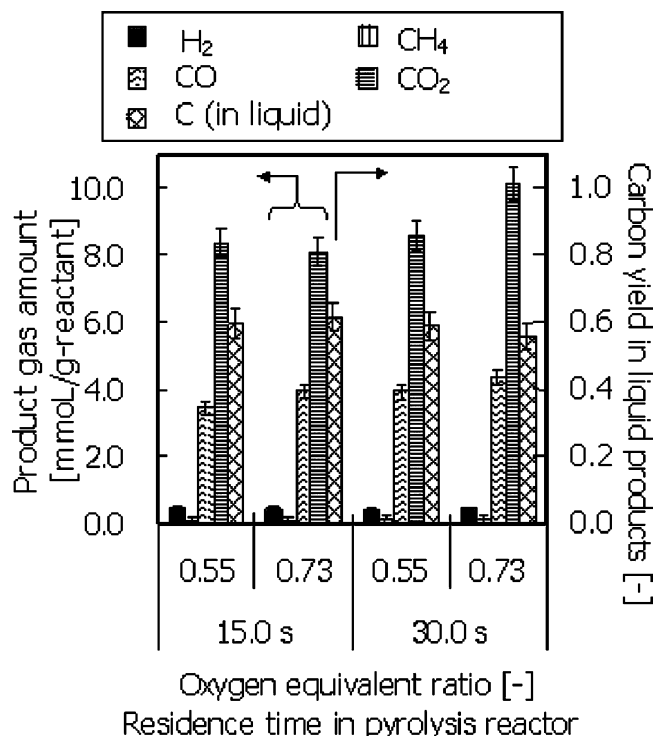


Figure 8. Effect of pyrolysis reactor length and oxygen equivalent ratio on product gas and carbon yield of liquid products in glucose–lignin mixture gasification without catalytic reactor (3000, 1000 ppm, 673 K, 25.7 MPa, residence time in the oxidation reactor 14.7 s, without catalytic reactor).

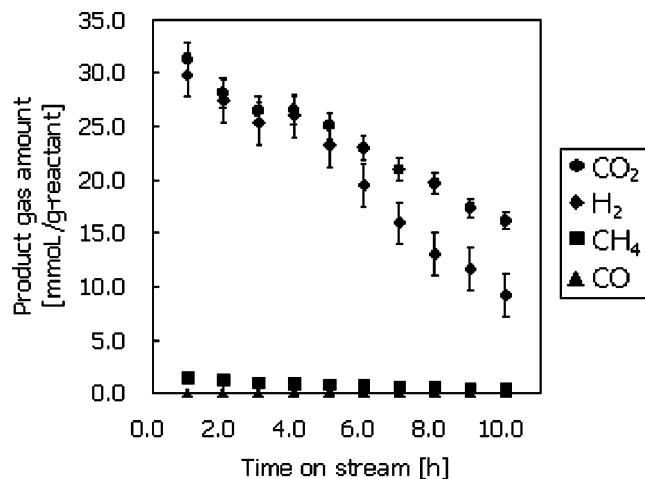


Figure 9. Effect of residence time in the oxidation reactor (cf. Figure 5) on gasification of glucose–lignin mixture (3000, 1000 ppm, respectively, 673 K, 25.7 MPa, residence times in the pyrolysis reactor and in the oxidation reactor are 30.0 and 7.3 s, respectively, O_2 equivalent 0.55, catalyst amount 5.4 g).

Figure 8 provides glucose–lignin mixture gasification without catalytic reactor on the condition of two different residence times in the pyrolysis reactor, and two different O_2 equivalent ratios (0.55, 0.73). Main gaseous products were CO and CO_2 . The larger amount of oxidant loading causes a decrease of carbon yield of the liquid products when the residence time is 30 s. However, in the case of shorter residence time in the pyrolysis reactor, an obvious difference in carbon yield of liquid products is not observed even with increasing oxidant loading. This means that appropriate residence time in the pyrolysis reactor is necessary for effective

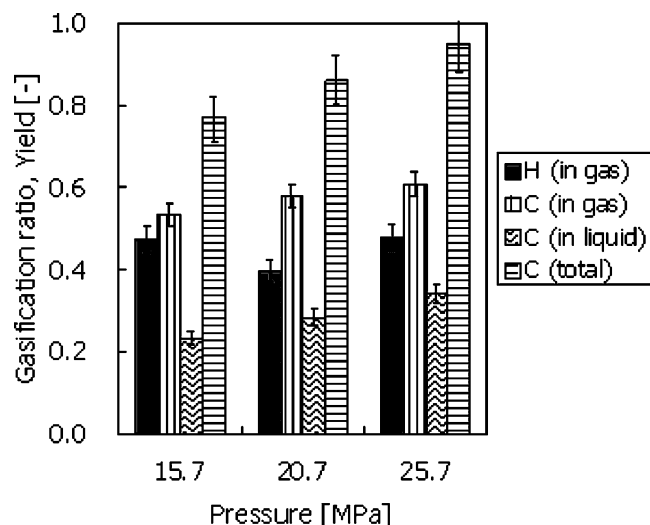


Figure 10. Pressure effect on carbon, hydrogen basis yields in glucose gasification (10 000 ppm, 673 K, residence time in the pyrolysis reactor 19.9 s, residence time in the oxidation reactor 22.0 s, O₂ equivalent 0.36).

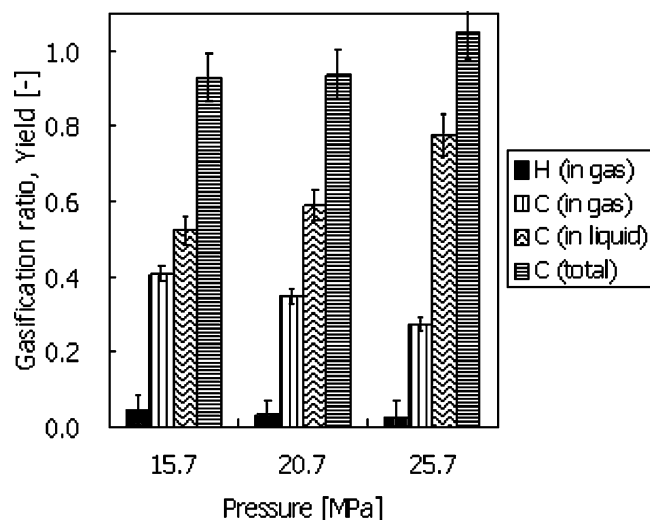


Figure 11. Pressure effect on carbon, hydrogen basis yields in glucose-lignin mixture gasification without catalytic reactor (1500, 500 ppm, respectively, 673 K, residence time in the pyrolysis reactor and in the oxidation reactor, 19.9 s and 22.0 s, respectively, O₂ equivalent 0.36).

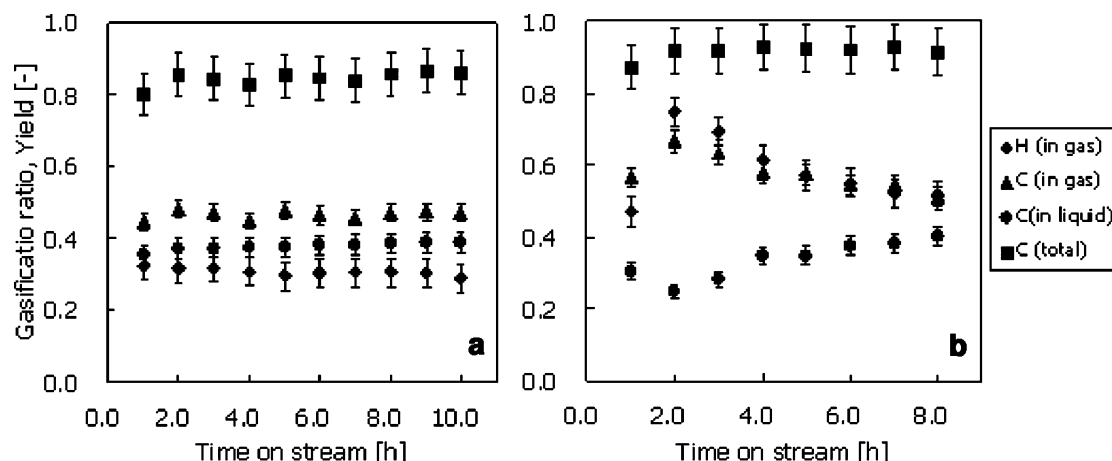


Figure 12. Pressure effect on carbon, hydrogen basis yields in glucose-lignin mixture gasification (1500, 500 ppm, respectively, 673 K, (a) 20.7 MPa, (b) 25.7 MPa, residence time in the pyrolysis reactor and in the oxidation reactor, 15.0 and 14.7 s, respectively, O₂ equivalent 0.55, catalyst amount 5.4 g).

reaction in the oxidation reactor. And this result shows that the pyrolysis process is important in our reactor system.

Moreover, the results of Figure 8 are completely different from the experiments using the three-reactor system including a catalytic reactor (Figures 5 and 6). At first, H₂ product amounts are very small. This fact indicates that most H₂ is formed in the catalytic reactor through the water-gas shift reaction on the catalyst surface or other catalytic reaction in the catalytic reactor. Second, the carbon yields of liquid product are around 0.6 while it presents about 0 at the first data point of the experiments with catalytic reactor (Figures 5 and 6). Therefore, not only CO, but also liquid products react and decompose in the catalytic reactor.

We have performed an experiment with making the oxidation reactor volume half the size of the one used in the experiment of Figures 5b and 6b, and have validated the effect of residence time in the oxidation reactor. The result is shown in Figure 9 and it has a totally different profile from that shown in Figures 5b and 6b. The H₂ product amount is much smaller than that in Figure 5b throughout the operation, and the decline of product gas amount along the time-on-stream is sharp, which is a sign of catalyst deactivation. This deactivation is caused by tarry products that are not decomposed in the oxidation reactor. Thus, the residence time in the oxidation reactor needs to be more than 14.6 s for effective tar decomposition in this experiment.

Pressure Dependency. Figure 10 shows the results of a glucose (1 wt %) gasification experiment with different pressure conditions from 15.7 to 25.7 MPa using the three-reactor system. The main gaseous products are H₂, CO₂, and CO in these experiments. The carbon gasification ratio, as well as carbon yield of liquid products, increases with increasing pressure. Consequently, the total carbon balance comes close to 1 at the condition of 25.7 MPa. There are many studies reported in the literature that investigated the pressure dependency of glucose decomposition and gasification in subcritical and supercritical water.^{7,34} Kabyemela et al.³⁴ observed a shift to higher kinetic rates for glucose decomposition as the conditions changed from subcritical to supercritical. It can be considered that these higher kinetic rates of decomposition promote the glucose decomposition into low-molecular-weight material that can be easily gasified via catalytic reaction in

these experiments. Consequently, we obtained higher gasification efficiency at 25.7 MPa, and this indicates that char or tarry products easily form and hardly decompose in lower pressure or lower water density conditions. In other words, polymerization that forms char and tarry products is restrained at higher pressure or higher water density conditions.

We have also examined the pressure dependency in glucose–lignin mixture gasification. Figure 11 shows the results of the experiments without catalytic reactor on the conditions of three different pressures with O₂ equivalent of 0.36 and without catalytic reactor. In this pressure region, the amount of each gas product decreases as the pressure goes up. Simultaneously, carbon yield of liquid products increases. In contrast to the experiments of glucose with catalyst shown in Figure 10, these experiments show that higher pressure restricts the gasification reaction. The reason for this disagreement is the lack of catalyst. Figure 12 provides the experiments utilizing the catalytic reactor. The gasification characteristics were totally different between 20.7 and 25.7 MPa. Both of the carbon and hydrogen gasification ratios at 20.7 MPa show lower values than the ones at 27.5 MPa. It can be considered that the liquid products of 20.7 MPa are not easily decomposed and catalyst is deactivated at the early stage of operation. On the other hand, liquid products at the condition of 25.7 MPa were comparatively easier to decompose. Thus, the gasification efficiency is better than the one at the condition of 20.7 MPa. According to these results, supercritical condition is very favorable for gasification of biomass using our reactor system.

Conclusions

Gasification of a glucose solution and a glucose–lignin mixture solution was conducted at a temperature of 673 K in supercritical water using the flow reactor system that we proposed. The reactor system is composed of three reactors: a pyrolysis reactor, an oxidation reactor, and a catalytic reactor with nickel catalyst. The reactions occur in each reactor as follows. In the pyrolysis reactor, there are mainly two kinds of reactions: decomposition and polymerization. The decomposition proceeds in the early stage of the reaction. However, long residence time in this reactor causes undesirable polymerization of biomass fragment. Consequently, moderate residence time in the pyrolysis reactor is favorable in our reactor system. In the oxidation reactor, tar and/or char products are effectively decomposed via radical reaction led by oxidant to low-molecular-weight products that can be decomposed in the catalytic reactor. With residence time in the oxidation reactor that is too short, high-molecular-weight compounds such as tarry products decompose insufficiently. In the catalytic reactor, CO is converted to H₂ and CO₂ via water–gas shift reaction, and low-molecular-weight liquid compounds are also decomposed to gas. However, heavy molecular compounds such as tarry and/or char products are not easily decomposed via catalytic reaction.

We also investigated the pressure dependency, and revealed that supercritical condition is suitable for gasification of biomass, because the tar and/or char products are decomposed easily.

Finally, we conclude that we can settle the char plug problem and can achieve a high gasification ratio, getting high content of hydrogen gas in its production gas, in the biomass gasification in supercritical water

by employing an oxidation reactor even at low temperature (around 673 K). Considering practical use, the concentrations of reactant in our experiments were still too dilute. To develop our system for gasifying dense biomass, a bigger oxidation reactor, in which tarry products will decompose owing to enough reaction time, will help. Moreover, the favorable residence time for dense biomass gasification might be different from that found for the dilute one. These considerations will be the subjects of our next work.

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