Effect of Activated Carbon Catalytic on Supercritical Water Gasification of Glycine as a Model Compound of Protein

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Aqueous solutions (1.0-5.0 wt%) of glycine, which is a model compound of proteins, was gasified in supercritical water using a tubular reactor at temperature of 500-650 °C and pressure of 25 MPa for a residence time of 63-188 s. Activated carbon (0.5 wt%) was employed as a catalyst in order to improve gasification efficiency. The identification and quantification of gaseous products were conducted and the total organic carbon was measured for the liquid effluent. Based on the experimental results, the reaction rate parameters were determined for the carbon gasification efficiency of glycine in supercritical water, assuming a first-order reaction. The results showed that an elevated temperature would be required for achieving high carbon gasification efficiency. The activated carbon catalyst was found to be ineffective for glycine.

Key Words
Biomass, Supercritical water gasification, Glycine, protein

1. Introduction

The increasing worldwide consumption of fossil fuels has not only led to a major shortage of energy resources but also accelerated global warming 1). One approach to reducing the use of fossil fuels is the utilization of biomass energy, which is a renewable and carbon neutral energy resource. Among the various technologies, fuel gas production from biomass is extremely attractive from the viewpoint of the efficiency associated with use of the product gas. A variety of biomass resources can be used to provide energy, including conversion to H₂, a process that can be undertaken via two main gasification technologies: thermochemical and biochemical. Thermochemical gasification of biomass is likely to be a cost-effective process for producing fuel gas. However, one of major problems with this technology is the formation of tars and char, which are produced as the biomass does not react directly with steam at atmospheric pressure 21-26). A great deal of research has been carried out in order to solve this problem. In particular, Calzavara et al. 26) found that energy efficiency reached up to 60% when they conducted gasification in supercritical conditions.

Supercritical H₂O, whose temperature and pressure are above critical values (Tc = 374 °C, Pc = 22.1 MPa), has an excellent extracting capability that is superior to that of liquid

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H₂O. Generally, it is known that the dielectric constant of supercritical H₂O is much lower than that of H₂O at room temperature. Therefore, supercritical H₂O behaves as an effective inorganic solvent for many bio-derived compounds. The excellent reactivity of supercritical H₂O could make it a highly promising reaction medium for converting various biomass sources into value-added fuel products \(^{61-12}\). Thus, supercritical H₂O gasification, where biomass is treated in supercritical water to form combustible gas such as H₂ and CH₄\(^{13,14}\), is an innovative thermochemical method for converting wet biomass and organic waste into fuel gases.

There are many kinds of model biomass compounds, in addition to the real materials, which have previously been gasified in supercritical H₂O \(^{51-29}\). To achieve high gasification efficiency, an activated carbon catalyst is known to be effective \(^{30}\). However, it was recently reported that the effectiveness of this catalyst differs from feedstock to feedstock. It has been found to be effective for glucose- and cellulose-containing feedstocks, but quite limited for fermentation residue \(^{31}\). It is therefore extremely important to find out for which biomass materials the activated carbon catalyst is effective; however, there has so far been no report on a systematic investigation to achieve this. In particular, its effectiveness for the gasification of compounds with heteroatoms, such as proteins, is of interest. In a previous study, Xu and Antal \(^{20}\) investigated sewage sludge gasification in supercritical H₂O. They prepared a cornstarch paste and used activated carbon as a catalyst. However, plugging of the reactor occurred after only 2 h of operation, and no reaction rate equation, which is of significant engineering importance, was provided in the report.

Glycine is the simplest amino acid, and can be a good model compound of proteins. The purpose of this study is to assess the effectiveness of activated carbon for the supercritical water gasification of glycine.

### 2. Experimental

#### 2.1 Experimental setup

All gasification runs were performed using the tubular flow reactor schematically illustrated in Fig. 1. The reactor was made of SS316 steel tubing (i.d., 2.17 mm; o.d., 3.18 mm) with a length of 12 m. Activated carbon from coconut shell (PDX-1, Kuraray Co., Ltd) with median particle size of 29 μm was used in this work and its concentration was fixed at 0.5 wt%. Feedstock containing the activated carbon catalyst was fed into the reactor by a piston pump (Toyo Koatsu Co.). Unless otherwise stated, the reactor pressure was maintained at 25 MPa and the desired temperature was reached before the addition of the feedstock. The residence time was changed in the range of 63 to 188 s by adjusting the feedstock flow rate. The reactor effluent was cooled down by the cooler before the remaining solid was separated from suspension by a solid-liquid separator and filter. The effluent was depressurized to atmospheric pressure by the back-pressure regulator and then sampled. The experimental conditions are shown in Table 1. The feedstock used in this study was a mixture of glycine and deionized H₂O, with activated carbon as the catalyst.

<table>
<thead>
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<th>Table 1 Experimental conditions</th>
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<tr>
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![Fig. 1 Experimental apparatus](image-url)
2.2 Analytical methods

The gas generation rate was determined by measuring the time for effluent gas to fill a vial of known volume. The gaseous products were detected by GC with a thermal conductivity detector (GC-TCD) with He as the carrier gas. CH₄, C₂H₆, and C₃H₆ were detected using GC with a flame ionization detector (GC-FID) with He as the carrier gas. H₂ was detected by GC-TCD with N₂ as the carrier gas.

The liquid product was analyzed by a total organic carbon (TOC) analyzer to quantify the amounts of carbon in the liquid product (non-purgeable organic carbon, NPOC) and in the dissolved gas product (inorganic carbon, IC). The carbon balance between the products (gaseous carbon, IC, and NPOC) and feedstock carbon was closed within the range from 0.96 to 1.1. No solid product was observed.

The authors did not recover activated carbon from the reactor effluent. As elucidated by Matsumura et al., activated carbon is known to react in SCW to produce H₂ and CO2. Therefore, the yield of gaseous carbon compounds produced from the gasification of activated carbon in the reaction was subtracted from the product gas when calculating the carbon gasification efficiency. The gasification rate of activated carbon catalyst needed for this purpose was determined only sending activated carbon to the reactor.

In this study, behavior of nitrogen was not followed, because it was beyond the scope of this study that effect of activated carbon is to be verified for glycine gasification, and because hetero atom behavior is difficult to trace by the small scale reactors as was employed in this study.

3. Results and Discussions

3.1 Effect of feedstock concentration

The effect of glycine concentration on the carbon gasification efficiency (CGE) is shown in Fig. 2. The CGE for all runs are calculated on the basis of the carbon content in glycine solution feedstock as defined in

\[
CGE = \frac{n_{CGE}}{n_{CGE} + n_{gas}} \times \frac{n_{gas}}{n_{CGE}} \quad (1)
\]

where \(n_{CGE}\) = initial amount of carbon [mol], \(n_{gas}\) = amount of gasified carbon [mol], \(n_{total}\) = total amount of carbon in gaseous products obtained after subtracting the effect of activated carbon gasification [mol], \(n_{inorganic}\) = total amount of inorganic carbon in the liquid products [mol], CGE = carbon gasification efficiency [%].

The experiment was conducted for glycine concentrations of 1.0, 3.0, and 5.0 wt% at 600 °C and 25 MPa with a residence time of 94 s. It can be seen that a high feedstock concentration resulted in lower carbon gasification efficiency, which is likely due to the production of tarry material. In a previous report on glucose gasification, the order of the reaction of tarry material production was found to be higher than unity, with high concentration resulting in a preference for tarry material production over gasification. The same trend was therefore expected here. Thus, at higher concentration, the effect of tarry material production cannot be neglected. As the intention of this study was to assess the gasification characteristics, the effect of tarry material production needed to be omitted so that the gasification rate was first order. For this reason, we employed the low feedstock concentration of 1 wt% in the subsequent experimental runs.

The effect of activated carbon was found to be negligible, indicating that this particular catalyst is not effective for enhancing the supercritical water gasification of glycine. Matsumura et al. classified biomass feedstock into three groups in terms of the effect of activated carbon; high cellulose content, low cellulose content, and lignin-containing, among which the low cellulose content group was not affected by the activated carbon catalyst. Glycine does not include cellulose or lignin, and so is most suited to the low (or no) cellulose content group. The lack of an effect by the carbon catalyst on the glycine feedstock therefore is in agreement with these previous results.

The effect of feedstock concentration on gas composition is shown in Fig. 3. A low feedstock concentration gave a higher H₂ content, while a higher feedstock concentration provided a higher CH₄ content. Thermodynamics has been found to be effective to predict the gas composition, where gas composition to minimize Gibbs free energy is calculated. Thermodynamics for supercritical water gasification predicts that higher feedstock concentration favors methane production. Thus, the experimental result agrees with thermodynamic prediction. Thermodynamics also predicts that little CO is to be found due to the water gas shift reaction with existence of large amount
of water, but CO is observed because the H_2O gas shift reaction is slow, and has not reached the equilibrium. The amount of CO_2 was found to increase when activated carbon was applied to high feedstock concentration, possibly due to its effect as catalyst for H_2O gas shift reaction.

### 3.2 Effect of residence time

An aqueous solution of 1.0 wt% was gasified at 600 °C and 25 MPa, for different residence times with and without the catalyst. The employed residence times were 188, 94, and 63 s, by adjusting the feedstock flow rate. It can be seen in Fig. 4 that the carbon gasification efficiency increased with residence time. Assuming that the gasification reaction rate is first order in terms of the ungasified carbon, the following equation is obtained.

\[
\frac{dn_{C_2}}{dt} = -k_0 \exp\left(\frac{-E_a}{RT}\right)(n_{C_2} - n_{C_2})
\]

which leads to

\[
n_{C_2} - n_{C_2} = n_0 \exp\left(\frac{-E_a}{RT}t\right)
\]

\[
CGE = \frac{n_{C_2}}{n_0} = 1 - \exp\left(\frac{-E_a}{RT}t\right)
\]

where \(n_0\) = initial amount of carbon [mol], \(n_{C_2}\) = amount of gasified carbon [mol], \(k_0\) = pre-exponential factor [s\(^{-1}\)], \(E_a\) = activation energy [J mol\(^{-1}\)], \(R\) = gas constant [J mol\(^{-1}\) K\(^{-1}\)], \(T\) = Temperature [K], \(t\) = time [s] and \(CGE\) = carbon gasification efficiency [-].

Fitting with this first-order-reaction rate equation is also shown in Fig. 4, and is in good agreement with the experimental data, indicating that 1.0 wt% is sufficiently dilute for the gasification characteristics to be expressed as a first order reaction with little error. This is also in agreement with many other reports on the effect of residence time on biomass gasification, where the gasification efficiency approached unity with time in an exponential manner \(^{17-19}\). Again, the effect of activated carbon was found to be negligible.

### 3.3 Effect of reaction temperature

The effect of temperature on the carbon gasification efficiency is shown in Fig. 5. As is characteristic for supercritical H_2O gasification, the efficiency increased significantly with increasing temperature. As previously found, the effect of the activated carbon catalyst was negligible. Assuming the Arrhenius rate law, a pre-exponenti-
tial factor of $2.73 \times 10^4 \text{s}^{-1}$ and an activation energy of 106.9 kJ mol$^{-1}$ were obtained from the experimental results without activated carbon. Fig. 6 shows the Arrhenius plot to show the validity of this assumption. Good agreement between experimental and theoretical results using the Arrhenius parameters was obtained, as shown in Fig. 5. The effect of reaction temperature on the gas composition is shown in Fig. 7. H$_2$ content is not affected by the reaction temperature so much. This may be characteristic to the decomposition of glycine. Thermodynamics predicts higher H$_2$ content for higher temperature. However, to achieve this equilibrium, methane generation has to proceed. Glycine, which is a small molecule with no methyl group, may not easily produce methane. This is just speculation, and further study is wanted.

4. Conclusions
Gasification of glycine was conducted using a tubular flow reactor. When the feedstock concentration was high, carbon gasification efficiency became lower. At a sufficiently low concentration of 1 wt%, the carbon gasification reaction followed the first order reaction rate. Its reaction rate constant was well expressed by the Arrhenius equation with a pre-exponential factor of $2.73 \times 10^4 \text{s}^{-1}$ and an activation energy of 106.9 kJ mol$^{-1}$. The product gas was composed of H$_2$, CO, CO$_2$, CH$_4$, and a small amount of C$_2$H$_6$ and C$_2$H$_4$. The effect of operation parameters on its composition agreed with the thermodynamic predictions. The activated carbon catalyst was found to be ineffective for glycine.

References