1. Introduction

Water under supercritical conditions ($T_c \approx 374 \degree C$, $P_c \approx 22.1$ MPa) has an excellent extracting capability, superior to that of liquid water. Many organic compounds, which cannot be dissolved in normal water, can be dissolved in supercritical water because it behaves like an organic solvent. This is mainly due to the dielectric constant of supercritical water, which is much lower than that of liquid water and alcohols. There are fewer and weaker hydrogen bonds between water molecules under supercritical conditions, especially at higher temperatures. With this change, the water turns into a nonpolar-like solvent with high solubility of organic compounds and gases. Thus, supercritical water behaves as an effective solvent for many bio-derived compounds. In addition, supercritical water has excellent reactivity, which makes it a very promising reaction medium for converting various types of biomass into value-added fuel products.$^{1-6}$

Supercritical water gasification of high-moisture-content biomass is a promising technology for combustible gas production such as $H_2$ and $CH_4$$^{7-10}$. It is an innovative thermochemical methodology for converting wet biomass and organic waste into fuel gases. In a previous study, many different model biomass compounds, in addition to the real biomass, have been gasified in supercritical water.$^{11-33}$ To understand the reaction mechanism of supercritical water gasification of biomass, the correlation between kinetic rate and temperature has been found to be useful.$^{34}$ The gasification rate of alanine was identical to that of glycine. The effect of the methyl group in alanine is the production of methane and the dilution of nitrogen so that the alkaline effect is suppressed. The former explains the higher methane yield, and the latter results in a high carbon monoxide yield.

Keywords
Biomass, Supercritical water gasification, Glycine, Alanine, Protein
compound, in supercritical water\(^{38}\), the determination of gasification of other amino acids and comparison of their gasification rates should be interesting. Especially if we can compare two similar compounds that differ by only one functional group, it might give some insight into the effect of the functional group on decomposition rate in supercritical water. Thus, the purpose of this study is to compare the gasification rate of glycine and alanine. By gasifying alanine, which is different from glycine by one methyl group, the effect of the methyl group should be clarified.

2. Experimental

2.1. Experimental Procedure

The experimental setup employed in this work is shown in Fig. 1. Tubing made of SS316 steel (ID: 2.17 mm, length 12 m) was used as a reactor. The reactor was made into coil with an approximately coil diameter of 8 cm and placed horizontal inside electrical temperature-controlled furnace. An aqueous solution of alanine (1.0-3.0 wt%) was delivered to the reactor by a high-pressure pump at a feedstock flow rate of 2 g/min. The reaction temperature was varied from 500 to 600 °C (residence times in a range of 94-119 s) and reaction pressure was controlled at 25 MPa. After passing through the reactor, the effluent was cooled by a heat exchanger, depressurized by a back pressure regulator, and then sampled. The experimental conditions are shown in Table 1. The feedstock was prepared by mixing alanine with deionized water. The experiment was repeated at least three times.

2.2. Analytical Methods

The gas generation rate was measured by the time for effluent gas to fill a vial of known volume by water replacement. The gaseous product was analyzed using gas chromatography (GC). Carbon dioxide and carbon monoxide were detected by GC with a thermal conductivity detector (GC-TCD) with helium as the carrier gas. Methane, ethene, and ethane were detected using GC with a flame ionization detector (GC-FID) with helium as the carrier gas. Hydrogen was detected by GC-TCD with nitrogen 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 the dissolved carbon 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 0.94 to 1.02. No solid product was observed.

The carbon gasification efficiency (CGE) for all runs was calculated on the basis of the carbon content in alanine solution feedstock as defined in

\[
\text{CGE} = \frac{n_{C_{\text{gas}}}}{n_{C_{0}}} = \frac{n_{C_{\text{gas}}} + n_{IC}}{n_{C_{0}}} \quad (1)
\]

where \(n_{C_{0}}\) = initial amount of carbon [mol], \(n_{C_{0}}\) = total amount of gasified carbon [mol], \(n_{C_{\text{gas}}}\) = amount of carbon in gaseous products [mol], \(n_{IC}\) = amount of inorganic carbon in the liquid products [mol].

3. Results and Discussions

3.1. Effect of Feedstock Concentration

The effect of feedstock concentration on carbon gasification efficiency is shown in Fig. 2. The experiment was conducted for alanine concentrations of 1.0, 2.0, and 3.0 wt% under 600 °C, 25 MPa, and a residence time of 94 s. The effluent product was colorless at 1.0 wt% and became slightly yellowish at higher concentrations. The effluent product was colorless at 1.0 wt% and became slightly yellowish at higher concentrations. The carbon gasification efficiency of alanine is not affected by the feedstock concentration employed here, which corresponds to first order behavior. For the case of glycine, the carbon gasification efficiency decreased with concentration. This is expected to be due to tarry material production at high concentrations. It is known that the order of the reaction for tarry material production is higher than unity for the case of glucose\(^{33}\). The same can be expected for amino acids. To determine the gasification characteristics, the effect of tarry material production should be omitted. It is not possible to completely get rid of it, but judging from the effect of residence time, 1.0 wt% was found to be...
sufficiently dilute so that the gasification characteristics is expressed as a first order reaction with a small error\(^3\). For the case of alanine, the effect of tarry material production is negligible, and we can safely assume first order kinetics. Maybe the methyl group has the ability to suppress tarry material production.

The effect of feedstock concentration on gas composition is shown in Fig. 3. Thermodynamics predicts that little carbon monoxide is to be found due to the water gas shift reaction with the existence of large amounts of water, but carbon monoxide is observed because the water gas shift reaction is slow, and has not reached equilibrium. Increase in feedstock concentration results in increased hydrogen and carbon dioxide yields. Remembering that increase in feedstock concentration did not affect the carbon gasification efficiency, increase in hydrogen and carbon dioxide yields implies the proceeding of the water gas shift reaction. A corresponding reduction in carbon monoxide yield supports this idea. Considering that amino groups can produce ammonia or amine molecules, as was observed by Sato \(\text{et al.}\)\(^{39}\), the alkalinity of the liquid should also increase with feedstock concentration. This alkali might have functioned as the catalyst for the water gas shift reaction. Alkali stabilizes the carbon dioxide, and enhanced water gas shift reaction is expected.

**3.2. Effect of Reaction Temperature**

A 1.0 wt% solution of alanine was gasified at 25 MPa over a temperature range of 500-650 °C. Feedstock flow rate was fixed at 2.0 g/min. The liquid sample of 500 °C of reaction temperature had light yellow color and it became lighter and colorless at higher reaction temperature. The resulting carbon gasification efficiency is shown in Fig. 4. The carbon gasification efficiency increases with reaction temperature. As is characteristic for supercritical water gasification, the efficiency increases significantly with increasing temperature, as was observed for glucose by Xu \(\text{et al.}\)\(^{7,15}\). Figure 4 also shows the carbon gasification efficiency of 1.0 wt% glycine\(^3\). Glycine gasification was conducted four times, and alanine gasification was conducted three times to obtain sufficient reproducibility. Considering the experimental error of the carbon gasification efficiency, the gasification rates of glycine and alanine are identical. This fact implies that the methyl group in alanine does not have a significant effect on carbon gasification efficiency. One of the possibilities is that the carboxyl group, which is common to both glycine and alanine, is reacting first. Since the carbon atom is not strongly electrophilic or nucleophilic, the methyl group will not affect the reactivity of the carboxyl group. This mechanism can explain why the methyl group does not affect the carbon gasification rate.

Assuming that the gasification reaction rate is first order in terms of the feedstock carbon amount, and assuming the Arrhenius rate law, the following equation is obtained.

\[
\frac{dn_{c_g}}{dt} = k_0 \left\{ \exp \left( -\frac{E_A}{RT} \right) \right\} (n_{c_0} - n_{c_g})
\]  

which leads to

\[
n_{c_0} - n_{c_g} = n_{c_0} \exp \left[ -k_0 \left( \frac{E_A}{RT} \right) t \right]
\]
The parameters in Eq. (4) were determined by fitting to the experimental data. Assuming the same reaction rate, the pre-exponential factor and the activation energy of glycine and alanine were determined to be $7.37 \times 10^5$ s$^{-1}$ and 131 kJ/mol, respectively. The fitting result using these parameters is also shown in Fig. 4. Good agreement between experimental and calculation results are obtained.

Gas composition of alanine gasification as a function of reaction temperature is shown in Fig. 5. The product gas composition for glycine is also shown for comparison purposes. It is clear that in comparison to glycine, alanine results in a higher yield of methane. This methane would have been produced from the methyl group. Another clear difference between glycine and alanine is that water gas shift reaction proceeds to a greater extent for glycine. Since both amino acid solutions were created at 1 wt%, and considering that molecular weight is smaller for glycine, the number of nitrogen atoms is higher for the case of glycine; thus, a stronger alkali effect is expected. Again, the alkali can stabilize carbon dioxide, resulting in a greater progress of the water gas shift reaction.

In this respect, the effect of the methyl group in alanine should be two-fold: (1) it is converted into methane, and (2) it dilutes nitrogen so that the alkaline effect is suppressed. The former explains the higher methane yield, whereas the latter results in the high carbon monoxide yield.

In this study, the authors did not attempt to identify or quantify individual compounds remaining in the liquid phase. However, Sato et al. have analyzed the products from alanine decomposition in high pressure and high temperature condition, and detected ammonia and ethyl amine as nitrogen containing compounds. This behavior of nitrogen will be our next target.

4. Conclusions

Gasification of alanine was conducted using a tubular flow reactor. When the feedstock concentration was high, the carbon gasification efficiency does not much change, but 1.0 wt% of glycine is sufficiently dilute for gasification. The carbon gasification reaction of alanine followed first order kinetics. Gasification rate is identical for both glycine and alanine, and the reaction rate parameters were determined. Its reaction rate constant was well expressed by the Arrhenius equation with a pre-exponential factor of $7.37 \times 10^5$ s$^{-1}$ and an activation energy of 131 kJ mol$^{-1}$. The product gas was composed of hydrogen, carbon dioxide, carbon monoxide, methane, and a small amount of ethane and ethene. The effect of the methyl group in alanine is the production of methane, and the dilution of nitrogen so that the alkaline effect is suppressed. The former explains the higher methane yield, whereas the latter results in the high carbon monoxide yield.

References

1) Cansell, F., Beslin, P., Berdeu, B., *Environ. Prog.*, **17**, (4), 240 (1998).
2) Goto, M., Nada, T., Kodama, A., Hirose, T., *Ind. Eng. Chem. Res.*, **38**, 1863 (1999).
3) Antal Jr., M. J., Allen, S., Schulman, D., Xu, X., *Ind. Eng. Chem. Res.*, **39**, 4040 (2000).
4) Bridgwater, A. V., *Chem. Eng. J.*, **91**, 87 (2003).
5) Kruse, A., Gawlik, A., *Ind. Eng. Chem. Res.*, **42**, 267 (2003).
6) Calzavara, Y., Joussot-Dubien, C., Boissonnet, G., Sarrade, S., *Energy Convers. Manage.*, **46**, 615 (2005).
7) Xu, X., Matsumura, Y., Stenberg, J., Antal Jr., M. J., *Ind. Eng. Chem. Res.*, **35**, 2522 (1996).
8) Yoshida, T., Oshima, Y., Matsumura, Y., *Biomass Bioenergy*, **26**, 71 (2004).
9) Matsumura, Y., Minowa, T., Potic, B., Kersten, S. R. A., Prins,
要 旨

アラニンの超臨界水ガス化特性

Thachanan SAMANMULYA①, 井上 修平②, 井上 陽仁③, 川井 良文④*, 久保田 晴仁⑤, 宗本 洋人⑥, 野口 琢史⑦, 松村 幸彦⑧

① 広島大学大学院工学研究科機械システム工学専攻, 739-8527 広島県東広島市鏡1-4-1
② 広島大学大学院工学研究院エネルギー・環境部門, 739-8527 広島県東広島市鏡1-4-1
③ 復建調査設計(株), 732-0052 広島市東区光町2-11-31
④ 中電プラント(株), 734-0001 広島市南区出汐2-3-18
⑤ 中国電力(株), 739-0046 広島県東広島市鏡3-9-1
⑥ 広島県立総合技術研究所西部工業技術センター, 737-0004 広島県呉市阿賀南2-10-1
⑦ 東洋大学高等, 733-0002 広島市西区倉木町2-1-22

反応温度500～650℃, 反応圧力25 MPa, 潜留時間86～119 s の条件下で1.0～3.0 wt%のアラニン水溶液の超臨界水ガス化を行った。さらに, 得られた炭素ガス化度を著者らの以前の研究で得られたグリシンの炭素ガス化度と比較した。ガス化生成物の同定と定量をガスクロマトグラフ（GC）で行い, また液相中の有機炭素（TOC）の分析も行った。アラニンの炭素ガス化反応速度とともに上昇し, そのガス化速度は1次反応速度式に従った。また, その温度依存性はアレニウスの式で表された。アラニンのガス化速度はグリシンと同じであることが確認された。アラニンのメチル基の効果はメタンの生成と窒素の希釈によるカルバニ効果の抑制であった。前者は高いメタン収率を, 後者は高い一酸化炭素収率を説明する。