Renewable energy is a promising solution to the problem of global warming and increased energy consumption. Biomass is one of the potential sources that can provide renewable energy. Gasification of biomass is one of the methods available to produce renewable energy. Fuel gases such as hydrogen and methane can be produced by the conversion of carbon and hydrogen in biomass (1-2). The generation of biomass energy will not add to the greenhouse effect causing global warming because this process is “carbon neutral” or has a net carbon balance of almost zero. Although gasification of biomass releases CO₂ into the atmosphere, this carbon can be taken up by plants during photosynthesis. Many types of biomass are available, including wet biomass. Unfortunately, the evaporation heat of water is higher than the heat of biomass combustion if the wet biomass has high water content, so the drying process before gasification is unfavorable. Supercritical water gasification is a promising technology that uses wet biomass with high water content as a reaction medium for biomass conversion to produce hydrogen and methane (3-5). Water under supercritical conditions (T_c = 374 °C or 647 K, P_c = 22.1 MPa) is a better solvent than liquid water. Supercritical water behaves like an organic solvent that can dissolve organic compounds, which are normally insoluble in liquid water. This advantageous characteristics, among a range of other interesting properties, is obtained only under particular temperatures and pressures of the system. The good solvent properties of supercritical water are mainly due to its dielectric constant, which is much lower than that of liquid water and alcohols. The ionic product and dielectric constant of water decrease dramatically on approaching the critical point, resulting in the formation of a nonpolar-like solvent that exhibits high solubility for organic compounds and gases. Ionic reactions are reduced and radical reactions are enhanced instead, indicating that the reaction pathway can be controlled by manipulating the water conditions. The reactions that usually proceed are the supercritical water oxidation of industrial and toxic wastes, and the supercritical water gasification of biomass. During these reactions, the cellulose, hemicellulose, polysaccharide, and protein present in the biomass are hydrolyzed to yield monosaccharides and smaller compounds (e.g., glucose, xylose, amino acids, and organic acids), which are utilized further as bio-chemicals and bioethanol. Therefore, supercritical water gasification has excellent reactivity, and is a very promising reaction medium for converting various types of biomass into value-added fuel products (4-12).

Many studies of supercritical water gasification tech-
ology have demonstrated the potential of this innovative thermochemical methodology for converting wet biomass and organic waste into combustible gases, such as hydrogen and methane\textsuperscript{13,14}. To investigate the gasification characteristics of various biomass species, a wide range of biomass compounds have been gasified in supercritical water as models of real biomass containing these compounds\textsuperscript{15\textendash}30. For example, glucose is a compound of cellulose and hemicellulose\textsuperscript{31,32} and guaiacol is a model compound of lignin\textsuperscript{33}. Many types of real biomass materials have also been gasified\textsuperscript{34}. However, the gasification rate of specific feedstocks is still difficult to predict. For example, not much is known about the gasification behavior of proteins, an important component of biomass. The study of protein gasification behavior is significant, especially for food waste and animal matter. Amino acids are good candidate model compounds of protein, and are produced by the hydrolysis of protein. The correlation between kinetic rate and temperature is useful to understand the reaction mechanism of supercritical water gasification of biomass\textsuperscript{35}. Radicals and ionic reactions between intermediates are distinguished by conformity to Arrhenius behavior\textsuperscript{31,33,36}. Previously, we studied the gasification characteristics of glycine, alanine, valine, leucine, and proline\textsuperscript{37\textendash}39, and found that the gasification behavior of these amino acids are not always the same. However, the gasification rates of glycine and alanine in supercritical water were identical, and so can be considered as a standard for investigating amino acid gasification. Other amino acids behave differently from the standard amino acids due to the different stability of the bond between the carboxyl group and other components (amino group and functional group) and the different stability of the produced radicals. However, more gasification data is needed to predict the gasification behavior of amino acids. Our previous work\textsuperscript{39} showed that decomposition of the amino acid leads to the production of radicals. Aminobutyric acid and serine are particularly interesting because their decomposition results in the formation of different radicals, but their gasification characteristics have not yet been studied.

The present study is investigated the effects of ethyl and hydroxymethyl functional groups on gasification behavior by studying the gasification characteristics of aminobutyric acid and serine. Figure 1 shows the molecular structure of aminobutyric acid and serine, with the structure of alanine for comparison. These amino acids vary by the functional group attached to the alpha carbon, i.e., methyl, ethyl, and hydroxymethyl, respectively.

2. Materials and Methods

2.1. Materials

The aminobutyric acid and serine feedstocks were prepared by dissolving commercially available amino acids in deionized water.

2.2. Experimental Procedure

All gasification experiments were performed using the tubular flow reactor schematically illustrated in Fig. 2. Briefly, a SS316 steel tube with a length of 12 m and an inner diameter of 2.17 mm was used as the reactor. The reaction temperature was varied from 400 to 650 °C and reaction pressure was fixed at 25 MPa. The residence time was changed in the range of 86-222 s by controlling water density at each reaction temperature with a fixed feedstock flow rate of 2.0 g/min and reactor length of 12 m. Before the addition of the feedstock, the reactor pressure was maintained at 25 MPa by feeding only deionized water controlled by a back-pressure regulator, and the reactor temperature was raised to the required temperature. An aqueous solution of 1.0 wt% amino acid was fed into the reactor at a fixed feedstock flow rate of 2.0 g/min. After passing through the reactor, the effluent was cooled down in a heat exchanger, depressurized through a back-pressure regulator, and then sampled.

2.3. Analytical Methods

The rate of gas generation was measured using a water displacement method which measured the time required for the effluent gas to fill a vial of known
volume. The gaseous product was characterized and quantified using gas chromatography (GC). Carbon dioxide and carbon monoxide were detected by GC with a thermal conductivity detector (GC-TCD) using helium as the carrier gas. Methane, ethene, and ethane were detected using GC with a flame ionization detector (GC-FID) using helium as the carrier gas. Hydrogen was detected by GC-TCD with nitrogen as the carrier gas.

The liquid product was quantified the amounts of carbon in the liquid product (non-purgeable organic carbon, NPOC) and the dissolved carbon gas product (inorganic carbon, IC) by a total organic carbon (TOC) analyzer.

Carbon gasification efficiency was defined as the ratio of the total carbon in the gas product to that in the feedstock solution.

Assuming that the gasification reaction follows the first order Arrhenius rate law in terms of the feedstock carbon content, the following equation is obtained:

$$\frac{dn_{C_{gas}}}{dt} = k_0 \left\{ \exp \left( -\frac{E_a}{RT} \right) \right\} (n_{C_0} - n_{C_{gas}})$$ (1)

which leads to

$$n_{C_0} - n_{C_{gas}} = n_{C_0} \exp \left[ -k_0 \left\{ \exp \left( -\frac{E_a}{RT} \right) \right\} t \right]$$ (2)

$$CGE = \frac{n_{C_{gas}}}{n_{C_0}} = 1 - \exp \left[ -k_0 \left\{ \exp \left( -\frac{E_a}{RT} \right) \right\} t \right]$$ (3)

where $n_{C_0}$ = initial amount of carbon [mol], $n_{C_{gas}}$ = 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 [-].

The parameters in Eq. (3) were determined by fitting to the experimental data of carbon gasification efficiency.

3. Results and Discussion

3.1. Aminobutyric Acid Gasification

Gasification of glycine and alanine in the experimental temperature region followed the first order reaction rate with respect to the amount of carbon feedstock. We assumed that the gasification rate of aminobutyric acid is also a first-order reaction here. Figure 3 shows the carbon gasification rate of aminobutyric acid relative to the reported results for glycine and alanine, expressed as the carbon gasification efficiency at each temperature. The gasification characteristics of glycine and alanine were identical as shown by the dashed line. As is characteristic for supercritical water gasification, the efficiency increased significantly with higher temperature, as observed for glucose. The gasification efficiency of aminobutyric acid increased with reaction temperature; this is consistent with Arrhenius behavior (indicated by the solid line in the figure). The error bars represent the standard deviation of replicated experimental runs.

As mentioned above, glycine, alanine, and aminobutyric acid differ only in the functional group attached to the alpha carbon. Decomposition of these amino acids leads to the production of hydrogen, methyl, and ethyl radicals, respectively. Figure 4 shows a schematic of the decomposition pathways of these amino acids adapted from previous work. The electron donation tendencies of hydrogen, methyl, and ethyl radicals are similar. Therefore, the bond strength between the carboxyl group and the alpha carbon, and its effect on the stability of this bond should be almost the same. This is consistent with the identical gasification rates of these amino acids: the bond between the carboxyl group and the other parts (amino group and functional group)
is likely to be cleaved first; considering the instability of the radicals produced in the following stage, this is expected to be the rate determining step for the gasification. Hydrogen, methyl, and ethyl radicals are produced from glycine, alanine, and aminobutyric acid, respectively, and all these small radicals should react rapidly to produce gaseous molecules such as hydrogen, methane, and ethane.

The composition of gases generated from the amino acids as a function of reaction temperature is shown in Fig. 5(a). Aminobutyric acid gasification resulted in increased methane fraction with higher reaction temperature. This can be explained as follows: aminobutyric acid decomposition produces an ethyl radical ($R = \text{C}_2\text{H}_5$), which can react further to produce butane, as shown in Fig. 4. Butane can undergo decomposition to produce methane, ethylene, ethane and hydrogen$^{39}$. At low reaction temperature, a carbon monoxide fraction was also observed in the product gas, possibly owing to incomplete gasification. However, this fraction decreased with higher reaction temperature. At 650°C, the fraction of carbon monoxide decreased and the fractions of carbon dioxide and hydrogen increased, due to the promotion of the water-gas shift reaction at high reaction temperature. Ethylene and ethane were also formed as a result of aminobutyric acid gasification; and are also reported to form during alanine gasification$^{39}$.

### 3.2 Serine Gasification

The carbon gasification efficiency is shown in Fig. 6. Similar to aminobutyric acid, the gasification rate of serine could also be well explained with a first order Arrhenius equation. The carbon gasification efficiency increased with higher reaction temperature. The gasification of serine was faster compared to glycine and alanine. The data shown in Fig. 6 are the average of triplicate experimental runs with standard deviation less than 5%, indicated in the error bars. Serine decomposition is also shown in Fig. 4. The decomposition of serine proceeds via the breaking of the bond between the carboxyl group and the 2-hydroxy-1-aminoethyl group; this is consistent with previous reports$^{39}$. The difference between alanine and serine is that one hydrogen atom in the methyl group of alanine is replaced with a hydroxyl group. The oxygen atom in this hydroxyl group is highly electronegative, thus lowering the electron density of the bond between the carboxyl group and the 2-hydroxy-1-aminoethyl group and weakening the bond. Therefore, serine is more reactive than alanine. The 2-hydroxy-1-aminoethyl radical formed is expected to further decompose to produce the hydroxymethyl radical, as shown in Fig. 4. The hydroxymethyl radical is a primary radical and its reactivity may lead to high carbon gasification efficiency. These radicals can react with each other to form ethylene glycol and with hydrogen radical to form methanol. These products are reactive compounds that can undergo further decomposition and gasification. Figure 6 also shows the carbon gasification efficiency of 1.0 wt% glycine and alanine$^{38}$.

The composition of the product gas of serine gasification as a function of reaction temperature is shown in Fig. 5(b). At low reaction temperatures, the reaction does not proceed to completion. The product gas
mainly consists of carbon monoxide, carbon dioxide, and hydrogen. These gases are produced during the initial decomposition of serine, as shown in Fig. 4. The methane fraction increases with reaction temperature, but the increase is not as great as that observed in the case of aminobutyric acid. The product gas has a low content of ethylene and ethane. Another clear difference between the composition of the product gases obtained with aminobutyric acid and serine is the higher hydrogen fraction derived from the latter due to the high reactivity of the hydroxyl group.

3.3. Analysis of Products

Carbon balance between the products and the feedstock carbon is defined by the following equation.

\[
\text{Carbon balance} = \frac{n_{\text{Cgas}} + n_{\text{IC}} + n_{\text{NPOC}}}{n_{\text{C0}}}
\]

where \(n_{\text{Cgas}}\) = amount of gasified carbon [mol], \(n_{\text{IC}}\) = amount of inorganic carbon dissolved in liquid phase products [mol], \(n_{\text{NPOC}}\) = amount of carbon in liquid phase products [mol] and \(n_{\text{C0}}\) = initial amount of carbon [mol].

The carbon balance of all runs was within the range of 0.89 to 1.00. A less solid particle was observed. The liquid phase products emitted a pungent odor and were light yellowish as was observed for amino acids. As shown in Fig. 4, amino acid should form carbon dioxide and hydrogen, and ammonia in the liquid phase product. This conjecture is supported by the previous results that determined total nitrogen recovery was around 90% from supercritical water gasification in the liquid phase product as ammonia.

3.4. Comparison of Gasification Rates of the Employed Amino Acids

Carbon gasification efficiencies of the employed amino acids are compared in Fig. 7. The previously reported carbon gasification efficiencies amino acids, glycine, alanine, valine, leucine, and proline, are also included for reference. The carbon gasification efficiency increased with higher reaction temperature. Serine was clearly the fastest to gasify, which is explained by the high electronegativity of the hydroxyl group, produced from serine decomposition. Decomposition of the other amino acids produced primary radicals, and their gasification rates are similar, including that of aminobutyric acid. However, unlike the other amino acids (with the exception of valine), the gasification rate of proline was largely insensitive to reaction temperature, although proline produces a primary radical. This could be due to stabilization of the transition state of the ring structure. Valine had the lowest gasification rate; possibly due to the formation of secondary radicals, which are relatively stable and can combine to form bulky molecules.

Gasification of glycine and alanine was found to follow first order reaction kinetics over this range of reaction temperatures, so we assumed that the gasification reaction rate of aminobutyric acid and serine are also first-order with respect to the amount of carbon feedstock. The pre-exponential factors and activation energies of the employed amino acids were determined by fitting to the experimental data of carbon gasification efficiency. Table 1 shows the resulting pre-exponential factors and activation energies of aminobutyric acid and serine, and those of glycine and alanine for reference. The fitting results using these parameters are also shown in Figs. 3, 6, and 7. The calculated results and experimental data are in good agreement. The pre-exponential factor and activation energy of aminobutyric acid are close to those of glycine, alanine, and leucine because the rate determining step, the carboxyl radical production, is the same in all three cases. The rate of carbon gasification of serine is faster than those of the others; resulting from the formation of a hydroxyl group, which is highly reactive.

<table>
<thead>
<tr>
<th>Table 1 Reaction Rate Parameters of Supercritical Water Gasification of Glycine and Alanine, Aminobutyric Acid and Serine</th>
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<tr>
<td><strong>Pre-exponential factor</strong> [s(^{-1})]</td>
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<td>---------------------------------------------------------------</td>
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<tr>
<td>Glycine and alanine(^{39,395})</td>
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<tr>
<td>Aminobutyric acid</td>
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<td>Serine</td>
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4. Conclusions

Carbon gasification efficiencies of aminobutyric acid and serine are higher than 80% at 650 °C. Supercritical water gasification of the employed amino acids can be characterized by first order kinetics with the Arrhenius equation rate constant, and the reaction parameters were determined. Gasification rate of serine was higher than those of glycine and alanine, whereas that of amino-butyric acid was nearly the same as those of glycine and alanine. The weak bond between the carboxyl group and the 2-hydroxy-1-aminoethyl group was affected by the oxygen atom in the hydroxyl group of serine, so serine was more reactive than glycine and alanine.

References

要  旨
タンパク質モデル化合物のアミノ酸およびセリンの超臨界条件下でのガス化特性

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タンパク質ガス化挙動の研究は、バイオマスエネルギー生産のため、とりわけ食品廃棄物や動物排せつ物の問題のために重要である。アミノ酸およびセリンのガス化特性を、連続式反応器を用いて超臨界条件下で測定した。これら二つのアミノ酸の濃度は1.0重量％、反応温度は400～650℃、滞留時間は86～222 s、反応圧力は25 MPaであった。生成物を同定し、ガスクロマトグラフィーにより定量、さらに水相中の全有機炭素も決定した。炭素ガス化率は反応温度とともに増加傾向を示した。ガス化反応速度は一次反応速度で表され、その温度依存はアレニウスの式によって説明される。アミノ酸のガス化率は、セリンより速く、グリシンおよびアラニンと同程度であった。セリンのヒドロキシル基中の酸素は極めて電的に陰性であり、このためにグリシンおよびアラニンよりもセリンは反応性に富んでいると考えられる。