

Acidic and Basic Amino Acids Gasification Characteristics under Supercritical Water Conditions

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Keywords: Amino acids, Hydrothermal, Supercritical water, Gasification, Biomass

Abstract: Animal biomass wastes and aquatic biomass are alternative biomass materials for renewable energy production which are contained low or no lignocellulosic. Protein is one of major contents in food waste, animal matter, and algae. The 2 selected amino acids, glutamic acid and arginine, were chosen to determine the gasification characteristics. Aqueous solution 1.0 wt% of those two amino acids was gasified under supercritical water conditions by using a tubular flow reactor. Reaction temperatures were varied ranging between 500 and 650 °C and pressure was fixed at 25 MPa. Aqueous feedstock flow rate also fixed at 2.0 g/mL for a residence time of 86-119 s. Identification and quantification of the gas products were examined by gas chromatography (GC). The aqueous phase product was also determined the dissolved carbon by the total organic carbon (TOC) analyzer. An increasing reaction temperature improved the carbon gasification efficiency. The gasification rate of glutamic acid and arginine follow Arrhenius behaviors and are explained well by the first order kinetics equation. Gasification characteristics of glutamic acid and arginine were also compared to those of glycine and alanine. The effect of the functional group in arginine is an increasing alkalinity that made pH of liquid products are above 9.

1 INTRODUCTION

Nowadays, the world energy consumption is tendency rises with the rising of fossil fuel depletion and the global environmental problem. Then, renewable energy such as biomass-derived energy becomes an attractive issue to reduce the fossil fuel production and develop to be a sustainable energy resource. Generally, organic compounds in biomass cannot be dissolved in normal conditions water due to they are non-polar molecules. Under supercritical conditions ($T_c = 647 \text{ K}$ or 374 °C , $P_c = 22.1 \text{ MPa}$), supercritical water became a better solvent more than a normal conditions water that behaves like an organic solvent. Supercritical water dissolved organic compounds, the lignocellulosic compounds, polysaccharide, and protein, which presented in biomass and hydrolyzed to form glucose, xylose, amino acids, and organic acids which are further utilized as feedstocks of bio-ethanol or bio-chemicals or bio-fuel productions. Then,

supercritical water gasification has excellent reactivity, which makes it a very promising reaction medium for converting various types of biomass into value-added fuel products. Furthermore, supercritical water gasification has been developed not only to solve the problem of tar and char formation which initiated low conversion efficiency and reactor plugging but also increases gasification efficiency (Antal et al., 2000).

Many works have studied and revealed that supercritical water gasification technology is an innovative thermochemical methodology for converting wet biomass and organic waste into combustible gases, such as hydrogen and methane (Matsumura et al., 2013). A wide variety of model biomass compounds have been separately gasified in supercritical water in order to investigate the gasification characteristics of substantial biomass species as the representative of real biomass containing these compounds. But, the gasification rate of specific feedstocks is still miserable to

predict. There are not much known about the gasification characteristics of non-lignocellulosic biomass which has low or no cellulose, hemicellulose and lignin content. Protein, which is non-lignocellulosic, is a common important component of biomass, organic waste, food waste, animal matter, and algae which are usually wet biomass. Then, protein gasification characteristics is important to study that its molecule is different from carbohydrate and has N-containing. Amino acids are good representative model compounds of protein due to they are produced by the hydrolysis of protein. So far, glycine, alanine, valine, leucine, and proline have been studied their gasification characteristics (Samanmulya et al., 2014). These employed amino acids showed the different gasification behavior but only the gasification rate of glycine and alanine are practically identical, and they were considered to be a standard for determining amino acid gasification. By the different stability of the bond between the carboxyl group and amino group and functional group, the other three amino acids behave variously from the standard amino acids and the different sensitivity of the produced radicals also affect to their gasification characteristics. Then, more gasification characteristics data is required to be able to predict the gasification characteristics of amino acids. Moreover, the correlation between kinetic rate and temperature are useful to hypothesize and understand the reaction mechanism of supercritical water gasification of biomass (Promdej and Matsumura, 2011). The reactions between intermediates were differentiated to be radical and ionic reactions by their compatibility to Arrhenius behavior (Yong and Matsumura, 2013). Therefore, Arrhenius rate law has attracted attention to determine supercritical water gasification characteristics of amino acids.

Glutamic acid and arginine are of interest because they are mostly found in a variety of foods including animal source and plant source. They are classified in different category which are acidic and basic, respectively, and moreover, their gasification characteristics have not much been studied yet. This study purpose is to determine the effect of two carboxyl groups, guanidine functional group, acidity and alkalinity on supercritical water gasification. Furthermore, the obtained reaction products were evaluated based on qualitative and quantitative, and the kinetics parameters were also elucidated for the reaction rate of glutamic acid and arginine gasification.

2 EXPERIMENTAL SECTION

2.1 Experimental Procedure

All gasification experiments were performed using the tubular flow reactor which was schematically illustrated in our previous study (Samanmulya et al., 2014). Briefly, a SS316 steel tube with a length of 12 m and an inner diameter of 2.17mm was used as the reactor. The reaction temperature was varied from 500 to 650 °C (residence times in a range of 86–119 s) and reaction pressure was fixed at 25 MPa. Before the addition of the feedstock, the reactor pressure was maintained at 25 MPa by feeding only deionized water and controlled by back-pressure regulator, and the reactor temperature was reached the desired temperature. Glutamic acid and arginine, obtained from Nacalai Tesque with purity >98%, aqueous solutions of 1.0 wt% were prepared by dilution in deionized water and fed into the reactor at a feedstock flow rate of 2 g/min. After passing through the reactor, the effluent was cooled down in a heat exchanger, depressurized by a back-pressure regulator, and then sampled.

2.2 Analytical Methods

The rate of gas generation was measured using a water displacement method in which we 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.

Although, gasification of nitrogen contained molecule that can produce syngas with NO_x but N-containing molecule is finally converted to N₂ via intermediate compound of NH₃ generation in supercritical water gasification system and no NO_x is occurred (Goto et al., 1998 and Yakaboylu et al., 2013).

3 RESULTS AND DISCUSSION

3.1 Glutamic Acid Gasification

Based on the previous studies, decomposition schematic of glutamic acid was proposed as shown in Figure 1. The schematic has been adapted from previous work (Samanmulya et al., 2014). 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 can be expected to be the rate determining step for the gasification. Decomposition of glutamic acid leaves propionic radical ($\text{CH}_2\text{CH}_2\text{COOH}$) which is rather unstable. It further decomposes and produces ethylene and carboxyl radical which are gasified easily.

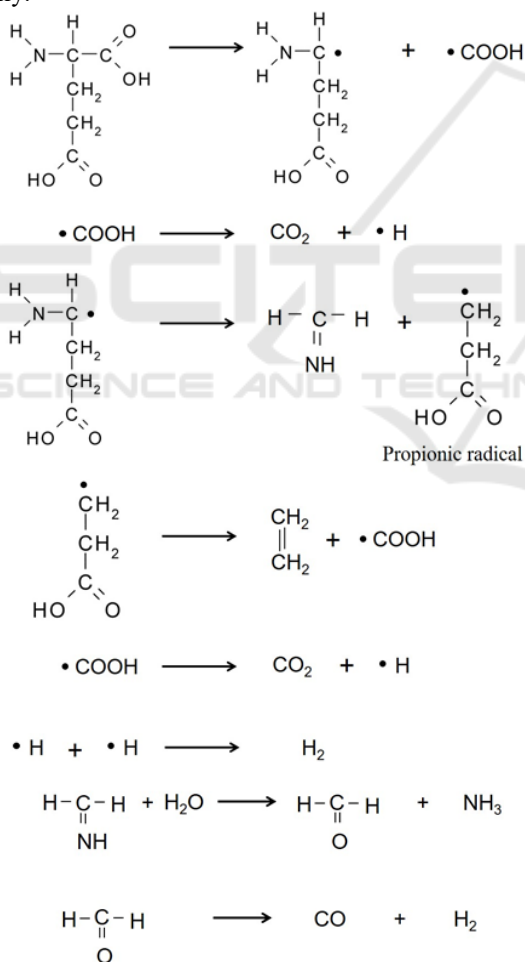


Figure 1: The proposed decomposition schematic pathway of glutamic acids under supercritical water conditions.

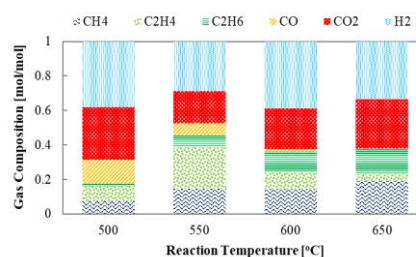


Figure 2: Effect of temperature on the product gas composition of glutamic acid gasification.

The effect of reaction temperature on product gas composition is shown in Figure 2. A fraction of ethylene is evident in gas composition, which is explained by the production of ethylene from decomposition of propionic radical ($\text{CH}_2\text{CH}_2\text{COOH}$). Ethylene is further consumed to produce other gases at later stages, which leads to a lower ethylene fraction at higher temperatures, while methane fraction is increased.

3.2 Arginine Gasification

Decomposition of amino acids leads to the production of radicals (Samanmulya et al., 2014). Figure 3 shows a schematic of the proposed decomposition pathways of arginine, the employed amino acids. This schematic has been adapted from previous work (Samanmulya et al., 2014). The same hypothesis as mentioned in glutamic acid gasification, propyl-guanidine may produce from arginine decomposition and it is a big molecule that should stay longer than small radicals. Propyl-guanidine will further decompose to produce small molecules and product gas leaving ammonia in liquid phase. Water gas shift reaction will be promoted by this alkalinity. The carbon monoxide reducing is evident in gas composition when the reaction temperature increased. Moreover, we had observed the pH of liquid products which were above 9.

The composition of generated gases from the arginine gasification as a function of reaction temperature is shown in Figure 4. Arginine gasification results in an increased methane fraction with increasing reaction temperature while carbon monoxide was decreased. This can be explained as methanation. At low reaction temperature, we also observe a carbon monoxide fraction in the product gas, possibly owing to incomplete gasification. However, this fraction reduces with increasing reaction temperature. At 650°C, the fraction of carbon monoxide was reduced while those of carbon

dioxide and hydrogen were increased, owing to the promotion of the water-gas shift reaction at high reaction temperature. Ethylene fraction is evident in product gas composition which supports the proposed arginine decomposition schematic as shown in Figure 3.

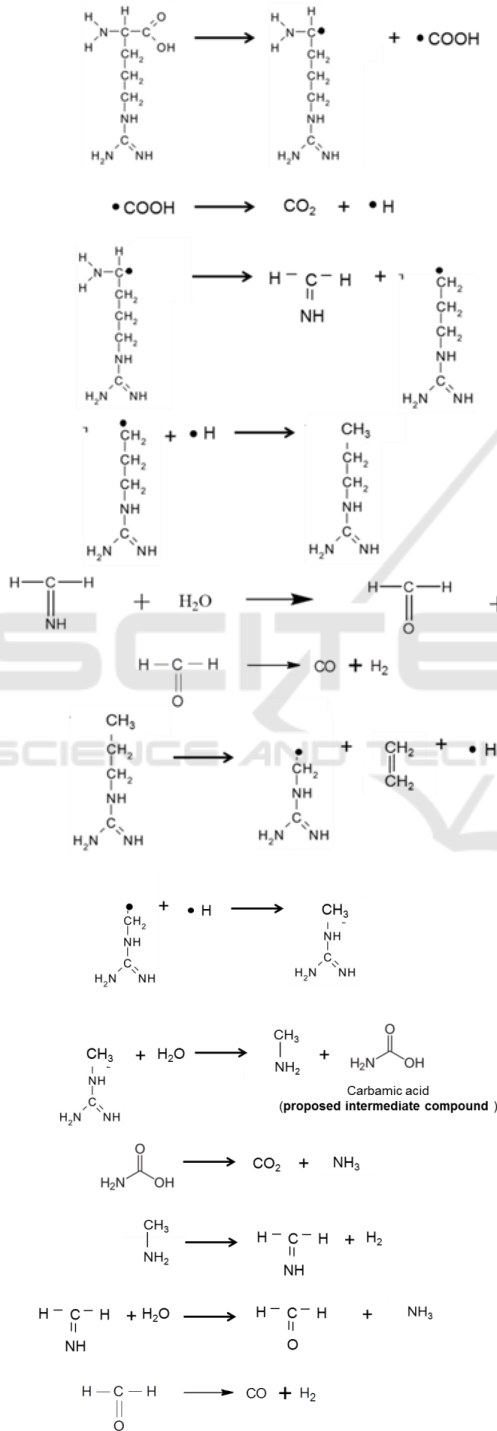


Figure 3: The proposed decomposition schematic pathway of arginine under supercritical water conditions.

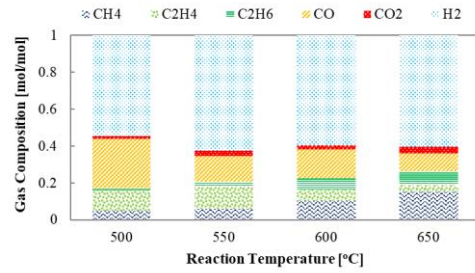


Figure 4: Effect of temperature on the product gas composition of arginine gasification.

3.3 Reaction Rate of Glutamic Acid and Arginine Gasification

Carbon gas product yield or carbon gasification efficiency (CGE) is defined as the ratio of the amount of carbon basis in the gas product to that in the feedstock solution.

$$CGE \equiv \frac{n_{Cg}}{n_{C0}} = \frac{n_{Cgas} + n_{CIC}}{n_{C0}} \quad (1)$$

where n_{C0} denote the initial amount of carbon [mol], n_{Cg} denote the amount of gasified carbon [mol], n_{Cgas} denote the total amount of carbon in gaseous product obtained from GC [mol], n_{CIC} denote the total amount of inorganic carbon in liquid product [mol], and CGE denote carbon gasification efficiency [-].

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

$$\frac{dn_{Cg}}{dt} = k_0 \left\{ \exp\left(\frac{-E_a}{RT}\right) \right\} (n_{C0} - n_{Cg}) \quad (2)$$

which leads to

$$n_{C0} - n_{Cg} = n_{C0} \exp\left[-k_0 \left\{ \exp\left(\frac{-E_a}{RT}\right) \right\} t\right] \quad (3)$$

$$CGE \equiv \frac{n_{Cg}}{n_{C0}} = 1 - \exp\left[-k_0 \left\{ \exp\left(\frac{-E_a}{RT}\right) \right\} t\right] \quad (4)$$

where 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], and t = time [s].

The experimental data of carbon gasification efficiency was fitted to Eq. (4) and the parameters were determined.

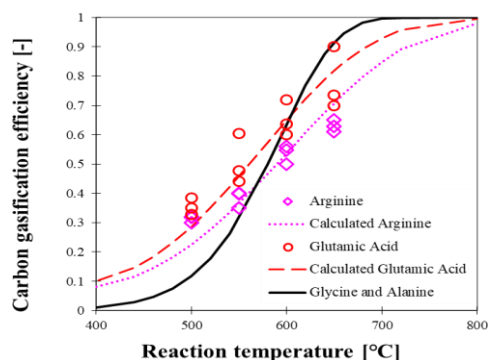


Figure 5: Gasification characteristics of the employed amino acids relative to the reported results for glycine and alanine.

Table 1: Reaction rate parameters of Supercritical Water Gasification for Glycine, Alanine, Valine, Leucine, Proline, Glutamic Acid and Arginine

Amino acids	Pre-exponential factor [s ⁻¹]	Activation Energy [kJ/mol]
Glycine and Alanine	7.37×10^5	131
Valine	6.97×10^1	70
Leucine	7.37×10^5	135
Proline	1.96×10^2	73
Glutamic Acid	4.50×10^2	77
Arginine	2.50×10^2	75

Figure 5 shows the effect of reaction temperature on carbon gasification efficiency of the employed amino acids relative to the reported results for glycine and alanine. Note that the gasification characteristics of glycine and alanine are identical and they are shown by a solid black line. The gasification efficiency increased with reaction temperature as was observed for glucose (Xu et al., 1996), which implies the Arrhenius behavior. The gasification efficiency of the employed amino acids is consistent with Arrhenius behavior indicating by the red dashed and pink dotted line in the figure.

The reaction parameters were pre-exponential factor and activation energy which are shown in Table 1 including with those of glycine, alanine, valine, leucine and proline for comparison purpose. The fitting results using these parameters are also shown in Figure 5. Gasification rate of arginine is slower than that of glycine and alanine although the activation energy is also lower. The calculated results and experimental data are in a good agreement. Experimental results and theoretical results using the Arrhenius parameters from Table 1 showed good correlation.

4 CONCLUSION

The supercritical water gasification of glutamic acid and arginine can be characterized by first order kinetics with the Arrhenius equation rate constant, and the reaction parameters were determined. The gasification rate of the two selected amino acids were lower than that of glycine and alanine, even the activation energy is lower that of glycine and alanine. Glutamic decomposition produces propionic acid radical and it further decomposes and produces ethylene and carboxyl radical which are easily to gasify. Arginine decomposition leads to produce propyl-guanidine and it will further decompose to produce small compounds and product gas, especially for ethylene that has evident in product gas composition.

ACKNOWLEDGMENT

This study was supported by Thermal Engineering Laboratory, Hiroshima University.

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