論 文 の 要 旨

題　目 SUPERCRITICAL WATER GASIFICATION CHARACTERISTICS OF AMINO ACIDS

(アミノ酸の超臨界水ガス化特性)

氏　名　Thachanan Samanmulya

Wet biomass, organic waste or sewage, contains so high moisture content that the heat of vaporization of water exceeds the heat of combustion of the biomass, the conventional dry gasification is not satisfied anymore. One of possible method is the steam reforming of biomass. The major problem in gasification by steam reforming is the formation of tars and char as the biomass does not react directly with steam at atmosphere pressure.

Supercritical water gasification (SCWG) process is as one of the promising alternatives, taking an advantage of the high moisture content by using the water as a reaction medium. The free radical condition of the supercritical water, moreover, promotes the gasification reaction. Supercritical water has some very usual properties, which are different from those of liquid or gas. Many organic compounds cannot be dissolved in normal water. But supercritical water behaves like an organic solvent. Organic materials can be dissolved in it. Supercritical water in particular has the ability to dissolve materials not normally soluble in liquid water or steam. These properties make supercritical water a very promising reaction medium for the conversion of biomass to value-added products. At supercritical conditions beyond the critical point of water (374 ^{o}C and 22.1 MPa), water is an effective solvent for organic components and gases, and also plays an important role of an H^+/OH^- ions as acid/base catalyst due to its unique solvent properties (e.g. density, dielectric constant and ion product). Thus, SCWG can convert wet biomasses into fuel gases, such as hydrogen and small hydrocarbon gases (e.g., CH_4, C_2H_4, and C_2H_6).

Although SCWG results in fewer amounts of the tarry materials than that from the dry gasification due to the enhanced organic solubility in the supercritical water conditions, these by-products (tarry material) acts as the inhibitor for the complete gasification.

The prediction of gasification rate in supercritical water is still difficult, and it is a big problem in reactor design. The investigation of reaction mechanism of biomass in SCWG process is helpful to insight into what reaction taking place during the heating up period of this process. To determine the reaction mechanism of biomass in SCWG process, the utilization of model compound is effective. Amino acids have been chosen to be a model compound of protein. Because the behavior of the proteins is important, especially for food waste and sewage from household, but have not yet to be clearly determined.

To achieve high gasification efficiency, an activated carbon catalyst is known to be effective. 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. 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. Glycine is the simplest amino acid, and can be a good model compound of proteins. The purpose of the first study is to assess the effectiveness of activated carbon for the supercritical water gasification of glycine.

Glycine gasification was performed using the tubular flow reactor which 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.). The reaction 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 gas generation rate was determined by measuring the time for effluent gas to fill a vial of known volume. The gaseous product was analyzed using gas chromatography (GC). CO_2 and CO were detected by GC with a thermal conductivity detector (GC-TCD) with He as the carrier gas. CH_4, C_2H_4, and C_2H_6 were detected using GC with a flame ionization detector (GC-FID) with He as the carrier gas. H_2 was detected by GC-TCD with N_2 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).

Glycine gasification had performed to determine the effect of feedstock concentration, the effect of residence time, and the effect of reaction temperature with a comparison of with and without activated carbon as a catalyst. 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 2.73×10^{4} s^{-1} and an activation energy of 106.9 kJ mol^{-1}. The product gas was composed of H_2, CO_2, CO, CH_4, and a small amount of C_2H_6 and C_2H_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 gasification.

As the gasification rate of glycine have already measured, the determination of gasification of other amino acids and comparison of their gasification rates would be interesting. Alanine was chosen to be the next target because they are 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. Then, the purpose of the second study is to compare the gasification rate of glycine and alanine, which are different by hydrogen and methyl as a functional group. The effect of the methyl group would be elucidated. The effect of feedstock concentration and the effect of reaction temperature were also determined.

Alanine gasification was conducted in the same apparatus as previous of glycine gasification. The same range of reaction temperature had been used, 500 to 650 ^{o}C, but the concentration of alanine were 1.0, 2.0, and 3.0 wt%. The gasification efficiency of alanine is not affected by the feedstock concentration employed here, which is likely to first order behavior. But glycine, the gasification efficiency decreased with increasing concentration. This is expected of tarry material production occur 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 from our previous research team's work. 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 as we had reported in the first work. In 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. However, amino groups can produce ammonia or amine molecules, which were observed as ammonium ion in our liquid samples, the alkalinity of the liquid should also increase while increased 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.

Increasing reaction temperature, gasification efficiency of alanine trends to increase sharply as was observed by our previous of glycine and agrees with the results of glucose that was conducted by Xu et al (1996). As the experimental data of the carbon gasification efficiency, the gasification rates of glycine and alanine are identical. Then, the pre-exponential factor and an activation energy of glycine had been corrected to 7.37×10^5 s^{-1} and 131 kJ mol^{-1} respectively as same as alanine. 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. Gas composition of glycine and alanine have been compared. The methane gas would have been produced from the methyl group of alanine that is shown in a higher fraction. Another clear difference between glycine and alanine is that water gas shift reaction proceeds to a greater extent for glycine.

As the gasification of glycine and alanine are identical. It is interesting that if other amino acids are also gasified with the same, we will be able to safely apply this gasification rate to other amino acids and likely proteins as well. Thus, valine and leucine are chosen to be candidate of amino acids which are in the same aliphatic classification with glycine and alanine. The difference by functional groups of valine and leucine, which are propyl and butyl, would give some insight effect on gasification characteristics. However, structure of compounds may effect on gasification. Then, proline was also chosen to show the gasification of amino acids which is cyclic structure. So, valine, leucine and proline gasification characteristics are the third target.

All above mention amino acids was performed in the same apparatus and the same supercritical water gasification conditions as previous work. Surprisingly, and to our disappointment, the gasification rate of valine is much lower than that of glycine and alanine. Valine was decomposed and produced isopropyl radicals in supercritical water conditions. This radical are much different than glycine and alanine which are hydrogen and methyl that can react rapidly with others radicals or molecules. Isopropyl radicals are quite stable which are called the secondary radicals. In additional, the reaction of isopropyl radicals with each other generates 2,3-dimethylbutane, which is a liquid-phase product. The formation of this bulky molecule could lead to the production of polymers because radicals of higher carbon numbers are more stable than smaller radicals and are relatively easily produced. This may the reason why the gasification of valine is low. Its reaction rate constant was well expressed by the Arrhenius equation with a pre-exponential factor of 6.97×10^{1} s^{-1} and an activation energy of 70 kJ mol^{-1}.

Leucine contains isobutyl as a functional group and releases it in supercritical water conditions. Isobutyl radicals from leucine decomposition are primary radicals that it can react with water to produce isopropyl alcohol and methyl radical can be removed from it to react and generate methane. As isobutyl radicals were defined to be primary radicals as hydrogen of glycine and methyl of alanine, accordingly, their gasification rates are similar but an activation energy of leucine is a bit higher which is 135 kJ mol^{-1}.

Gasification rate of proline is higher than valine and determined a pre-exponential factor of 1.96×10^{2} s^{-1} and an activation energy of 73 kJ mol^{-1}. The radical produced from proline is primary and will decompose easily. This explains why its gasification rate is almost equal to those of glycine and alanine. However, gasification of proline is less sensitive to reaction temperature than that of glycine, alanine, and leucine. This may be due to stabilization of the transition state of the carboxyl radical–producing reaction by the ring structure.

Finally, we had made a purposed reaction network of the 5 amino acids that can be well clarified those of decomposition and radicals production. These reaction network may explain why the gasification rate is same for glycine, alanine, and leucine ,and different for valine and proline. The reaction rate constant of each 5 amino acids was well expressed by the Arrhenius equation with a sufficiently low concentration of 1 wt%.