論文の要旨

題目 REACTION KINETICS OF GLUCOSE DECOMPOSITION IN SUPERCritical WATER GASIFICATION
（超臨界水ガス化におけるグルコース分解の反応速度）

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Supercritical water gasification (SCWG) is a promising technology for gasifying the biomass with high moisture content or organic waste into combustible gas such as $\text{H}_2$ and $\text{CH}_4$ from the view points of environmental and economic. At hydrothermal conditions beyond the critical point of pure water (374 ºC and 22.1 MPa), water is an effective solvent for organic components and gases, and also plays an important role of an $\text{H}^+/\text{OH}^-$ ions as acid/base catalyst due to its unique solvent properties (e.g. density, dielectric constant and ion product). As the environmental and potential reaction medium of water, biomass is easily decomposed in SCWG process but concurrently polymerizations of the biomass can occur. Polymerization reactions that produce char and tar materials can cause serious problems in the SCWG process because they not only reduce the gasification efficiency, but also can plug the reactor. Conditions for polymerization and char formation become more favorable in the heating up section at lower temperatures in the SCWG process, which makes it difficult to completely gasify biomass material. Therefore, 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 elucidate the reaction mechanism of biomass in SCWG process, the utilization of model compound is effective. The model compound in most biomass is glucose obtained from the rapid hydrolysis of cellulose, which is one of the major components of lignocellulosic biomass. Thus, glucose can be used to potentially reproduce the reaction characteristics of SCWG. A lot of side products are found during the hydrothermal gasification. Glucose decomposition is not a typical pyrolysis to produce gaseous products. Numerous linear (as glyceraldehyde, dihydroxyacetone and pyrvaldehyde) and ring compounds (as 5-hydroxymethylfurfuraldehyde (5-HMF) and furfural) are produced. To insight into the behavior of hydrothermal glucose decomposition, the proposed reaction
network of glucose could be used to explain the reaction kinetics of glucose in SCWG process. Conceptually, glucose undergoes isomerization to fructose, dehydration to 5-HMF and furfural and also decomposition to other water-soluble products (TOC). Fructose also further produces 5-HMF, furfural and TOC. These three intermediate compounds subsequently polymerize to form char product, meanwhile, only TOC concurrently gasify to gaseous product.

Reactions taking place in SCWG generally include both ionic and radical reactions. The ionic reactions should proceed more in the subcritical region where the dielectric constant and the ion product are high. In contrast, the radical reactions should be favored in steam and less dense supercritical water. Both reactions proceed competitively around the critical point of water. Based on the proposed reaction network of glucose decomposition in SCWG process, it could have both radical and ionic reactions and that might be controlling the reaction pathway. No one has thoroughly investigated the experiment of model biomass in SCWG process to classify which are ionic or radical reactions. Thus, the purpose of this research is to investigate the reaction mechanism underlying the reaction kinetics of glucose decomposition. The behavior of each reaction rate on the process variable parameter (temperature, pressure and catalyst) is investigated and the type of reactions can be further classified.

Glucose solution (1.5 wt%) was carried out in a tubular reactor at subcritical (300-350 °C) and supercritical water (400-460 °C) conditions at pressure of 20-25 MPa. The addition of catalysts (HCl and NaOH) was also investigated which represented the addition of $\text{H}^+$ and $\text{OH}^-$ in supercritical water gasification. The concentrations of catalyst ranged from 0.01 to 0.05 mol/dm$^3$ (at room temperature). The speedy heating of the glucose solution to the reaction temperature was achieved by mixing with the preheated water before the reactor entry. The product effluent obtained was also suddenly cooled down by mixing with the cold water. This feature allowed the precise formulation of the reaction kinetics. Product yields of glucose, fructose, char, gas, furfural, 5-HMF, glyceraldehyde, dihydroxyacetone, pyruvaldehyde and TOC were examined.

Glucose decomposition is rapid, and it accelerated with temperature rise from sub- to supercritical water temperature. Glucose is almost completely decomposed in 60 s even at the lowest
subcritical temperature of 300 °C and in only 0.5 s at the supercritical temperature of 460 °C. Fructose was both rapidly formed and rapidly decomposed, its rate increasing with temperature. Other intermediate compounds; 5-HMF, furfural and TOC; increased and stay constant in the subcritical region, but hose in the supercritical region further slowly decreased. Gas product continuously increased with temperature up to the supercritical temperature. No char product was observed in beyond supercritical water temperature owing to the low dielectric constant under supercritical temperatures inhibited char production, which is ionic reaction essential to form the aromatic compounds.

As the experimental results, proposed reaction network of the glucose decomposition was developed for the hydrothermal gasification, by assuming the first-order reaction. The result showed the rates of glucose decomposition had two different behaviors; Arrhenius and non-Arrhenius, at supercritical water condition. It implied that the glucose decomposition consisted of radical and ionic reactions: the former showing the Arrhenius behavior, and the latter showing the non-Arrhenius behavior. The gasification rate following Arrhenius behavior, which is radical reaction, is promoted by high temperature condition. As the results of behaviors of individual rate constants with temperature, the classification of reactions which ionic or radical reactions was successful. The reactions of TOC formation from glucose, 5-HMF and furfural are radical reactions, meanwhile the isomerization of glucose, the dehydrations of glucose and fructose and the char formation from 5-HMF, furfural and TOC are ionic reactions.

Change of pressure of in each reaction temperature slightly affected the change of product distribution of glucose decomposition in supercritical water gasification. The rate constants of ionic reactions influenced with pressure changing at supercritical water region only. It is due to the fact that the change of ion product of water at supercritical water temperature is dominant. As the results of rate constants on pressure effect, they support the criterion of classification of type of reaction on the Arrhenius plot.

The addition of HCl catalyst representing the presence of H⁺ on glucose decomposition in SCWG was clearly catalyzed both gasification and polymerization; meanwhile, glucose isomerization
was not observed. At subcritical water temperature, increases in HCl concentration enhanced both gasification and polymerization. At supercritical water temperature, these increases slightly suppressed the gasification but promoted the formations of furfural and 5-HMF. The addition of NaOH representing the presence of OH\(^-\) was not influenced the polymerization at supercritical water temperature. On the basis of the proposed reaction network and parameter fitting for the experimental results, it can be concluded that polymerization is enhanced to a greater extent in terms of the reaction rate coefficient. Glucose decomposition, glucose dehydration, 5-HMF and furfural dehydration, and gasification were all enhanced by the addition of H\(^+\). The rate constants for the ionic reaction increased in the presence of an acid catalyst whereas that for the radical reaction did not.

Finally, the reactions in the reaction network of glucose decomposition in supercritical water gasification can be well classified into ionic and radical reactions by changing the operating parameters: temperature, pressure and catalysts based on the proposed reaction network.