論 文 の 要 旨

題　目 STUDY ON THE LIGNIN DECOMPOSITION IN SUBCRITICAL AND SUPERCRITICAL WATER: DETAILED REACTION PATHWAYS, MECHANISM, AND KINETICS
（亜臨界水と超臨界水におけるリグニンの分解：反応経路、メカニズム、反応特性の解明）

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Hydrothermal gasification of biomass is a promising technology for high moisture content compounds. The different nature of biomass compounds especially the three main constituents (cellulose, hemicellulose, and lignin) can significantly affect its decomposition behavior in sub- and supercritical water especially towards gasification pathways. In addition, although supercritical water gasification (SCWG) of wood biomass is proved to be feasible, there is also high char formation for certain types of wood biomass. It is subsequently observed that there is correlation between the high char formation with high lignin content in these biomasses. Therefore, this studies shows the probability that lignin might be the inhibitor of the gaseous formation pathway. This is a major complication for biomass conversion under hydrothermal conditions, as char formation is undesirable and the gaseous formation pathway is favored. Understanding the lignin chemistry and its mechanism in sub- and supercritical water is a challenge since its structure is extremely complex due to its long polymer chains with abundance aromatic rings in addition to hydroxyl and methoxyl substituent. In addition, although it is established that there is a rapid depolymerization of lignin and simultaneously higher char yield obtained under supercritical conditions, the mechanism are not established conclusively. It is important to conduct preliminary study using monomeric model compounds of lignin such as benzene, phenol, and guaiacol to elucidate the primary pathways of gaseous formation in comparison to char from phenolic and aromatic groups in lignin constituent. These compounds are the simplest model compounds for lignin with important structural features similar to lignin. Therefore, by establishing the primary pathways of these compounds decomposition under hydrothermal conditions, it could be used to establish the overall reaction network for lignin itself. This could be achieved by varying the reaction temperature from subcritical to supercritical conditions.

The effect of wood addition on SCWG of poultry manure is investigated for broiler-derived wastes consisting of manure and the bedding material such as wood sawdust. The effect of wood addition on SCWG of poultry manure was investigated for broiler-derived wastes consisting of manure and the bedding material such as wood sawdust. SCWG of poultry manure (0.5 wt%) with Eucalyptus wood (0–0.3 wt%) was conducted in a continuous-flow reactor for temperature range of 550–650 °C and pressure of 25 MPa. For SCWG of poultry manure, wood additions affect the gasification efficiency. During the reaction, not only decomposition of both but also reactions between these decomposition products occurred. The addition of Eucalyptus wood to the poultry manure changed its decomposition behavior. Cellulose and hemicellulose in the Eucalyptus wood were easily decomposed in SCW compared to poultry manure. However, at higher loading of wood in the feedstock mixture, the existence of inhibiting compounds from lignin decomposition decelerated the gaseous formation pathway. Although activated carbon improved the reaction efficiency and showed its potential as a

reaction catalyst, the CGE remained considerably low. Therefore, this study shows the significance effect of lignin compounds towards the SCWG of wood biomass and indicate the importance of understanding its mechanism and decomposition behavior. However, due to the complexity of its chemical structure, there has been no attempt made to elucidate a detailed mechanism.

Decomposition of phenol and benzene was studied in SCW at 370–450 °C and 25 MPa with short residence times (0.5–100 s). Under these conditions, we conclude that decomposition of phenol and benzene is considerably slow although char and gaseous formation are observed in addition to other intermediate compounds such as catechol and naphthalene. Char formation pathways are competing with gas production especially with enhanced temperature and residence time. Phenol decompositions are faster than benzene due to resonance-stabilized phenoxy radicals, which are believed to play key role in enhancing its reactions in SCW. In addition, formation of phenol from benzene obeys Arrhenius behavior. On the other hand, benzene formation from phenol decreases with temperature in SCW (non Arrhenius behavior). This implies that the reaction is largely influenced by dielectric constant and ionic product that are reduced tremendously as the temperature increases. Other pathways are mainly free radical reactions. The activation energy of benzene decomposition (91.16 kJ/mol) in SCW is much higher than phenol (53.06 kJ/mol). The reaction rate parameters elucidated for each reaction pathway as deduced in the overall reaction network for phenol and benzene decomposition in SCW shows good agreement with one another. This study shows the importance of substituent group (hydroxyl group) in the benzene ring structure to enhance the decomposition rate that ultimately lead to higher char formations. It is key information and could explain the high char formation often associated with lignin decomposition under hydrothermal conditions due to its diverse and complex structure with various substitution groups in the benzene ring.

Guaiacol decomposition was subsequently studied under hydrothermal conditions of 300–450 °C and residence time of 0.5–40 s. It is observed that even at short residence times, guaiacol are converted into various organic liquid and gaseous compounds, in addition to its repolymerization to form a solid. This is an important indication of the rapid char formation resulting from the degradation of the aromatic ring substituents, and in particular, the methoxyl groups. Although there is evidence of ring opening mechanism, the minimal yield of acids (acetic acid and formic acid) indicates that the aromatic rings are generally preserved and unaffected by the hydrothermal reactions, in contrast to their substituent groups. Furthermore, we also discovered that there was rapid conversion of these intermediate phenolic compounds in the reactions. The importance of temperature on the guaiacol conversion is another integral part of the study and showed similar results to those obtained using phenol and benzene. It is interesting to note that although the overall guaiacol conversion follows Arrhenius behavior, some individual pathways do not. The decreasing rate of benzene formation and its subsequent decomposition with temperature is an interesting observation and indicates that it is likely occurs through ionic reactions, in contrast to phenolic formations, which are mainly derived through radical reactions.

The lignin decomposition was studied in sub- and supercritical water (300–450 °C) and residence times of 0.5–10 s. Lignin was depolymerized into various liquid and gaseous compounds, in addition to undergoing repolymerization to form char at very short residence times, which indicated its high reactivity under hydrothermal conditions. In addition, temperature played an integral role in deciding the dominant pathway because of the existence of ionic and radical based pathways.

Although the overall lignin decomposition in sub- and supercritical water followed Arrhenius behavior, some of the individual pathways diverged from the Arrhenius behavior. Unlike hydrothermal decomposition of other biomass compounds (cellulose and glucose) in which solid yields are drastically suppressed, char formation arising from decomposition of lignin was enhanced under supercritical conditions. This could be attributed to the diminishing in the number of aliphatic groups that ultimately resulted in the formation of a highly aromatic char. In addition, the reaction rate parameters elucidated for each reaction pathway as deduced in the overall reaction network for softwood lignin, guaiacol, phenol, and benzene decomposition in sub- and supercritical shows good agreement with one another.