

# Studies on Kinetic Analysis and Modeling of Biochar Gasification

ザイダ ファイザ ザハラ

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氏 名 : Zayda Faizah Zahara

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(バイオチャーのガス化の反応速度解析とモデリングに関する研究)

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### Thesis summary

Biomass, most importantly, lignocellulosic biomass, is expected to play important roles as an energy resource and also a major chemical feedstock in the future. In fact, biomass (including wastes) is already a significant global energy source, accounting for over 70% of all renewable energy production, and making a contribution to the world final energy consumption in 2015 that was roughly equivalent to that of coal. Moreover, promoting the utilization of biomass is advantageous in reducing the emission of carbon dioxide. Some technologies have been developed to transforming biomass chemical energy into power and heat through thermochemical conversion processes. It is believed that a most efficient one is gasification with respect to energy efficiency, process flexibility and industrial applicability.

A key factor to improve the efficiency of the gasification is reaction kinetics since it is essential for designing the gasifier. Among the thermochemical reactions involved in the gasification, that of biochar (charcoal from the pyrolysis of biomass) is the rate-determining step. The biochar (as well as the parent biomass) fortunately and inherently contains more or less amount of metallic species such as K, Na, Ca and Fe, which can play catalytic roles in the biochar gasification. Taking the most advantage of this nature leads to more rapid and energy-efficient conversion of the biochar. However, quantitative understanding of the kinetics as well as mechanism of the catalytic gasification has not been reached. Motivated by this fact, this thesis makes a particular focus on the kinetics and mechanism of biochar gasification under the catalysis of inherent metallic species, aiming at quantitative description of the kinetics over the entire range of the biochar conversion into gas with oxidizing agents, i.e., CO<sub>2</sub> and steam. This thesis also discuss hydrothermal pretreatment of biomass, which is expected to upgrade it as a solid fuel with a strong focal point of fates and behaviors of the inherent metallic species.

Chapter 1 of this thesis comprehensively reviews the potential of biomass as an energy resource and chemical feedstock as well as the thermochemical technologies for the biomass conversion. A particular focus is made on gasification of char with a consideration of mechanism, kinetics, and process. It is believed that, in the presence of catalytic species, the structural-based or the oversimplified kinetic model is not plausible to describe the char conversion. Hence, the kinetic model should consider the non-catalytic gasification and catalytic gasification in parallel.

Chapter 2 discussed the results of the gasification of eighteen chars from the pyrolysis of six trios of sugarcane bagasses (SCBs; original, water-washed, and acid-washed) with CO<sub>2</sub> at 900°C. This study aimed at the quantitative description of the rate of gasification catalyzed by inherent metallic species and correlation of the catalytic activity and its change during the gasification with the metallic species composition. The measured kinetics was described quantitatively over a range of char conversion, 0–0.999, by a model that assumed progress in parallel of the catalytic gasification and non-catalytic one, together with the presence of a catalytic precursor and 3–4 types of catalysts having different activities and deactivation characteristics. A series of regression analyses was scrutinized and reached expression of initial catalytic activity as a linear function of Na, K, Ca, Fe and Si concentrations in the char with a correlation factor ( $r^2$ ) > 0.98. The catalyst precursor was contributed fully by the water-soluble Na, K and Ca. Si was responsible for the catalyst deactivation during the pyrolysis, but not during the gasification. The chars produced from original SCBs followed a linear relationship between the initial catalytic deactivation rate and initial activity ( $r^2$  > 0.99),

while such a linear relationship was not valid for those formed from the water-washed SCBs. This was explained mainly by more rapid deactivation of Fe catalyst in the chars from water-washed SCBs than that in the chars formed from the original SCBs. Na and K in char from the original SCBs, originating from the water-soluble ones SCBs, chemically interacted with Fe catalyst slowing down its deactivation.

Chapter 3 discussed the results of the steam gasification of chars from the pyrolysis of sugarcane bagasses (SCBs) prepared in the different types of preparation as described in Chapter 2. The gasification process was carried out in the thermogravimetric analyzer (TGA) at 850°C, while the concentration of gasifying agent is 20 vol.% steam/N<sub>2</sub>. The parallel kinetic model was able to describe the measured profiles of the catalytic gasification with the assumption of one to two types of catalysts. The results from this chapter were compared to the study of gasification of the similar char in CO<sub>2</sub> which has been scrutinized in Chapter 2. The results from steam gasification showed rapid transformation and progression of catalyst precursor to catalyst during gasification thereby causing the unnecessary of the assumption of catalyst precursor in the kinetic model. This quick transformation was supposedly due to the formation of very mobile catalytic species in the char due to the interaction with steam and this catalyst mobility was lesser in CO<sub>2</sub> gasification. There was no evidence of the effect of SiO<sub>2</sub> on the catalyst deactivation during gasification. Therefore, the catalytic species experienced self-deactivation and volatilized during gasification. Chapter 3 further suggested that Na, K, and Ca was actively involved in the char conversion and the interaction between Na/K and Fe were suppressed. Thus, Fe played as a single catalyst and deactivated faster during the steam gasification.

Chapter 4 described the results of the investigation of heat treatment in hot-compressed water (hydrothermal treatment) at 250 °C. The process was able to upgrade the woody biomass to solid with particular features by converting a major portion of carbohydrate (cellulose and hemicellulose) into the water-soluble matter and solvent-soluble lignin-like material, removing more than 90% of the alkali and alkaline earth metallic (AAEM) species. The upgraded biomass is available in the production of metallurgical coke that has mechanical strength higher by more than six times than that of conventional one from coals, and activated carbon with specific surface area well above 2,000 m<sup>2</sup> g<sup>-1</sup> without any additives/chemicals. Repeated use of product water maximizes the yield of upgraded biomass, maintaining its ability of leaching of AAEM species. It is well described here that with the absence of AAEM species, the char conversion rate in steam decreased significantly compared to the reactivity of the char from non-treated biomass. Further leaching by HCl resulted in a near-identical trend with that of char from upgraded biomass, indicating that although not fully eliminated the AAEM species, the HT eradicated the catalytic AAEM species. It is noted from this chapter that specific surface area might not be the important factor in the biomass char reactivity, but the catalysis of AAEM species was the compelling circumstances in gasification.

Chapter 5 summarized the findings described in the preceding chapters.