

## Study on Mechanism and Kinetics of Key Reactions in Gasification of Lignite

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(褐炭ガス化において鍵となる反応機構および速度論に関する研究)

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## 論 文 内 容 の 要 旨

### Thesis Summary

Low temperature gasification is an important option for future industries due to its flexibility in terms of feedstock and end-use application. It integrates chemical energy from various organic resources with thermal energy into a simple form of product, i.e. syngas, while current gasification technology involves inevitable chemical energy loss due to high operating temperature and large degree of exothermic oxidation. Lignite gasification with  $\text{CO}_2$  is proposed as a promising option applicable to the advanced technology due to the features of lignite that has high reactivity arisen from abundant metallic species and activity toward tar vapor caused by large surface area when converted to char. Such features are directly associated with key chemical reactions in low temperature gasification, which are deactivation of catalytic activity induced by inherent minerals and elimination of tar over char surface. As extensive application of the characteristics is encouraged, comprehensive understanding of the phenomena is indispensable to cope with the technical issues. Qualitative understanding of catalytic behavior and tar decomposition in the presence of char has been accumulated, while quantitative examination, particularly precise kinetic analysis, has been insufficient. Therefore, this study aims at investigation of kinetics of the above-described key reactions.

Chapter 1 overviews key reactions in lignite gasification and purpose of this study.

Chapter 2 describes mechanism of deactivation of catalytic effect of inherent metallic species in  $\text{CO}_2$  gasification of coke from lignite. Inherent metallic species such as Na, Ca and Fe are highly dispersed in the organic matrix of coal in forms of organically bound cations or pore-condensed inorganic salts. In the course of pyrolysis, such metallic species transform into nano-sized or greater particles (metals, oxides or carbonates) that can catalyze the gasification forming redox cycles. Lignite also contains inherent  $\text{SiO}_2$ , which can react with the metallic species to form silicates, resulting in catalyst deactivation over the range of pyrolysis, carbonization and gasification, and thereby reducing the char/coke reactivity.

The inherent catalyst deactivation was experimentally simulated by blending a Victorian lignite with  $\text{SiO}_2$ , briquetting the  $\text{SiO}_2$ /lignite blend, carbonizing the briquette, and then gasifying the coke with  $\text{CO}_2$ . The kinetic analysis of the gasification employed a comprehensive model, which assumed progress in parallel of non-catalytic and catalytic gasification. The model quantitatively described the measured kinetics of the coke gasification with different  $\text{SiO}_2$  contents over a range of coke conversion up to 99.9%. The kinetic analysis revealed that the  $\text{SiO}_2$  deactivated substantial and entire portions of the most active catalyst and its precursor, respectively, before the gasification (i.e., during the carbonization). The catalyst deactivation also occurred during the gasification, but mainly following a self-deactivation mechanism that involved no silicates formation.

Chapter 3 proposes a continuous measurement method for decomposition of aromatic vapors on char surface. Elimination of tar (i.e., aromatic compounds) has been an important technical issue of gasification of coal and biomass operated at temperature lower than  $1000^\circ\text{C}$ . It is recognized that use of char is a most effective way to eliminate the tar. Kinetics of thermal decomposition of benzene on lignite-derived char was investigated at  $900^\circ\text{C}$ .

Benzene vapor was continuously forced to pass through a micro fixed bed of char with residence time as short as 7.6 ms, and then detected continuously by a flame-ionization detector. Results showed the presence of two different types of char surfaces; consumptive Type I surface and non-consumptive (sustainable) Type II surface. Type I surface of a partially CO<sub>2</sub>-gasified char had an capacity of carbon deposit from benzene over 20 wt%-char and an high initial activity. Both of them decreased with increasing carbon deposit due to consumption of micropores accessible to benzene, and finally became zero leaving Type II surface that had a low but very stable activity. The chars without gasification had capacities of Type I surfaces smaller by two orders of magnitude than the partially gasified char, while the Type II surfaces had activities similar to that of the partially gasified char. It was found that Type II surface converted benzene into not only carbon deposit but also diaromatics and even greater aromatics. Composition of the greater aromatics was unknown because they were deposited onto the reactor wall immediately after passing through the char bed.

Chapter 4 re-evaluates diffusional effects on catalytic and non-catalytic gasification of lignite char with CO<sub>2</sub> in a thermogravimetric analyzer. Successful gas diffusion to internal/external char surface is a presumption for determination of the precise reaction rate. Experimental conditions such as flow rate, particle size and initial amount of sample are thus carefully chosen to avoid or minimize inhomogeneous contact between gas and solid. Insufficient flow rate and inappropriate particle size would lead to misinterpretation of kinetics due to char gasification controlled not kinetically but by mass transport.

Effects of total gas flow rate, particle size and initial char weight (in other words, thickness of char bed) on the rate of gasification were investigated at atmospheric and isothermal conditions by employing a TGA. Chars derived from lignite and that from demineralization were gasified with CO<sub>2</sub> at 900 °C. In non-catalytic gasification, it was found that the total gas flow rate of 700 ml/min and the particle size of 125 μm were the minimal condition for minimizing the resistance arisen from gas film. The rate of non-catalytic gasification was highly affected by the diffusional limits within the bed/pores as well as inhibition induced by CO. On the other hand, catalytic gasification showed no dependency on flow rate when the char bed was sufficiently thin. Only small differences were observed by changing initial char weight due to decreases in CO<sub>2</sub> partial pressure within the bed. It was believed that the rate of catalytic gasification was affected by no or negligible CO inhibition.

Chapter 5 summarizes the findings described in the preceding chapters.