

Studies on Low-temperature Gasification of Biomass and Lignite with Minimized Tar Emission and Loss of Chemical Energy

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論文題名：Studies on Low-temperature Gasification of Biomass and Lignite with Minimized Tar Emission and Loss of Chemical Energy (タール発生と化学エネルギー損失を最小化したバイオマスおよび褐炭の低温ガス化に関する研究)

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論文内容の要旨

Gasification is a most effective thermochemical or catalytic process to convert solid carbonaceous fuels into syngas, which consists mainly of H_2 and CO and plays roles of platform material common between energy and chemical sectors. The gasification should therefore be performed with minimized loss of chemical energy (LCE) of the original fuel, in other words, with minimized and maximized consumptions of oxygen and steam, respectively, which necessitate solid-to-gas conversion of the fuel at lower temperatures.

In Chapter 1 of this thesis are comprehensively reviewed existing studies on the gasification of low-rank solid fuels such as biomass and lignite to be operated at temperature well below $1000\text{ }^{\circ}C$, drawing novel concepts such as control of key reactions of intermediates, rearrangement of homogeneous/heterogeneous reactions in series/ parallel, and chemical recuperation of thermal energy. These concepts lead to proposal of two different types of gasification. One is fluidized-bed steam gasification of not a parent fuel but its char from mild pyrolysis, and it is termed Type-III gasification. A tar-free nature of the char enables to avoid emission of problematic tar. Type-III gasification can accept high-temperature heat from power devices such as solid-oxide fuel cells and drive the gasification without oxygen, recuperating the heat to chemical energy of syngas (causing net gain of chemical energy). Employment of Type-III gasification in a type of integrated gasification/fuel-cell combined cycles (IGFC) can theoretically realize electrical efficiency of power generation even over 80%. The other is steam-oxygen gasification in which the pyrolysis of solid fuel and catalytic gasification/reforming of the pyrolysates (*i.e.*, char, tar and gaseous hydrocarbons) are isolated from each other. This type of gasification is termed Type-IV gasification. Complete conversion of the pyrolysates at temperature as low as $700\text{ }^{\circ}C$ and chemical recuperation of syngas by the endothermic pyrolysis can realize LCE of 3–4%, which is smaller than that for current high-temperature gasification by a factor of 5 or more. The main objective of the author's studies was to experimentally prove the concepts of Type-III gasification and Type-IV one.

In Chapters 2, 3 and 4 are described results of the studies on Type-III gasification. Chapter 2 reports the results on the pyrolysis to produce tar-free chars from biomass (cedar, mallee and pine) and lignite (Loy Yang). These fuels were pyrolyzed at $450\text{--}750\text{ }^{\circ}C$. Resulting chars were further subjected to Curie-point pyrolysis (CPP) at $920\text{ }^{\circ}C$ in which the volatile products were analyzed by gas chromatography/mass spectrometry (GC/MS). The CPP-GC/MS successfully identified mono-aromatic hydrocarbons and tar (di- to hepta-aromatic hydrocarbons and oxygen-containing aromatics), and quantified them even with yields as

low as 10^{-4} to 10^{-8} wt%. It was clarified that production of char with residual tar content of ≤ 0.01 wt% requires the pyrolysis temperatures of ≥ 550 °C and ≥ 600 °C for the biomass and lignite, respectively. Such minimum temperatures were first demonstrated by this study.

The pyrolysis of biomass was further considered with a purpose to accurately estimate quantity of heat required for the pyrolysis, the result of which is reported in Chapter 3. The estimation requires that of the overall enthalpy of vaporous tar that contains high-molecular-mass and unidentifiable compounds. The author first developed equations that estimate the enthalpy of vaporous tar as a function of temperature only from its overall elemental composition, *i.e.*, C, H and O contents, within errors smaller than 0.2 MJ/kg-biomass. Those equations enabled to estimate the overall quantity of heat for driving the pyrolysis of different types of biomass, which was in a range of 1.1–1.6 MJ/kg at 500–550 °C.

Chapter 4 describes the results of the experimental examination of the Type-III gasification of tar-free char from Ca-loaded lignite. Thorough kinetic analysis of steam gasification of the char revealed the optimum loading of Ca (1.0 wt%-lignite) and the mechanism of gasification that was valid over the entire range of char conversion. A newly developed kinetic model, which considers simultaneous progress of non-catalytic gasification and Ca-catalyzed gasification of two different modes together with catalyst deactivation, successfully predicted characteristics of continuous steam gasification of the char in a fluidized bed at 800 °C, the result of which demonstrated that the Ca catalyst enables steady-state operation of the gasification, *i.e.*, 100% carbon conversion of the char in continuous operation, even under atmospheric pressure.

In Chapter 5 are mentioned results of experimental simulation of Type-IV gasification of Biomass loaded with K_2CO_3 . The biomass was converted in a continuous reactor that consisted of an auger pyrolyzer and a fixed-bed reformer/gasifier in series. It was demonstrated that the biomass (K-loading; 1.5 wt%) was converted to syngas with dynamic carbon conversion of $\approx 100\%$ and tar emission well below 100 mg/Nm³-dry-gas under the following conditions; O_2/C molar ratio ≈ 0.2 , H_2O/C molar ratio ≈ 0.5 , gasification/reforming temperature ≈ 700 °C and pyrolysis temperature ≈ 550 °C. This set of the conditions satisfied those required for achieving CEL of 3–4%. The concept of Type-IV gasification has thus been proven by this study.

Applicability of Type-IV gasification was also examined for lignite. The results are described in Chapter 6. The continuous gasification of K_2CO_3 loaded lignite was performed in the way very similar to that mentioned in Chapter 5. It was demonstrated that the lignite(K-loading; 3.05 wt%) was converted to syngas with dynamic carbon conversion of $\approx 100\%$ and tar emission well below 30 mg/Nm³-dry-gas under the following conditions; O_2/C molar ratio ≈ 0.21 , H_2O/C molar ratio ≈ 0.60 , gasification/reforming temperature ≈ 750 °C and pyrolysis temperature ≈ 550 °C. This set of the conditions satisfied those required for achieving CEL of 3–4%. The concept of Type-IV gasification has thus been proven by this study.

Chapter 7 draws the general conclusions of this work. The most important conclusion is that this work has proved the concepts of both Type-III gasification and Type-IV one of biomass and lignite.