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Studies on Pyrolytic and Hydrothermal Conversion of Biomass and Lignite

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(熱分解および水熱分解によるバイオマスおよび褐炭の転換に関する研究)

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論文内容の要旨

Thesis Summary

Biomass is the only renewable source on energy and organic carbon that has the potential to reduce our overreliance of fossil fuels and mitigate environmental issues. Effective utilization of biomass in the current energy system, which is essential to the establishment of a circular, bio-based economy, necessitates the development of new technologies to overcome the limitations of the structural recalcitrance, low bulk density and high moisture content of biomass. With this perspective, this thesis has been devoted to the combined pyrolytic and hydrothermal conversion of biomass, the implementation of which is expected to achieve a simple and selective production of light oil, clean biochar or/and fuel gas, with sufficiently high recoveries and relatively moderate reaction conditions.

First, the robust structure of biomass, composed of different chemical components (cellulose, hemicellulose and lignin), impedes an effective valorization of that and therefore, fractionation of the biomass into individual components is frequently applied in modern biorefinery such as the pulp and emerged 2nd ethanol industries. To data, various pretreatment technologies have been developed including alkaline-based methods (e.g., Kraft pulping, sulfate pulping) and acid-catalyzed Saccharization (e.g., organosolv pulping, concentrated acid hydrolysis, subcritical water hydrolysis), in which the lignin fraction is isolated as a typical by-product. Lignin though embodies the largest source of bio-aromatics, and the utilization of this feedstock for the production of chemicals has come into the spotlight. However, the recalcitrant condensed structure of the isolated lignin renders a difficult value-added use but mostly as a cheap energy source. We recognize that amongst the existing thermochemical technologies, pyrolysis is the simplest way to convert the lignin into biochar and monomers. Therefore, the conversion of a Klason lignin by a proposed pyrolysis process was investigated, the results of which are discussed in Chapter 2. Second, biomass-derived aqueous stream in modern biorefinery is another by-product with very limited applications, which otherwise must then be treated before discharging to the environment. The aqueous phase of bio-oil from pyrolysis is a representative waste stream, the composition of which is more or less similar to that of effluent water from hydrothermal treatment of biomass. This type of by-products mainly contains water and lots of organic compounds such as phenolic compounds, alcohols and carboxylic acids, etc. Treatment of the pyrolytic aqueous phase by hydrothermal gasification could not only reduce its total organic content but also enable energy recovery in the form of CH₄/H₂ fuel gases, which are the main

driving force for Chapter 3. Regardless of the hazardous properties, the pyrolytic aqueous phase is highly acidic and thus shows great promise as an alternative of mineral acids for leaching alkali and alkaline earth metals (AAEMs) from biochar, which could mitigate ash-related issues during char-related applications. The leaching of char with the aqueous phase was in-detail investigated in Chapter 4. Third, as a promising method to process highly wet feedstocks, hydrothermal gasification was further applied to lignite-to-syngas conversion (Chapter 5).

Six chapters including the detailed works and a general summary are involved in this thesis. Chapter 1 gives a general overview of the core topic of the present work. The importance of biomass as an energy source is presented, along with the technologies for its energetic exploitation. The focus is then moved to hydrothermal processes and, in particular, to hydrothermal gasification. After presenting the most relevant physical and chemical properties of hot-compressed water, the state of the art for HTG is drawn. Finally, the objectives of the present work are stated.

Chapter 2 describes a particular type of pyrolysis that recycles the heavier portion of bio-oil (HO) entirely to pyrolysis, employing the parent feedstock for their capturing or/and recycling. Continuous pyrolysis of a cedar lignin with HO recycling was simulated by repeating fix-bed pyrolysis of HO-loaded lignin up to nine times, and demonstrated the steady state of yields of gas, water, char and light oil (LO) that consisted solely of monomers and furans and lower acids, with neither discharge of HO from the system nor accumulation therein. Theoretical yields of the products were compared with the experimental values, which confirmed the HO–lignin interactions. The recycled HO underwent not only self-pyrolysis/carbonization but also co-pyrolysis or/and carbonization with the lignin, resulting in the char formation and degradation into LO, in particular, phenolic monomers such as catechol, guaiacol and their derivates.

Chapter 3 proposes a sequential conversion of biomass into syngas and clean biochar, without use of external chemicals. Aqueous pyrolytic phase of bio-oil was used as a useful agent to leach alkali and alkaline earth metallic species from the char, and then was subjected to HTG in a continuous flow reactor at 350°C for 280 min, employing a 4.6 wt% ruthenium/activated-charcoal catalyst. The leaching transforms 92% of K form the char to the solution and the resultant carbon conversion by the subsequent HTG was 99% while a CH₄-rich fuel gas and clean water abundance in K were produced.

Chapter 4 in-detail investigated repeated leaching of char with pyrolytic aqueous phase at ambient temperature in a batch mode. The leaching of AAEMs is initially rapid and followed by a slower rate towards equilibrium, which can be broadly described by a pseudo-second order model. In terms of the leaching kinetics of K, Mg and Ca, the leaching almost reaches equilibrium within 1 h, with near-steady removal rates of 65, 55 and 74%, respectively. Repeated leaching of biochar with the aqueous phase up to 18 times enables the internal recycling of the pyrolytic products.

Chapter 5 demonstrated a sequence of degradation, dissolution and catalytic hydrothermal gasification of lignite in alkaline water. A Victorian lignite was subjected to hydrothermal treatment (HT) in an aqueous solution of NaOH at 250°C, and then oxidation with pressurized O_2 at 100°C. The sequential HT and oxidation near-completely solubilized the lignite. The resulting solution was successfully converted by CHTG in a flow reactor at 350°C for 10 h, employing a 16 wt% ruthenium/activated-charcoal catalyst. The initial carbon conversion to gas was as high as 98% while CH₄, CO₂ and H₂ were produced. The catalyst deactivation was in detail discussed and caused mainly by the coke deposition that is related to the heavier portion (molecular mass >1,000) of the solubilized lignite.

Chapter 6 summarizes the general conclusions, perspectives and recommendations based on the finding in the preceding chapters.