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主 論 文 の 要 旨

論文題目 **Utilization of lignin to obtain olefin and aromatic compounds through hydrogenation and subsequent fast pyrolysis processes**
(リグニンの水素化と急速熱分解の逐次的プロセスによる基幹化学原料製造に関する研究)

氏 名 **ZHANG Lijuan**

論 文 内 容 の 要 旨

This study focused on the utilization of lignin. Based on the major global issues such as greenhouse gas emissions and the excessive exploration of fossil fuel, clean renewable sources are required to replace fossil fuels, among them lignocellulosic biomass the most prospective candidate. The study of hydrogenation on biomass or biomass derivatives has proved that it improves the efficiency of generating high-value chemicals. And lignin, one of the three major components in lignocellulosic biomass, is internally rich in phenolic units and has significant research potential. Hydrogenation process as a pretreatment was conducted on lignin in this work, so that the hydrogenated lignin is expected to have greater pyrolytic properties and produce more olefins and aromatic hydrocarbons in fast pyrolysis. Thermal catalytic hydrogenation (TCH) of lignin has been extensively discussed, while hydrogenolysis or depolymerization of lignin mainly occurred under severe conditions and an energy-intensive process. Hence, electrochemical hydrogenation (ECH) used as an alternative pretreatment technology

for lignin was checked in this work, and the pyrolytic property of hydrogenated lignin in fast pyrolysis was investigated. In this work, the hydrogenation of lignin through the TCH and ECH processes was compared, including the effect of catalyst types and reaction conditions on hydrogenation efficiency, pyrolysis reactivity, product selectivity, and technical limitations. The advantages and disadvantages of the two technologies for lignin utilization have also been compared, which provides a more favourable knowledge base and theoretical basis for the subsequent research work. Besides, techno-economic analysis of this two-stage process (hydrogenation coupled with fast pyrolysis) was also checked based on experimental data. In order to verify the feasibility of this two-stage process, ASPEN Plus software was used to conduct process simulations for plant scale. A comprehensive economic assessment of the process was performed, including a comparative analysis of the impact of both the feedstock and hydrogenation methods on overall profitability.

The first part of work (in Chapter 3) shows the primary experiment study of hydrotreatment on alkaline lignin (AL) with relatively mild conditions, as well as the characterization of hydrogenated alkaline lignin (HAL), particularly the behaviour during fast pyrolysis were further investigated. The recovery of the HAL samples decreased with the increasing of reaction temperature from 60 wt.% to 41 wt.% in the range of 150-250 °C. The hydrotreated products were analyzed by Elemental Analysis and FTIR (for HAL), and GC-MS (for bio-oil). The HAL samples were found to have a higher hydrogen/carbon atomic effective ratio (H/C_{eff} ratio) than AL. Compared to the internal structure of the lignin before and after hydrotreatment, the side chain groups were removed from AL during the process. After that, from the fast pyrolysis of HAL samples, it was observed that more light hydrocarbons and aromatic compounds were

formed than that of AL. Furthermore, fast pyrolysis in the hydrogen atmosphere revealed that more volatile fractions released compared to the helium atmosphere. The total olefins yield for HAL (at 250 °C for 7 hours) compared to AL increased from 1.02 wt.% to 3.1 wt.%.

Chapter 4 presents this two-stage process that consists of catalytic hydrogenation and subsequent fast pyrolysis on organosolv lignin (EOL). The results showed that 48-87 wt.% of solid product could be recovered as hydrogenated lignin (H-EOL) after hydrogenation at 200-250 °C for 1-7 hours. The chemical structure of H-EOL was comprehensively investigated by the means of Elemental analysis, FTIR, ¹³C & ¹H NMR, and TGA. Furthermore, the behaviour of fast pyrolysis of H-EOL was detected. H-EOL has higher hydrogen to carbon atomic effective ratio (H/C_{eff} ratio) and achieves the increasing reactivity of thermal decomposition. H-EOL yields light olefins double as much as raw organosolv lignin. And the formation of alkanes (C1-C4), benzene, and toluene was promoted to various degrees, while the yield of carbon monoxide, carbon dioxide, and vapour decreased. A novel process and efficient pretreatment method has been provided to verify on organosolv lignin, which is instructive for subsequent research.

Chapter 5 reports an electrochemical approach for hydrogenating alkaline lignin (AL), which uses relatively low-cost Ni foam as a working electrode under alkali electrolyte. The primary factors (such as power input, reactor type, temperature, reaction time, catalysts, and electrode substrates) of electrochemical hydrogenation were used to control the products' yield and features. The redox characteristics of the reaction system were directly compared with the cyclic voltammetry measurement under different parameters. After electrochemical hydrogenation (ECH), fast pyrolysis

was conducted on HAL samples to investigate the influence of electrochemical reactions on lignin. The maximum olefins and aromatics yield from HAL was increased to more than three times AL, accounting for 2.22 wt.% and 4.07 wt.%, respectively. Then, thermogravimetric analysis (TGA), elemental analysis (EA), Fourier-transform infrared spectroscopy (FTIR), and heteronuclear single quantum coherence (HSQC) 2D NMR were employed to characterize hydrogenated lignin samples (HAL), as well as gas chromatography–mass spectrometry (GC-MS) was conducted to investigate the oil-phase products. This work focused on this electrochemical hydrogenation coupled with fast pyrolysis process to give a possibility that converting lignin into not only liquid oil products, but solid hydrogenated lignin can be used to produce more olefins and aromatics in fast pyrolysis.

Finally, the techno-economic of the processes was also verified at the demonstration plant-scale in chapter 6. Aspen Plus was used to represent this two-stage on process simulation for converting lignin into valuable products in this chapter. Based on previous experimental data, the process was evaluated based by modelling a 1000 kg-feedstock/h. For the overall hydrogenation process coupled with pyrolysis reactions, process simulation buildup and optimization, heat exchange network creation, and economic evaluation were performed. The impact of different lignin feedstock (organosolv lignin and alkaline lignin) and hydrogenation technologies (thermal catalytic hydrogenation and electrochemical hydrogenation) on the overall economics was calculated and compared as different Scenarios. Simulations revealed that the annual profit of the whole process was mainly influenced by the product's value and the reaction materials, especially hydrogen and the solvent of the hydrogenation reaction. The economic and energy consumption of this two-stage process proved that the heat

exchanging network can decline the energy consumption of the whole process and utilization of phenolic compounds after hydrogenation has large effect on the total revenue.