

Modeling and Kinetic Study of Degradative Solvent Extraction of Biomass Wastes

Xianqing Zhu,[†] Jian Tang,[†] Xian Li,^{*,†} Wei Lan,[†] Kai Xu,[†] Yuan Fang,[†] Ryuichi Ashida,[‡] Kouichi Miura,[§] Guangqian Luo,[†] and Hong Yao^{*,†}

[†]State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China

[‡]Department of Chemical Engineering and [§]Institute of Advanced Energy, Kyoto University, Kyoto 615-8510, Japan

ABSTRACT: The degradative solvent extraction (DSE) has been found to be an effective method to convert and upgrade biomass wastes into high-quality extracts with various applications. However, the reaction pathways and kinetics of this DSE process are still not clear and need to be clarified. Hence, in this study, the biomass was treated in 1-methylnaphthalene at various conditions (300–350 °C and 0–90 min) by the DSE method and separated into five products: residue (unreacted biomass), two extracts (deposit and soluble), liquid, and gas. A lumped reaction model was proposed to simulate this biomass DSE process. The kinetic parameters were estimated by the least squares fit based on the experimental data and the model, which was optimized by the MATLAB optimization program. The results showed that the proposed model was valid and well-capable of describing the biomass DSE process. It can be concluded that different conversion pathways existed at 300 and 350 °C. At 300 °C, the dominant reactions were the conversion of residue (unreacted biomass) to the extraction products [deposit ($k = 0.0104 \text{ min}^{-1}$), soluble ($k = 0.0042 \text{ min}^{-1}$), and liquid ($k = 0.0044 \text{ min}^{-1}$)]. The deoxygenation reactions mainly occurred at relatively mild conditions. While at 350 °C, the rate-controlled process was the conversion of high-molecular-weight extract (deposit) to low-molecular-weight extract (soluble) ($k = 0.0155 \text{ min}^{-1}$). A comprehensive understanding of the reaction pathways of the biomass DSE conversion process was provided.

1. INTRODUCTION

As a result of the concerns of fossil fuel exhaustion and climate change, renewable alternative resources are receiving more and more interest and growingly considered as potential substitutes for fossil energies. Among them, biomass is one of the most important and abundant renewable energy resources, which accounts for around 10–13% of the world primary energy consumption.^{1–3} In addition, biomass has less negative impacts on the environment compared to fossil fuels, owing to its low sulfur and nitrogen contents as well as CO₂-neutral characteristic.^{4–6} Therefore, biomass is expected to play a more vital role in energy production in the near future. The existing biomass utilization technologies mainly include thermochemical conversion technologies (such as pyrolysis, gasification, and combustion)^{7–9} and biochemical conversion technologies (such as digestion and fermentation).¹⁰ Generally, thermochemical processes have higher utilization efficiencies than biochemical processes in terms of the much lower reaction time and the superior capability to convert most of the organic compounds in biomass, especially for lignin.¹¹ The thermochemical processes are the most common methods up to date. However, the inherently disadvantageous features of biomass, such as high moisture and oxygen contents and low energy density, lead to its low economic efficiency and limit its practical application for conventional thermochemical technologies.¹² Hence, to realize the efficient utilization of biomass feedstocks, it is necessary to achieve the dewatering and deoxygenation of them before introducing them into traditional thermochemical processes. This process is referred to as biomass upgrading.

Currently, two main biomass upgrading technologies, slow pyrolysis (torrefaction)^{13–16} and hydrothermal carbonization,^{17–20} have been employed to upgrade and convert biomass into carbonaceous solid products (biochar and hydrochar). Slow pyrolysis of biomass is typically performed between 200 and 300 °C with a low heating rate in the absence of oxygen. Hydrothermal carbonization is the conversion of biomass to hydrochar using subcritical water at moderate temperatures (180–300 °C). In general, these two methods could increase the carbon content and reduce the oxygen content of the biomass feedstocks to some extent and narrow the difference between the diversities of biomasses. However, the carbon contents of biochars produced from slow pyrolysis are generally lower than 65%, and the oxygen contents are still as considerably high as 25–35%.²¹ As for hydrothermal carbonization, it is commonly carried out under harsh subcritical conditions with the pressure higher than 16 MPa, which requires a complex and expensive reaction system. Moreover, the ash contents of both biochar and hydrochar are higher than those of the corresponding raw biomasses, which can result in ash-related problems during further utilization.

Apart from the traditional technologies mentioned above for biomass upgrading, an alternatively novel method (termed degradative solvent extraction, abbreviated to DSE) has been recently proposed to upgrade and convert a wide variety of biomass wastes into several high-quality solid fractions in our

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