

A Study on the Pyrolysis Behavior and Product Evolution of Typical Wood Biomass to Hydrogen-Rich Gas Catalyzed by the Ni-Fe/HZSM-5 Catalyst

Xueqin Li^{1,2,3} Peng Liu⁴ Youqing Wu² Zhiwei Wang^{1,3*} Tingzhou Lei^{4*}

(1. School of Environmental Engineering, Henan University of Technology, Zhengzhou 450001, China; 2. Department of Chemical Engineering for Energy Resources, School of Resources and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China; 3. Institute for Carbon Neutrality, Henan University of Technology, Zhengzhou 450001, China; 4. National-Local Joint Engineering Research Center of Biomass Refining and High-Quality Utilization, Institute of Urban and Rural Mining, Changzhou University, Jiangsu 213164, China)

Abstract: **【Objective】** Catalytic pyrolysis is an efficient method of biomass thermal conversion. Under the action of a catalyst, pyrolysis products can be cracked into short-chain intermediate products by the dehydration or decarboxylation of long-chain bio-oil molecules and inhibit the occurrence of secondary cracking reactions; thus, high-quality target products can be obtained by directional conversion. Therefore, the overall pyrolysis process of biomass can be considered the decomposition of polymer chains in biomass macromolecules to produce condensable volatiles (bio-oil), no condensable gases, and biochar via externally supplied heat under an inert atmosphere. But the outcomes of biomass pyrolysis are heavily dependent on its reaction conditions. However, at present, the research on the pyrolysis mechanism of biomass pyrolysis is mostly based on the structure of biomass raw materials and pyrolysis products to deduce the possible reaction path in the process of pyrolysis or to speculate the possible evolution path of product functional groups by a method of theoretical calculation. More importantly, obtaining highquality hydrogen-rich gas by improving and optimizing reaction conditions not only serves as one of the important paths toward the development of biomass pyrolysis technology, but it also provides an important theoretical basis for promoting the utilization of biomass pyrolysis gas. **【Method】** PR and CR were used as staple wood biomasses to investigate the apparent kinetics of TG/DTG at different heating rates. Furtherly, relying on thermogravimetric behavior and pyrolysis kinetics, this study explored and optimized the process of the catalytic pyrolysis of wood biomass to hydrogen-rich gas in a fixed-bed reactor with pyrolysis temperature, catalysts, and H₂O steam as influencing factors, to comprehensive investigations on their pyrolysis behavior and product evolution; this was to determine the reaction path and mechanism of catalytic pyrolysis. **【Result】** Both PR and CR exhibited three consecutive stages of weight loss and the TG/DTG curves. The characteristic parameters shifted to a higher temperature as the heating rate rose. The activation energies and preexponential factor obtained from the law of mass action and Arrhenius equation for CR were 72.38 kJ/mol and 1147.11 min⁻¹ and located in 72.36 kJ/mol and 1144.36 miⁿ⁻¹ for PR. The pyrolysis mechanisms of wood biomass were mainly the process of carbon enrichment and depolarity functional group of organic components. H₂ was the most dominant gaseous product during the pyrolysis process, followed by C–O bond-containspecies (CO, CO₂), while CH₄ was abundant in pyrolysis gas. The high temperature was beneficial for promoting the pyrolysis of biomass, increasing pyrolysis gas yield, and reducing tar yield. In the presence of the Ni-Fe/HZSM-5 catalyst, the gas yield significantly increased to 117.9 mL/g-biomass at the pyrolysis temperature of 700°C. The catalytic pyrolysis of MWC could generate larger amounts

of oxygenated product. In particular, more hydrocarbons like aldehydes, acids, alcohols, ketones, phenols, furans, and esters were observed in the liquid products. Furthermore, the H₂O steam had more effect on the product evolution and yield of gaseous products. However, too much H₂O inhibits the cracking/reforming reaction of tar and also consumes a lot of energy. In particular, the gas yield and hydrogen conversion were 76.94% and 15.90%, and the H₂/CO was 2.07 under the H₂O steam flow rate of 1 mL/min. The yields of H₂, CO, and CO₂ were 107.35 mL/g-biomass, 53.70 mL/g-biomass, and 99.31 mL/g-biomass, respectively. **【Conclusion】**The thermo-chemical conversion of biomass wastes is a practical approach for the value-added reclamation of bioenergy in large quantities, and pyrolysis plays a core role in this process. The pyrolysis mechanism and product distribution of wood biomass were demonstrated through different indexes. It was concluded that wood biomass has great advantages in pyrolysis for producing hydrogen-rich gas, and it has a good application prospect as the raw material of alternative fuel. However, understanding how to carry out deep purification and the efficient utilization of high-temperature pyrolysis gas is an important direction for promoting the development of biomass technology.

Key words: woody biomass; Ni-Fe/HZSM-5 catalyst; pyrolysis behavior; products evolution; gaseous products