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Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review

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ABSTRACT

The past decades have seen increasing interest in developing pyrolysis pathways to produce biofuels and bio-based chemicals from lignocellulosic biomass. Pyrolysis is a key stage in other thermochemical conversion processes, such as combustion and gasification. Understanding the reaction mechanisms of biomass pyrolysis will facilitate the process optimization and reactor design of commercial-scale biorefineries. However, the multiscale complexity of the biomass structures and reactions involved in pyrolysis make it challenging to elucidate the mechanism. This article provides a broad review of the state-of-art biomass pyrolysis research. Considering the complexity of the biomass structure, the pyrolysis characteristics of its three major individual components (cellulose, hemicellulose and lignin) are discussed in detail. Recently developed experimental technologies, such as Py-GC–MS/FID, TG-MS/TG-FTIR, *in situ* spectroscopy, 2D-PCIS, isotopic labeling method, *in situ* EPR and PIMS have been employed for biomass pyrolysis research, including online monitoring of the evolution of key intermediate products and the qualitative and quantitative measurement of the pyrolysis products. Based on experimental results, many macroscopic kinetic modeling methods with comprehensive mechanism schemes, such as the distributed activation energy model (DAEM), isoconversional method, detailed lumped kinetic model, kinetic Monte Carlo model, have been developed to simulate the mass loss behavior during biomass pyrolysis and to predict the resulting product distribution. Combined with molecular simulations of the elemental reaction routes, an in-depth understanding of the biomass pyrolysis mechanism may be obtained. Aiming to further improve the quality of pyrolysis products, the effects of various catalytic methods and feedstock pretreatment technologies on the pyrolysis behavior are also reviewed. At last, a brief conclusion for the challenge and perspectives of biomass pyrolysis is provided.

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1. Introduction

Consumption of fossil fuels worldwide has increased tremendously in last few decades, which leads to several environmental issues, including greenhouse gas emissions and deteriorating air quality caused by pollutants such as SO_x, NO_x and fine particulate matter. Moreover, the fluctuation of fossil fuel prices and the depletion of fossil resources have shadowed the global economy. The production of carbon-neutral and low-emission fuels from renewable resources, such as biomass, is of growing importance in the gradual substitution of conventional fossils. Biomass is biological material from living, or recently living organisms produced directly or indirectly by photosynthesis, most often plants or plant-derived materials [1–3]. Biomass resources are widely available in nature. It is estimated that the global biomass production is approximately 100 billion tons per year [4]. As the only renewable carbonaceous resource, biomass has the potential to produce heat, electricity, fuel, chemicals, and other products [5,6]. The International Energy Agency (IEA) suggests that bioenergy has the potential to provide 10% of the world's primary energy supply by 2035, and biofuels can replace up to 27% of world transportation fuel by 2050 [7].

Biomass can be converted into fuels and chemicals through biochemical or thermochemical processes. Digestion (anaerobic and aerobic) and fermentation are typical biochemical processes used to produce methane and alcohols [8,9]. The main thermochemical processes include pyrolysis, gasification, combustion, hydrothermal liquefaction and hydrothermal carbonization [10,11]. Among these thermochemical pathways, pyrolysis, the thermal decomposition of organics in the absence of oxygen, has been extensively developed as a promising platform to produce fuels and chemicals from various types of biomass. Pyrolysis produces char, liquid and gas products, the distribution of which strongly depends on the reaction conditions. Fast pyrolysis of biomass at rapid heating rates and short hot vapor residence times (<1 s) produces liquid with yield up to 75 wt.% [12,13]. The pyrolysis liquid, which is normally called bio-oil, can be further upgraded to transportation fuels and value-added chemicals. The char and gaseous products can be combusted to provide energy for the pyrolysis reaction or heat/power generation [12]. Many potential agricultural and environmental applications of char are also being explored to enhance the value chain of the pyrolysis process [12,14]. Techno-economic analysis showed that transportation fuel production from biomass via pyrolysis-based pathways had economic advantages over other conversion pathways, such as gasification and biochemical pathways [15–18]. Due to the huge demand for liquid transport fuels, biomass pyrolysis technology will attract increasing interest from both academia and industry [19].

Biomass slow pyrolysis, particularly wood carbonization and distillation, has been used by humans for more than a thousand years. Nevertheless, the pioneering studies on biomass pyrolysis were initiated in 19th century [20]. The effect of the reaction conditions on the yields of the solid, liquid and gas pyrolysis products was first reported in 1875 by Gruner [21]. However, little progress was made until the 1980s. During this stage, the kinetics of biomass/cellulose pyrolysis received significant attention. In 1956, Stamm [22] reported the kinetics of wood and cellulose thermal degradation and suggested that thermal degradation followed a first-order reaction model. In 1970, Roberts [23] reviewed the pyrolysis kinetics of biomass and related substances. The results showed that pyrolysis may proceed through different reaction routes. In 1979, the classic Broido–Shafizadeh (B–S) model for cellulose pyrolysis based on the formation of char, volatiles and gas via different pathways was proposed [24]. These findings provide some fundamentals for further development of biomass pyrolysis technology.