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Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters



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ABSTRACT

Pyrolysis is one of the thermochemical technologies for converting biomass into energy and chemical products consisting of liquid bio-oil, solid biochar, and pyrolytic gas. Depending on the heating rate and residence time, biomass pyrolysis can be divided into three main categories slow (conventional), fast and flash pyrolysis mainly aiming at maximising either the bio-oil or biochar yields. Synthesis gas or hydrogen-rich gas can also be the target of biomass pyrolysis. Maximised gas rates can be achieved through the catalytic pyrolysis process, which is now increasingly being developed. Biomass pyrolysis generally follows a three-step mechanism comprising of dehydration, primary and secondary reactions. Dehydrogenation, depolymerisation, and fragmentation are the main competitive reactions during the primary decomposition of biomass. A number of parameters affect the biomass pyrolysis process, yields and properties of products. These include the biomass type, biomass pretreatment (physical, chemical, and biological), reaction atmosphere, temperature, heating rate and vapour residence time. This manuscript gives a general summary of the properties of the pyrolytic products and their analysis methods. Also provided are a review of the parameters that affect biomass pyrolysis and a summary of the state of industrial pyrolysis technologies.

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1. Introduction

With the rapid increase in global energy demand and increasing environmental and sustainability challenges, biomass fuels as renewable energy sources have increasingly been considered as a key option to substitute conventional fossil fuels. Currently, biomass and waste contribute to around 10% of the global energy supply [1]. The full estimated potential of annual biomass availability is predicted to be as high as 1.08×10^{11} toe (tons of oil equivalent), which is almost 10 times the world's current energy need [2,3]. The abundant biomass reserves, its renewability, CO₂ neutrality, and technical grafting from coal industries have been the main driving forces for research and utilisation of biomass.

Thermochemical technologies for converting biomass into energy or chemicals mainly consist of combustion, pyrolysis, gasification, and high-pressure liquefaction [4]. Biomass pyrolysis with a long history of use, initially for the production of charcoal (biochar), has emerged as a frontier research domain. Biomass pyrolysis is generally defined as the thermal decomposition of the biomass organic matrix in non-oxidising atmospheres resulting in liquid bio-oil, solid biochar, and non-condensable gas products.

Depending on the heating rate and solid residence time, biomass pyrolysis can be divided into three main types including slow (conventional) pyrolysis, fast pyrolysis and flash pyrolysis [5,6]. Some other pyrolysis processes may also be conducted between these typical pyrolysis types [7]. Slow pyrolysis, termed carbonisation, has been conventionally applied for the production of charcoal. Due to the long residence time (lasting hours to days), relatively low temperature (\sim 300–700 °C), and the acceptance of a wide range of particle sizes (5–50 mm) [8], the thermal decomposition of biomass (mostly lignocellulosic types) proceeds under a very low heating rate with sufficient time allowed for repolymerisation reactions to maximise the solid yields. Fast pyrolysis typically involves high heating rates (> 10-200 °C/s) and short residence times (0.5-10 s, typically < 2 s) [8]. Bio-oil yield (dry biomass basis) can be as high as 50-70 wt%. The flash pyrolysis process is characterised by higher heating rates of 10³- 10^4 °C/s and shorter residence times (< 0.5 s), resulting in very high bio-oil yields which can achieve up to 75–80 wt% [9–11].

The future of research on biomass pyrolysis toward achievement of high energy efficiencies and tailoring the conditions to produce the desired product types takes into consideration the experience and knowledge of the influences of pyrolysis parameters on the process performance, including reaction rate, product selectivities and yields, product properties and energy efficiency [12]. The pyrolysis parameters for consideration involve feedstock type selection (biomass type, particle size, biomass pretreatment), reaction conditions (pyrolysis temperature, pressure, particle heating rate, residence time), reactor configurations and processes, and miscellaneous variables, such as the addition of catalysts and vapour condensation mechanisms [13]. This paper aims to review the properties and applications of pyrolysis products, as well as the effects of pyrolysis parameters on biomass pyrolysis product yields and properties.

2. Pyrolysis mechanism

The complexity of biomass pyrolysis arises from the difference in decomposition of the biomass components with varying reaction mechanisms and reaction rates which also partly depend on the thermal processing conditions and reactor designs. Interactions between the major constituents of the woody biomass, such as the cellulose, hemicelluloses, and lignin, during pyrolysis have been confirmed previously [14], which makes prediction of biomass pyrolysis characteristics simply based on the thermal behaviour of the three individual components very difficult. For example, the interaction between hemicellulose and lignin promotes production of lignin-derived phenols while hinders the generation of hydrocarbons [15]. Lignin also significantly interacts with cellulose during pyrolysis as lignin hinders the polymerisation of levoglucosan from cellulose thus reducing biochar formation, while the cellulose-hemicellulose interaction has a lower effect on the formation and distribution of pyrolysis products [16].

During biomass pyrolysis, a large number of reactions take place in parallel and series, including dehydration, depolymerisation, isomerization, aromatisation, decarboxylation, and charring [12,17,18]. It is generally accepted that the pyrolysis of biomass consists of three main stages: (i) initial evaporation of free moisture, (ii) primary decomposition followed by (iii) secondary reactions (oil cracking and repolymerisation) [19]. These stages are intermingled, with a possibility to observe their transitional behaviour through thermal analysis. The apparent specific heat of biomass during pyrolysis and the corresponding heats of reactions during different pyrolysis stages have been extensively studied in the past using computer-aided thermal analysis (CATA) under different heating rates [20–26].

Biomass decomposition generally occurs during the primary decomposition to form solid char at 200–400 °C, which is responsible for the largest degradation of biomass [27]. The secondary reactions proceed to take place within the solid matrix with further rising of the temperature [27].

The degradation pathways of the main biomass components have been investigated separately. Decomposition of hemicellulose, generally represented by xylan, mainly takes place between 250 and 350 °C, followed by cellulose decomposition, which primarily occurs between 325 and 400 °C with levoglucosan as the main pyrolysis product [28,29]. Lignin is the most stable component which decomposes at higher temperature range of 300–550 °C [30].

Among the three major biomass constituents of cellulose, hemicelluloses, and lignin, the decomposition of cellulose has been most widely analysed and best comprehended [31]. Fig. 1 illustrates the simplified reaction pathway of cellulose pyrolysis, which is the generally accepted Waterloo-mechanism [32]. Dehydrogenation, depolymerisation and fragmentation are the main competitive reactions dominant at different temperature ranges.

3. Properties and applications of products

3.1. Bio-oil

When bio-oil production is the primary product of interest, fast or flash pyrolysis are the conditions of choice to maximise the

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