



Assessment of pyrolysis polygeneration of biomass based on major components: Product characterization and elucidation of degradation pathways



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HIGHLIGHTS

- The cleavage of glycosidic bond was the first step for cellulose and xylan pyrolysis.
- Furans were produced accompanied by the formation of anhydro saccharides.
- The surface of cellulose formed a melted phase at low temperature.
- The depolymerization and dealkylation were the primary reactions during lignin pyrolysis.
- For the biomass polygeneration system, it is not suggested to pyrolyze over 750 °C.

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ABSTRACT

The pyrolysis behaviors of biomass components (cellulose, hemicellulose and lignin) were studied at various temperatures and the evolution mechanisms of the pyrolytic products were investigated with variant approaches. Anhydro-saccharides, light oxygenates and phenols were the main compounds in pyrolytic bio-oil from cellulose, xylan and lignin, respectively. The subsequent degradation of saccharides involved was the fragmentation to generate gaseous and light oxygenates, and these compounds formed competitively against the generation of phenols and aromatics. CO released from cellulose originated from the decomposition of saccharides while that from xylan was more likely to derive from the decarbonylation of ketones and decarboxylation of acids. H₂, CH₄ and light hydrocarbons formed during aromatization when exceeded 650 °C. Cellulose was the main contributor to the porosity of biomass chars and lignin was the main contributor for the mass of biomass chars. Furthermore, a new pathway for the pyrolysis of biomass and insights into how biomass materials used more efficiently and comprehensively, were provided.

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1. Introduction

Biomass is a renewable substitute of petroleum that can be converted to fuel gas, solid char and liquid oil or other chemicals through thermochemical processes, such as pyrolysis, combustion and gasification. Among those technologies, pyrolysis is one of the most promising conversion routes and plays a crucial role in biomass thermochemical conversion [1,2]. Biomass contains three major components (cellulose, hemicellulose and lignin) along with minor amounts of extractives (proteins, fatty, acids, resins) and ash [3]. Different kinds of biomass have different compositions. The biomass constituents are found to pyrolyze at different rates and by different pathways [4,5]. It is suggested that the pyrolysis of any biomass can be considered as the superposition of the three

major components [6]. So the elucidation of the pyrolytic behavior of individual components of biomass is essential to a better understanding of the intricate pyrolysis process of biomass.

Till now, numerous studies were carried out to investigate the degradation mechanism of biomass major components based on the properties of released products, such as gases [5,7–9], liquids [10–16] or solids [17,18]. Yang et al. [5] performed the pyrolysis of hemicellulose, cellulose and lignin in TGA and packed bed focusing on the gas releasing behaviors. The formation characteristics of gas compounds from cellulose pyrolysis were also investigated using entrained-flow reactor (EFR) [7] and FTIR at various conditions [8]. It was found that the formation of CO strongly depended on the temperature. CO₂ was mainly produced by the primary pyrolysis and barely affected by additional heating. Basilakis et al. [9] studied the gas released from pyrolysis of D-glucose, chlorogenic acid and xylan using FTIR quantitatively. The liquids from pyrolysis are also an important indicator for the elucidation of

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decomposition pathways. The effects of temperature and residence time on the formation of main liquid products from cellulose and hemicellulose were performed by Lu [10] and Shen [11,12] using Py–GC/MS and Py–GC–FTIR. Lu found that levoglucosan exhibited good thermal stability and its formation was favored at elevated pyrolysis temperature and time. However, Shen indicated that the yield of levoglucosan is inhibited at the elevated temperature. Patwardhan [13,14] pyrolyzed corn stover lignin and hemicellulose using a micro-pyrolyzer coupled with a GC–MS/FID and the liquid products were characterized. Guo et al. [15] and Wang et al. [16] analyzed the bio-oil from the pyrolysis of milled wood lignin (MWL). The degradation of MWL was dominated by the demethylation reaction and the cleavage of aliphatic hydroxymethyl at the γ -position, followed by the cracking of C_{α} – C_{β} and C_4 – C_{α} bonds. Hosoya et al. [17] investigated the pyrolysis of the model compounds of lignin in a closed ampoule reactor and found that the o-quinone methide was a key intermediate for lignin char formation during pyrolysis. Sharma et al. [18] analyzed the lignin char obtained under both pyrolytic and oxidative atmospheres and identified the surface area, presence of inorganics and aromaticity of char as potentially important factors in the formation of PAHs.

Other studies had focused on the pyrolysis parameters for maximizing the yields of individual products. Shen et al. found that the maximum bio-oil yield from cellulose was 72% at 580 °C, while that for hemicellulose was 45% at 475 °C [12,19]. The activated carbon was produced from wood components, cellulose, lignin, xylan and characterized by Khezami et al. [20]. It was found that only the char from cellulose had a significant BET-surface area of pores. Ferdous et al. [21] pyrolyzed Alcell and Kraft lignin in a fixed-bed microreactor to produce H_2 and medium Btu gas. The production of medium Btu gas was over 800 ml/g at 800 °C. As the total synthesis gas production was over 60 mol% of total gas, it could be an excellent candidate for liquid fuel production through Fischer–Tropsch synthesis. Piskorz et al. [22] performed the flash pyrolysis of cellulose to obtain levoglucosan and anhydro-oligosaccharides.

Although the pyrolysis of the biomass and its major components was investigated by many researchers, most of them focused on the possible mechanisms of the individual components and optimum conditions for producing single products. Generally, the yield and properties of gas, liquid and solid products from biomass pyrolysis were different and the optimum temperature for each product may vary. The by-products from biomass pyrolysis carry low economic value and are difficult to further process. Hence, the traditional processes may no longer meet the recent environmental and economic requirements.

The biomass-based polygeneration is one of the promising options to solve this problem as the production of solid char, liquid oil, and biogas can be synergistically optimized. Therefore, more efforts should be made to study the pyrolytic mechanisms of the three main components by taking into account the properties of products released comprehensively, i.e. products in gas, oil, solid forms. In this study, the pyrolysis characteristics of the major components of biomass were investigated to understand the mechanisms of their degradation thoroughly. Meanwhile, the relationship between biomass compositions and polygeneration was studied by examining the properties of the released products. Our findings may help better understand the mechanism of biomass pyrolysis and develop more efficient biomass utilization process.

2. Experimental

2.1. Materials

The three main components (cellulose, hemicellulose, and lignin) are provided by Sigma–Aldrich Co., Ltd. Cellulose, in the form

of white and microcrystalline powders of 20 μ m particle size. Alkaline lignin is in the form of dark brown powders. Customarily, xylan has been widely used as a model compound of hemicellulose in pyrolysis process. In this study, it is isolated from birchwood and in the form of yellow powder. The results of proximate and elemental analysis are listed in Table 1. It can be seen that the volatile content in cellulose is the highest (up to 95.5%) whereas that in lignin is the lowest (58.9%). Cellulose and xylan contains more oxygen and hydrogen than lignin due to the abundant hydroxyl group in carbohydrates.

2.2. Pyrolysis setup and procedures

Pyrolysis was conducted in a bench-scale tubular reactor (internal diameter 46 mm, length 400 mm). The experimental apparatus mainly consisted of a fixed-bed reactor, a controller system for temperature and purging gas and the systems for condensation, purification and analysis. Prior to each trial, the reactor was heated up to the designated temperature with nitrogen (99.999% 200 ml/min) as carrier gas and kept constant for 10 min. Afterwards, two porcelain arks with a thin layer of biomass particles (1 ± 0.001 g) were quickly pushed into the center of the reactor. The condensable volatiles were collected in the ice-water condenser while the non-condensable volatiles were filtered through a glass wool filter and dried using silica gel. After 15 min, the pyrolysis was finished and the sample holder was moved to the inlet and cooled down with nitrogen (1 L/min) to ambient temperature. The amounts of liquid bio-oil and char fractions were determined based on the weight differences of the glass tube and porcelain arks. The amount of gaseous products was calculated by combining all the gases collected during pyrolysis and converted from volume to weight percentage at ambient temperature and atmospheric pressure (the volume of 1 mol gas equals 24.45L at 1 atm and 25 °C) [23]. During the pyrolysis process, the mass balance during pyrolysis process was among 90–113%, which indicated that the process was feasible. Also, for each trial, it was repeated thrice with higher reproducibility with the relative error within 10% and all measured data presented were the average value.

2.3. Measurement of pyrolysis products

2.3.1. Determination of gaseous products

A dual-channel micro-GC system (Micro-GC 3000A, Agilent Technologies, USA), equipped with thermal conductivity detectors, was used to analyze quantitatively the gaseous products. Channel A was molecular sieve 5A for detecting H_2 , CO, CH_4 at 110 °C and channel B was PLOT U for checking CO_2 , C_2H_2 , C_2H_4 and C_2H_6 at 105 °C. A standard gas composed of H_2 (9.83 vol%), CO(20.7 vol%), CH_4 (9.89 vol%), CO_2 (20.1 vol%), C_2H_2 (0.49 vol%), C_2H_4 (0.5 vol%), C_2H_6 (0.5 vol%) with N_2 (37.99 vol%) was used as balance gas to calibrate gas species. Each gas sample was measured thrice to get the average value.

2.3.2. Specification of liquid oil

The composition of liquid oil was specified in detail using gas chromatography–mass spectroscopy (GC–MS, 7890A/5975C, Agilent) with a quartz capillary column (DB-WAX, length, 30 m; internal diameter, 250 μ m; film thickness, 0.25 μ m). The GC oven temperature program began with a 3 min hold at 50 °C followed by heating to 250 °C at 20 °C/min. The final temperature was held for 18 min. An injector temperature was set at 250 °C and a split ratio was 2:1. In each trial, 1 μ L of the sample was injected. The flow rate of the carrier gas (Helium) for the column was 1.0 ml/min. After 4.5 min of solvent delay, the sample was directly introduced into the ion source of a DB-WAX series mass-selective detector operated in an electron-impact ionization mode and scanned

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