Fuel Processing Technology 159 (2017) 19–26

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Improving hydrocarbon yield by two-step pyrolysis of pinewood in a fluidized-bed reactor

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ARTICLE INFO

Article history:
Received 8 November 2016
Received in revised form 15 January 2017
Accepted 16 January 2017
Available online xxxx

Keywords:
Biomass
Torrefaction
Catalytic pyrolysis
Aromatics
Olefins
Fluidized-bed

ABSTRACT

Two-stage fast pyrolysis of pinewood, was investigated with and without catalysts in a fluidized-bed reactor. The method is using low-temperature pyrolysis (torrefaction) to remove unfavorable compounds firstly and then using high-temperature catalytic pyrolysis to produce hydrocarbons. The effects of torrefaction temperature, residence time and atmosphere on product distribution were investigated. The results show that the acidity of produced liquids reduced with increasing torrefaction temperature and residence time. Torrefaction pretreatment of pinewood reduced the yields of acetic acid and guaiacol effectively during catalytic pyrolysis. The highest aromatic yield was obtained with torrefied pinewood at 250 °C, which was boasted 30% of that without torrefaction. Besides, torrefied biomass can obviously reduce coke deposition on ZSM-5 in the catalytic pyrolysis process compared with raw pinewood. Therefore, the two-step pyrolysis can be considered as a more effective and promising method for producing high-quality liquid fuels and chemicals.

1. Introduction

Motivated by the transition to be a more sustainable society based on clean energy technologies, biomass emerges as one of the most important renewable energy sources [1,2]. On one hand, due to its environmental benefits, biomass utilization implies a reduction in the carbon dioxide emissions and contributes to decrease the environmental impact caused by organic wastes [3–5]. On the other hand, it constitutes as a key factor in the economic development of rural areas and enhances energy access [6]. Thus, biomass which can be converted into fuels and chemical feedstock has been considered as an important renewable resource for the future [7–12].

However, biomass properties, such as heterogeneous and tenacious structure, hydrophilic nature, and high moisture content pose challenges to use biomass for energy production [9,10,13,14]. Torrefaction is a promising method for biomass pretreatment. It is a thermal treatment with a reaction temperature between 200 °C and 300 °C at atmospheric pressure in the absence of oxygen [15–17]. The process is characterized by relatively long residence time of the raw material in the reactor and low particle heating rates. During the residence in the reactor, biomass is partly decomposed releasing various types of volatiles. Specifically, the tenacious and fibrous structure of the raw biomass material is largely destroyed through the breakdown of hemicellulose and cellulose molecules during the torrefaction process [18–21]. It can effectively increase biomass energy density. It is also well known that the poor quality of bio-oil from biomass fast pyrolysis is mainly attributed to the existence of plenty of water and some easy-coking compounds [22–24]. These compounds can be removed in the torrefaction step [25].

Dozens of studies have been published on the evolution of vapors from biomass during torrefaction. Li et al. reported that a high temperature and long holding time produced a torrefied sample with low mass and energy yield, and aliphaticity decreased but aromaticity increased with increasing temperature due to the deoxygenation and dehydration reactions [26]. Chen et al. found that biomass torrefaction is controlled by heat and mass transfer, while surface oxidation is the dominant mechanism for biomass torrefaction in air [27]. Besides, pyrolysis of torrefied biomass has been paid a lot of attentions in the past years. Chen et al. showed that both bio-oil yield and number of functional groups containing oxygen decreased after torrefaction, while bio-char yield rapidly increased with increasing torrefaction temperature [28]. Zhao et al. has conducted wet and dry torrefaction of corncobs and found that hemicellulose could be effectively removed from corncobs by torrefaction. Dry torrefaction causes severe degradation and cross-linking of cellulose, wet torrefaction significantly enhances levoglucosan yield [29].

One of the most important challenges for catalytic pyrolysis of biomass to produce high-quality liquid fuels and chemicals is coking of catalysts [30,31]. Torrefaction treatment is found to influence the structure of biomass, and thus promotes the quality of bio-oil. Besides, the easily

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http://dx.doi.org/10.1016/j.fuproc.2017.01.025
0378-3820/

coking compounds in catalytic pyrolysis of biomass could be reduced in the torrefaction step. In particular, the process of biomass pyrolysis can be divided into two parts, "low-temperature pyrolysis" which is called "torrefaction" in the temperature ranging between 200 °C and 300 °C, and "pyrolysis" or "catalytic pyrolysis" in which biomass is converted into bio-oil or high-value liquid fuels and chemicals. Many works have been done about catalytic pyrolysis of biomass to produce aromatics and olefins without feedstock pretreatment [32–36]. However, the hydrocarbon yields are still low and catalyst deactivates very fast due to coking. In the two-step pyrolysis process, water and easily coking compounds are released in the torrefaction step, thus the catalyst's stability and hydrocarbon yield would be enhanced in the catalytic pyrolysis process.

In this work, pinewood was used as material to investigate the effect of torrefaction on the fuel properties during the two-step pyrolysis. The pyrolysis experiments of torrefied pinewood were performed using a fluidized-bed pyrolysis reactor with and without catalysts. The yield and quality of the pyrolysis products (bio-oil, bio-char and non-condensable gas) were analyzed, especially the composition of bio-oil in order to obtain torrefaction effects.

2. Experimental

2.1. Material

The feedstock used in the present study, pine sawdust (provided by a wood processing factory, Nanjing, Jiangsu), was grounded and sieved to obtain particles with sizes between 0.28 mm and 0.38 mm. The pine sawdust was dried at 105 °C for 12 h, and then stored for use. The elemental composition of pinewood (dry basis) was 44.88 wt% carbon, 4.17 wt% hydrogen, 0.96 wt% nitrogen, and 49.99 wt% oxygen (by difference). The proximate analysis of pinewood (dry basis) was 86.2 wt% volatile, 13.56 wt% fixed carbon and 0.24 wt% ash.

ZSM-5 was used as acid catalysts purchased from catalyst plant of Nankai University with Si/Al ratio of 25. The particle size of ZSM-5 catalysts was in the range of 0.075– 0.1 mm.

2.2. Torrefaction process

The torrefaction of pinewood was performed in a tubular furnace reactor. Torrefaction temperatures of 210 °C, 230 °C, 250 °C, 270 °C and 290 °C were conducted in which nitrogen was used as an inert carrier gas and residence time was 12 s. The residence times of 6 s and 24 s were also tested. The non-condensable gases in torrefaction process are mainly CO_2 and CO. For scale-up of the technology, the non-condensable gas would be used as carried gas. Therefore, CO_2 and CO were used as oxidizing and reducing carrier gases to understand their influences on biomass pyrolysis, respectively.

2.3. Pyrolysis system

The fluidized-bed system for biomass pyrolysis was shown in Fig. 1. The reactor was made of 304 stainless steel with inner diameter of 32 mm. The distributor was made up of 316 stainless wire-mesh with diameter of 300 mesh. Torrefied pinewood and catalyst were fed from the top of reactor. Pure nitrogen was usually used as a carrier gas with flow rate of 300 mL/min if not specified. A filter made up of 316 stainless wire-mesh with pore diameter of 200 mesh was set at the exit of fluidized-bed reactor to separate tiny catalyst and char particles. An ice water condenser was used to collect liquid product at 0 °C. In this experiment, the non-condensable pyrolysis gases were collected after passing through cotton wool and silica gel. The solid residues were sieved to separate bed material and char. Nitrogen gas with the concentration of 99.99% and flow rate of 300 mL/min were used as carrier gas for pyrolysis and catalytic pyrolysis. The reaction temperature was fixed at 600 °C according our previous study. 5 g of biomass was used as feedstock in each run. A mixture of quartz sand and catalyst was used in all the experiments. The particle size of quartz sand was from 0.05 to 0.075 mm, while that of the catalyst was from 0.075 to 0.10 mm because of its lower density. The mass ratio of sand to catalyst was 1. The total amount of the heat transfer material (sand and catalyst) in the fluidized bed was 20 g. The catalyst to pinewood ratio is 2.

2.4. Product characterization

Liquid products were analyzed with GC/MS (Agilent, 7890A–5975C). VF-5 capillary column (30 m × 0.25 mm × 0.25 μm) was used as chromatographic column. High purity helium (99.99%) gas was used as the carrier gas. The following temperature ramps were employed in the liquid analysis: from 40 °C to 50 °C at 5 °C/min, held at 50 °C for 3 min, ramped to 180 °C at 5 °C/min, held at 180 °C for 2 min, ramped to 280 °C at 10 °C/min, and held at 280 °C for 2 min. The gas products were analyzed using a Shimadzu 2014 GC system. A Restek Rtx-VMS capillary column (30 m × 0.25 mm × 1.4 μm) was used to qualify olefins and gaseous aromatics, while a SE30 packed column (30 m × 0.25 mm × 1.5 μm) was used to analyze methane, CO and CO_2. High purity helium was used as the carrier gas. The temperature ramps of oven temperature was as follows: held at 40 °C for 5 min, ramped to 100 °C at 5 °C/min, and held at 100 °C for 13 min.

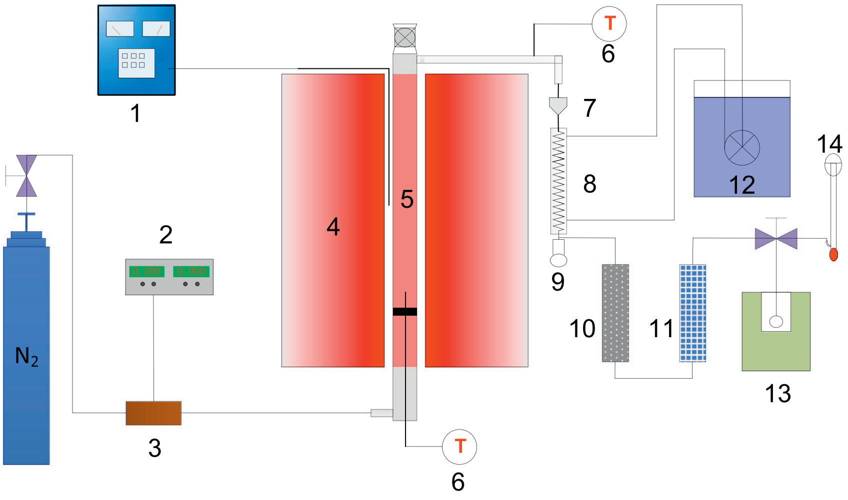

Fig. 1. Schematic diagram of a fluidized-bed system for biomass pyrolysis.