



Production high yields of aromatic hydrocarbons through catalytic fast pyrolysis of torrefied wood and polystyrene



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HIGHLIGHTS

- Pyrolysis of torrefied wood and polystyrene was used to produce aromatic hydrocarbons.
- Presence of polystyrene introduced more than twenty aromatic hydrocarbon compounds.
- Higher temperatures (600 °C) and zeolite catalyst improved the yield of aromatic hydrocarbons.
- Aromatic hydrocarbons were formed through a free radical reaction mechanism.

ARTICLE INFO

Article history:

Received 29 October 2015

Received in revised form 24 January 2016

Accepted 5 February 2016

Available online 12 February 2016

Keywords:

Py-GC/MS

Torrefied wood

Polystyrene

HZSM-5

Aromatic hydrocarbons

ABSTRACT

Catalytic fast pyrolysis of torrefied wood has been shown to improve the yields of aromatic hydrocarbons in the bio-oil. In this study, Py-GC/MS was employed on torrefied wood (TW), polystyrene (PS) and torrefied wood/polystyrene (TW/PS) with and without zeolite catalyst (HZSM-5) to produce a wide range of aromatic hydrocarbons. The effects of pyrolysis temperature, presence of polystyrene and catalyst on the yields and nature of aromatic hydrocarbons were investigated. Experimental results showed that the chemical composition of TW pyrolysis products was significantly different than that produced from TW/PS and TW/PS/catalyst. Presence of PS significantly reduced the yield of oxygenated phenolic compounds and produced more aromatic hydrocarbons compared to TW. More than twenty aromatic hydrocarbons were introduced during the co-pyrolysis of TW/PS and TW/PS/catalyst due to the presence of PS. The highest yields of aromatic hydrocarbons in co-pyrolysis samples were obtained at 600 °C, but higher temperatures slightly decreased the yield of most hydrocarbons. The major aromatic hydrocarbons were found to have high influence on the yields of pyrolysis products are: Styrene; α -methylstyrene; 2-phenyl-1,2,3,4-tetrahydronaphthalene; diphenylpropane and diphenylbutane derivatives. Most of aromatic hydrocarbons identified in this study were proposed to be formed through free radical reaction mechanism.

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1. Introduction

Biomass has a potential to be the only renewable energy source that can be used as an alternative to produce hydrocarbon fuels. In contrast to fossil oils, biomass is planted and collected annually which can provide a continuous energy supply. Biomass is also a clean and carbon-neutral energy source as carbon is recycled from the atmosphere [1]. In the US, the potential capacity of biomass is up to 1.3 billion dry tons annually which can replace a large portion of current petroleum consumption [2]. Biomass is complex, mainly composed from carbohydrates and lignin, it has high water and oxygen content as well as low bulk density and heating value.

These properties hinder its broad usage. Several technologies have been used to convert biomass to high-energy fuels in the form of solids, liquids, and gases. These technologies include torrefaction, pyrolysis, liquefaction, digestion, fermentation of biomass to ethanol, etc. [3,4]. Among these processes, pyrolysis and torrefaction has received an increasing attention as a strategy to produce biofuels from renewable resources.

Fast pyrolysis rapidly converts organic biomass into liquid products and gas in the absence of oxygen. This simple and low-cost technology can transform various feedstocks such as agricultural and forest residues into value-added biofuels and chemicals. Biofuels derived from biomass contribute a positive effect on the greenhouse gas emissions compared to petroleum-based transportation fuels [5]. Because of the above advantages, fast pyrolysis is considered to have a great potential to replace

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petroleum-based fuels and chemicals. Catalytic fast pyrolysis (CFP) is one of the most promising technologies for production of aromatic hydrocarbons from solid biomass [6,7]. Presence of catalyst enhances the aromatic yields of the bio-oil due to the rupture of C–C bonds associated with dehydration, decarbonylation, and decarboxylation [8]. Among all used catalysts, zeolite (HZSM-5) catalyst is particularly attractive because of its effectiveness in increasing the aromatic yield by selective deoxygenation of pyrolysis vapors [4,9]. HZSM-5 has a three dimensional pore structure with a pore size of 5.5–5.6 Å which make it suitable for the production of hydrocarbons [10]. HZSM-5 also has a short catalyst lifetime and low carbon efficiencies. Dehydrogenation and dehydration reactions that are catalyzed by HZSM-5 have been found to suffer further reduction in the hydrogen content, leading to coke formation. Incorporation of carbon-rich reactants into the catalytic fast pyrolysis with zeolite could possibly improve the above problems.

Compounds produced from CFP of biomass have a complex composition, high acid and water contents, low heating value and storage instability [11–13]. Pretreatment of biomass prior to the fast pyrolysis has been identified as one of the most promising techniques to improve the quality of liquid bio-oil [14,15]. Several pretreatment methods prior to the fast pyrolysis have been investigated, including water leaching, pretreatment with dilute acid and alkali, and hot compressed water treatment. Torrefaction can also be considered as a potential pretreatment prior to fast pyrolysis of biomass [15,16]. Torrefaction is a mild pyrolysis process which occurs around 200–300 °C in the absence of oxygen [17]. This temperature range selectively decompose the hemicellulose fraction because the thermal stability of biomass components are in the order: cellulose > lignin > hemicellulose [18]. This will enhance the aromatic hydrocarbon yields because cellulose and lignin can provide relatively higher aromatic yields compared to hemicelluloses [19–21]. Torrefaction can also reduce the bio-oil oxygen content significantly by losing CO, CO₂, H₂O and the removal of acidic components such as acetic acid, which in turn will increase the calorific value for the pretreated biomass [22]. Another advantage is the decreasing of energy required for the grinding of torrefied biomass by three to seven times lower than that required for raw materials [23].

Recently, co-pyrolysis of biomass and plastics has gained a lot of attention in the literature. The most important reason for the increasing awareness toward biomass/plastic co-pyrolysis is to obtain high quality and better quantity bio-oils compared with those obtained from biomass pyrolysis alone [24,25]. This is because plastics possess high hydrogen contents which provide more hydrogen and accordingly increase the bio-oil yield [25]. Many researchers studied the catalytic pyrolysis of plastics, and co-pyrolysis of biomass/plastics to increase the yield of aromatic hydrocarbons [26–31]. Other researchers tried to increase the yield of aromatic hydrocarbons through the catalytic pyrolysis of torrefied biomass [32–34]. However, to the best of our knowledge, no researchers have studied the effect of using both torrefied wood and plastic on the yield of aromatic hydrocarbons. Therefore, the aim of this study was to increase the aromatic hydrocarbon yields in the bio-oil through the catalytic fast pyrolysis of torrefied wood/polystyrene and ZSM-5 as catalyst. The effects of different pyrolysis temperature on the yield and nature of aromatics produced will be discussed extensively.

2. Materials and methods

2.1. Materials

The torrefied wood of pine chips (TW) used in this study was obtained from Agri-Tech Producers, LLC South Carolina while the

commercial polystyrene (PS) was obtained from TDL Plastics Inc. The Zeolite type catalyst (HZSM-5) was purchased from Acros Organics (Zeolite without alumina acid sites). Ratio SiO₂/Al₂O₃ = 40). The catalyst was heated in an oven at over 110 °C for two hours to eliminate moisture.

2.2. Characterization of TW and plastic

TW and PS were ground individually in a Hamilton beach blender, and sieved to a particle size of about 1–2 mm. Elemental analysis (C, H, N and O) was determined for TW by Exeter Analytical Incorporation (EAI CE-440) elemental analyzer, the amount of oxygen was determined by difference. Thermal gravimetric analysis (TGA) was applied on both TW and PS samples to determine their optimum pyrolysis temperatures. TGA experiments were performed, using a SDT Q600 thermo gravimetric analyzer. In each experiment, 2 mg of TW and PS powdered samples were placed in the crucible of the thermo gravimetric analyzer. Each sample was heated from room temperature to 900 °C at the heating rate of 100 °C/min and then held at 900 °C for 20 min in an inert atmosphere. Pure nitrogen was used as the carrier gas with a flow rate of 40 mL/min to maintain the inert atmosphere for the samples.

2.3. Py-GC/MS experiments

PS, TW, TW/PS and TW/PS/Catalyst were individually homogenized, by mixing thoroughly in a mortar. About 3 mg of each sample was individually held in a CDS quartz tube and packed with quartz wool. The ratio of TW to PS was (4:1) in co-pyrolysis experiments, and the ratio of pyrolyzed sample (TW/PS) to catalyst was (9:1) in all catalytic experiments. Each prepared sample of PS, TW, TW/PS and TW/PS/Catalyst was pyrolyzed individually and the pyrolysis products were identified. Pyrolysis experiments were conducted using a 5200 model pyrolyzer (CDS analytical Inc.). Based on the TGA results for TW and PS, pyrolysis experiments were performed at four different temperatures (500, 550, 600 and 650 °C). These temperatures are higher than the thermal decomposition temperature of each sample. Each pyrolysis experiment was repeated three times to determine the consistency of the experimental results. The biomass heating rate was 1000 °C/s at 10 s. pyrolysis time for all experiments. The interface temperature was set at 300 °C with the ramp at 100 °C/min. The pyrolysis vapors were carried directly by ultrahigh purity helium carrier gas stream (99.99%) through the transfer line to a Perkin Elmer Clarus 500 Gas Chromatograph /Mass Spectrometer (GC/MS) system. The transfer line temperature was set at 300 °C and the carrier gas rate was 2 mL/min. The gas chromatograph was equipped with a DB-5MS capillary column of 30 m × 0.32 mm ID × 1 µm film thickness. Samples were injected in the split less mode and the injector temperature was 270 °C. The initial oven temperature of the GC was 40 °C for 4 min. and then programmed at a rate of 4 °C/min to 280 °C, with a total run of 72 min. The mass spectrometer detector was an electron impact ionization device operating at 70 eV with a source temperature of 210 °C and interface temperature of 225 °C. The chemical component data obtained from GC/MS has analyzed using a chemical integration program together with NIST mass spectral search library). The peak area percentages for the three runs were added up and the average, calculated for each identified compound. However compounds that were associated with some peaks were not identified.

3. Results and discussions

3.1. Characterization of torrefied wood and polystyrene

Table 1 shows the results of ultimate, proximate analysis and the calorific heating values of wood and TW. Elemental analysis

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