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A comparative study on co-pyrolysis of lignocellulosic biomass with polyethylene terephthalate, polystyrene, and polyvinyl chloride: Synergistic effects and product characteristics

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ABSTRACT

Co-pyrolysis of waste biomass and plastics was investigated to find out whether the quality of pyrolysis products was improved. For the sake of yield and compositional comparison, three polymers (polyethylene terephthalate, polystyrene, and polyvinyl chloride) and two biomasses (walnut shells and peach stones) were tested in a fixed bed reactor. The maximum bio-oil yield was obtained at 500 °C as 20.81 wt % for walnut shell and 18.30 wt %, for peach stone pyrolysis, then co-pyrolysis experiments were performed at 500 °C. Based on the experimental findings, blending of polyethylene terephthalate, polystyrene, and polyvinyl chloride into biomass affected product yield substantially. To gain more insight into the effect of polymers, liquid and solid products were analyzed by various analytical techniques. Results showed a significant modification on the chemical structure tars after co-pyrolysis, and tar yield increased up to 49.80 wt%. Meanwhile, modifying the structures and enhancing the quality of the tars and chars seemed possible by co-pyrolysis.

1. Introduction

Disposal of organic wastes is a serious environmental problem of mankind considering accelerated industrialization and population growth. The accumulation of waste and the "throw-away philosophy" result in several environmental problems, health issues and safety hazards, and prevent sustainable development in terms of resource recovery and recycling of waste materials. On the other hand, these wastes have a huge potential in lowering the dependence on fossil fuels and producing energy through waste-to-energy (WTE) processes (Herbert and Krishnan, 2016; Taherzadeh and Karimi, 2008). Such technologies have been a viable waste management strategy in establishing sustainable waste disposal methods, and are capable of delivering clean energy and providing better end products in comparison to other disposal methods (Shen et al., 2016). When availability, and economic and environmental benefits are considered as the most crucial factors for proper selection of materials to be used in WTE technologies, it can be seen that non-edible biomass wastes have received increased attention in recent years (Dewangan et al., 2016; Ning et al., 2013). There are many different technologies that are being applied in biomass utilization, including biological, physical and thermochemical conversion. Transformation of the wastes into bioenergy can be efficiently achieved applying thermochemical methods such as combustion, pyrolysis and gasification (Alvarez et al., 2014; Kajaste, 2014). As an effective and promising thermochemical conversion technology, pyrolysis offers several advantages in energy production since it is flexible due to convenient manipulation of process parameters to optimize the product yield based on preferences.

Through pyrolysis process, long-chain polymer molecules are thermally degraded into smaller, less complex molecules by being heated in the absence of oxygen (Sharuddin et al., 2016; Strezov et al., 2008). Pyrolytic oil can be used in boilers and diesel engines for power generation while it may also be used to obtain valuable and useful chemicals, such as flavoring and resins (Bhattacharjee and Biswas, 2017; Guo et al., 2010; Van Putten et al., 2013). The solid product of pyrolysis, char, can either be directly used as fuel since it has a high calorific value or it can be used as feedstock to prepare carbonaceous products such as activated

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carbon. Other potential benefits of char are nitrate leaching, adsorption of inorganic and organic contaminants and reduction of trace-gas emissions from soil and atmosphere (Chen, D. et al., 2016; Lu et al., 2012; Zhao, B. et al., 2018). On the other hand, the gas product can be considered as a mixture composed of carbon oxides, light hydrocarbons, and hydrogen which can be utilized as gas fuel (Chen et al., 2003; Solar et al., 2016). The production of synthetic fuel and value-added intermediates from biomass seems attractive considering renewable nature of biomass (Dorado et al., 2015; Hasan et al., 2017). Still, most of the studies about pyrolysis are mainly focused on how to increase the yield of pyrolytic oil that are produced from lignocellulosic biomass and enhance its properties. The major challenges in converting lignocellulosic biomass to "drop-in" liquid fuels are related to the feedstock properties (Perkins et al., 2018). This is due to several oxygenated products, such as sugars, aldehydes, ketones, acids, and phenols which can be formed during pyrolysis of biomass. Presence of such compounds both lowers the calorific value of bio-oil, causes corrosiveness and instability and hence liquid product of biomass pyrolysis, bio-tar, requires additional separation steps (Chen et al., 2014; Nigam and Singh, 2011; Ro et al., 2017). Therefore, current studies focus on catalytic pyrolysis, hydro-pyrolysis, hydrothermal treatment or co-pyrolysis techniques in order to improve the quality of bio-oil.

Recently, positive effects of plastic blending in biomass have been reported in the literature since plastics can effectively balance the C, H, and O content of the feedstock and eliminate disposal problems of plastics (Chen et al., 2017; Kumagai et al., 2016; Soganciogl u et al., 2017). Lignocellulosic biomass sources are hydrogen deficient, whose H/C ratio usually vary between 0 and 0.3, therefore when they are pyrolyzed, yields of petrochemicals are relatively low. On the other hand, plastic wastes mainly consist of polyolefin, with a higher H/C value than biomass sources. Hence, carbon and hydrogen will be exchanged during the co-pyrolysis reaction, and increase the quality of petrochemicals with co-feeding of plastics with biomass (Chattopadhyay et al., 2016). To put it in other words, polymer blending to biomass creates more free radicals and may suppress formation of long-chain hydrocarbon compounds (Shadangi and Mohanty, 2015). This synergistic effect among plastic-derived olefins and lignin, cellulose, and hemicellulose-derived fragments would lead to a strong improvement on the properties of bio-oils (Chen, W. et al., 2016; Zhao, Y. et al., 2018). Another benefit of co-pyrolysis can be stated as raw material sustainability since using waste mixtures or different feedstock types can help resolve issues related to the limited supply of some feedstock types. Furthermore, it is the least capital intensive process with low operating costs (Melendi-Espina et al., 2015; Oyedun et al., 2014).

In the literature, numerous studies are focusing on the co-pyrolysis of plastics and biomass, in order to investigate product yields and distributions together with product characteristics (Bernardo et al., 2009; Paradela et al., 2009; Sajdak, 2017). Results showed that, positive or negative synergy depend on the type and contact of components, pyrolysis duration, temperature and heating rate, removal or equilibrium of volatiles formed, and addition of solvents, catalysts, and hydrogen-donors. Among these factors, the types of blending feedstock are a major factor that can significantly influence the synergistic effects; thus, synergistic effects on co-pyrolysis can be complicatedly varied (Abnisa and Daud, 2014; Sajdak, 2017). For instance, blending polymers such as polyethylene, polypropylene, polystyrene, polyurethane to specific biomass samples is generally known to increase liquid product yield (Dewangan et al., 2016; Suriapparao et al., 2018; Chattopadhyay et al., 2016) According to the previous researches polyvinyl chloride results in increase in solid product yield (Ephraim et al., 2018; Lu et al., 2018). However, distinctive properties of each biomass species make impossible to reach a general consensus on precise polymer-biomass interactions during co-pyrolysis.

In this study, walnut shells (WS) and peach stones (PST) were selected as biomass species since they are popular plantations and grown in many countries worldwide. About 10 million hectares of land is used for the cultivation of walnut and its annual production is approximately 3.5 million metric tons. On the other hand, an area of 1.5 million hectares is harvested to produce approximately 23 million tons of peach stones throughout the world (FAO, 2017). Hence, a considerable amount of non-edible wastes is discarded during the processing of these fruits. To the best of our knowledge, co-pyrolysis of walnut shells and peach stones with PET (polyethylene terephthalate), PS (polystyrene), and PVC (polyvinyl chloride) has not been reported in the literature yet. These synthetic polymeric wastes selected due to the considerable amount of usage and hence waste generation in the industrial and daily life. PET and PS include aromatic rings in their repeating units which can be produced by the polymerization of ethylene glycol with terephthalic acid and styrene, respectively. On the other hand, PVC is one of the most-widely produced polymer through polymerization of vinyl chloride monomer. Therefore, the aim of this study is to investigate the effect of biomass and different polymer characteristics during co-pyrolysis to evaluate the potentials of the co-pyrolysis products for recovery of chemicals. For this purpose, effects of polymer blending on liquid and solid product characteristics were analyzed and discussed in detail.

2. Methods

2.1. Preparation and characterization of raw materials

In this study, two biomass samples including walnut shell (WS) and peach stones (PST) were used for investigation. Waste PET, PS, and PVC samples were obtained from the post-consumer polymer waste collection establishment in Turkey. After grinding, all samples were sieved to obtain a uniform particle size between 1 and 1.25 mm to be used in a fixed-bed reactor. On the other hand, a particle size between 112 μm and 224 μm was used for TGA. The blends were prepared by mixing the samples at a definite ratio of 50 wt %. Prior to pyrolysis and co-pyrolysis experiments, TGA was performed for the raw materials and blends in a Setreram-Labsys Evo thermobalance. In each analysis, approximately 10 mg of sample was put uniformly in an Al_2O_3 ceramic crucible and heated from 25 °C to 1000 °C at a constant rate of 10 °C min^{-1} in a nitrogen atmosphere with a flow rate of 20 ml min^{-1}.

2.2. Pyrolysis experiments

The pyrolysis experiments were conducted in a fixed-bed reactor system, which is illustrated in Fig. 1. In each trial, 10 g of raw material (or blend with a 50 wt %) was put inside the reactor, and then the reactor was closed tightly with an input pipe for inert gas connection and output pipe was connected to the liquid product collecting traps. Before each run, nitrogen was purged through the reactor for 10 min to ensure an inert atmosphere.

The pyrolysis experiments were performed to study the effect of pyrolysis temperature in the range 400–700 °C and then co-pyrolysis experiments were carried out at 500 °C. A thermocouple was installed near the center of the sample chamber to enable measurement of the temperature and the desired temperature was adjusted using an automatic PID controller. The volatile products left the reactor together with the inert gas and condensable gases were converted to liquid as the volatile products passed through the traps containing salty-ice. The liquid products were recovered