Synergistic enhancement of product quality through fast co-pyrolysis of acid pretreated biomass and waste plastic

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ABSTRACT

With the increasing global production of plastics, co-pyrolyzing biomass and waste plastics has emerged as a promising way to improve the quality of pyrolysis products. In the present study, the possibility of enhancing the synergistic interactions between biomass and plastics was explored by co-pyrolyzing acid pretreated corn stover (CS) and polyethylene (PE) in the presence or absence of zeolite catalyst. During non-catalytic co-pyrolysis, the use of acid-pretreated CS was found to synergistically reduce char yield and increase both the yield and quality of CS-derived pyrolysis oil. When acid-pretreated CS was catalytically co-pyrolyzed with PE, the yields of aromatic hydrocarbons and alkene increased whereas the yields of solid residue and carbon oxides decreased to a much greater extent than co-pyrolyzing raw CS and PE. The synergistic effect was least significant with raw CS and PE, suggesting the presence of alkali and alkaline earth metals (AAEMs) in the biomass hinder the occurrence of synergy. The positive synergy was strongest with acid-infused CS and PE. When acid-infused CS was co-pyrolyzed with PE, not only did the yield of phenolic monomers increase, but levoglucosan yield also increased significantly. During catalytic co-pyrolysis, acid-infused CS and PE also produced the highest yield of aromatic hydrocarbon and lowest yield of solid residue. This study also showed that co-pyrolysis with PE mitigates char agglomeration associated with pyrolyzing CS alone.

1. Introduction

Biomass found in forest residues, agricultural wastes, perennial grasses and municipal solid waste stream is considered as promising alternatives to petroleum for fuels and chemicals due to their abundant availability at low-costs and carbon-neutral nature. Among biomass conversion technologies, fast pyrolysis is attractive because of its ability to convert biomass into liquid product within seconds. The liquid, also called bio-oil, has a higher energy density than original biomass, thus can be used as low-quality fuels or further upgraded to transportation fuels and chemicals. Although promising, the poor quality of bio-oil hinders the commercialization of biomass pyrolysis cost competitively [1]. Bio-oil is a complex mixture of oxygenated compounds. It has a poor storage stability and a heating value lower than petroleum-based fuels, attributed to the intrinsic oxygen content and hydrogen deficiency in biomass. When biomass is catalytically pyrolyzed, the properties of biomass also causes low hydrocarbon yields and the formation of catalytic coke.

Along with the rapid increase in the global production of plastics, co-pyrolysis of biomass and waste plastics has received increasing attention in recent years [2–4]. The co-pyrolysis approach can improve

the quality of bio-oil and simultaneously solve various environmental problems related to waste plastic disposal. Waste plastics are attractive feedstock for co-pyrolysis because of their low oxygen content and higher hydrogen content. In fact, the main municipal plastic wastes, such as polyethylene, polypropylene, polystyrene, are hydrocarbons themselves with no oxygen. When co-pyrolyzed, high hydrogen content and low oxygen content in the waste plastics could compensate for the intrinsic hydrogen deficiency in biomass to produce bio-oil with higher heating values. The benefits of co-pyrolyzing biomass and plastics are not only limited to the additive effect. Previous studies have shown that the product yield and quality of pyrolysis oil were improved compared to converting individual feedstocks separately, contributed by synergistic effects between biomass and plastics [5–12]. Such synergistic effects were observed during both non-catalytic and catalytic co-pyrolysis.

The mechanisms of synergistic reactions between biomass and plastics were often studied by co-pyrolyzing the plastics with biomass compositions, such as cellulose, xylan or lignin. In addition to the three major compositions, biomass also contains naturally occurring alkali and alkaline earth metals (AAEMs). AAEM is known to have strong detrimental impacts on biomass pyrolysis [13–15]. However, the

presence of AAEM in the co-pyrolysis feedstock was overlooked and its role during co-pyrolysis remains unknown. While its concentration varies depending on biomass type, even a very small amount of AAEM can significantly increases the formation of pyrolysis char and light gases from biomass at the expense of decreasing bio-oil yield. It has shown that AAEM catalyzes the homolytic ring opening of carbohydrates and dehydration reactions instead of depolymerizing the polysaccharides [16]. During catalytic pyrolysis, the presence of AAEM also reduces hydrocarbon yields and promotes catalyst deactivation [17]. Regarding biomass pyrolysis, the common approach to reduce the detrimental effect of AAEM is to acid-pretreat biomass prior to pyrolysis [14,18–21]. For example, biomass is washed using a diluted acid solution to remove any acid-dissolving AAEM. Alternatively, biomass is infused with a small amount of acid so the catalytic effect of AAEM is passivated without having to physically remove the inorganics. It was reported that the infused acid reacts with AAEM in biomass to form chemically less-reactive, yet thermally-stable salts [22]. The previous results have shown that both the acid pretreatments can improve the quality of bio-oil by increasing the production of anhydrosugars and reducing the yields of less valuable light-oxygenates and water [21]. Nevertheless, it was also reported that acid pretreated biomass is challenging to pyrolyze continuously due to char agglomeration inside reactors [23,24]. The char agglomeration can cause reactor clogging and defluidization, eventually leading to a forced shut down of the reactors.

As described above, co-pyrolyzing biomass and waste plastics, and acid-pretreating biomass both can improve the quality of pyrolysis products although their working mechanisms are completely different. In the present study, non-catalytic and catalytic co-pyrolysis of acid-pretreated biomass and plastic were conducted to: (1) determine the effect of AAEM on co-pyrolysis of biomass and plastics; (2) investigate the potential benefit of co-pyrolyzing acid-pretreated biomass with waste plastic compared to pyrolyzing raw biomass with the plastic. It is hypothesized that using acid-pretreated biomass during co-pyrolysis could affect synergy between biomass and plastics, therefore changing the overall product distribution. Specifically, raw corn stover (CS), acid-washed CS or acid-infused CS were co-pyrolyzed with polyethylene (PE) in the presence or absence of zeolite catalyst. CS is the most abundant agriculture residue in the US [25,26]. Compared to pyrolyzing woody biomass, pyrolysis of CS produces much lower bio-oil yield (65–75 wt% vs. 40–50 wt%) because of the high AAEM content in herbaceous biomass in comparison to woody biomass [27,28]. PE was selected in this study since it is the most common waste plastic. To our best knowledge, co-pyrolysis of acid-pretreated biomass and plastic is investigated for the first time in this work.

2. Materials and methods

2.1. Feedstock preparation and characterization

CS was obtained from the BioCentury Research Farm at Iowa State University. The size of CS was reduced to less than 70 µm by ball milling. Acid-pretreated CS samples were prepared by pretreating as-received CS with sulfuric acid (98%, Sigma Aldrich). To prepare acid-washed CS, a 5 g of CS was first mixed with 100 ml of a 0.1 M sulfuric acid solution. The slurry was then stirred at room temperature for 4 h. After the solution is filtered, biomass was further washed with deionized water until the rinsed water became neutral. The washed biomass was then dried in a muffle furnace oven at 50 °C for 24 h. To prepare the acid-infused CS, the amount of sulfuric acid equivalent to 4% of the CS mass was first diluted in a 15 g of deionized water. The acid solution was then added to 5 g of CS. After being stirred at room temperature for 2 h, the slurry was dried in the oven overnight. The concentration of acid infusion was chosen based on the method described in Ref. [22]. Proximate and ultimate analysis of the as-received raw CS and acid pretreated CS were conducted using standard methods. The inorganic

content in the raw CS was determined using Inductively Coupled Plasma (ICP) method.

PE powders with the particle sizes between 53 and 75 µm were purchased from Sigma Aldrich. NH_4ZSM-5 (CBV 2314, SiO_2/Al_2O_3 = 23:1) was purchased from Zeolyst International. The as-received catalyst was activated at 550 °C for 5 h to obtain a proton form HZSM-5 zeolite, and then pelletized and screened to 50–70 mesh sizes. Authentic chemicals of aromatic hydrocarbons, sugars, light-oxygenated compounds and phenolic compounds were purchased from Sigma Aldrich, Acros Organics and Fisher Scientific, respectively. A gas mixture (helium, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_4, C_4H_8 and C_5H_{10}) was customer-ordered from Praxair.

2.2. Pyrolysis

Fast pyrolysis was conducted in a Tandem micro-pyrolyzer system (Rx-3050 TR, Frontier Laboratory, Japan). The micro-pyrolyzer consists of two reactor ovens sequentially connected. The temperatures of the two ovens can be controlled independently from room temperature to 900 °C at 1 °C intervals. The schematic setup of the pyrolyzer can be found from previous literature [29]. A quartz tube was inserted inside the second reactor oven to hold catalyst if a separate catalyst bed is needed. In this study, an empty quartz tube was loaded in the oven.

For non-catalytic pyrolysis, 500 ± 10 µg of CS, PE or the mixture of CS and PE (1:1 ratio) was placed in a deactivated stainless steel cup, which was then dropped into the first reactor oven for pyrolysis. In the cases of catalytic pyrolysis, 250 µg of CS and PE were premixed with 5 mg of catalyst in a sample cup. The temperatures at both the reactor ovens were 600 °C, and helium was used as the carrier gas.

The volatile products evolved from non-catalytic or catalytic pyrolysis were characterized by an online Agilent 7890B Gas Chromatograph (GC) equipped with a mass spectrometer (MS), flame ion detector (FID) and thermal conductivity detector (TCD). Helium was also used as the purge gas in the GC, and its flow rate at the front inlet was 156 mL/min with a split ratio of 50:1. The temperature of the GC oven was kept at 40 °C for an initial 3 min, then increased to 280 °C at a heating rate of 6 °C/min. Finally, the GC was held at 280 °C for 3 min. Phenomenex ZB 1701 (60 m × 0.250 mm × 0.250 µm) column was used in both the MS and FID, and a Porous Layer Open Tubular (PLOT) (60 m × 0.320 mm) was used in the TCD. The vapor products were identified by the MS, and then quantified by the FID using calibration curves of individual compounds. Non-condensable gases were measured by the TCD that was pre-calibrated with the standard gas mixture. For non-catalytic pyrolysis, the mass of pyrolysis char was determined by weighing the sample cup before and after pyrolysis. The pyrolysis char was also analyzed using a CHNS elemental analyzer (Vario Micro Cube) to determine its carbon content. For catalytic pyrolysis, the mixture of char and used catalyst remaining in the sample cup was analyzed using the CHNS elemental analyzer for carbon content in the solid residue. In this study, the carbon mole-based product yields were reported for both non-catalytic and catalytic pyrolysis, and they were determined using following equation:

Carbon yield of a product (C%)

$$= \frac{The\ mole\ of\ carbon\ in\ the\ product}{The\ total\ mole\ of\ carbon\ in\ the\ feedstock} \times 100\%$$

During catalytic pyrolysis, the selectivity of individual aromatic or aliphatic hydrocarbons was determined using below equation:

Product selectivity(%)

$$= \frac{The\ mole\ of\ carbon\ in\ an\ aromatic\ or\ aliphatic\ hydrocarbon\ product}{The\ total\ mole\ of\ carbon\ in\ the\ aromatic\ or\ aliphatic\ hydrocarbon\ group} \times 100\%$$

In the above equation, the aromatic hydrocarbon group consists of all single and polyaromatic ring hydrocarbon products. The aliphatic hydrocarbon group consists of all alkene and alkane products.

Raw or acid pretreated CS with and without PE were also pyrolyzed