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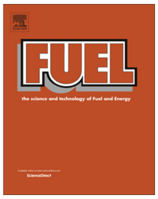

Catalytic co-pyrolysis of biomass and polyethylene in a tandem micropyrolyzer

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ABSTRACT

In the present study, catalytic fast co-pyrolysis of biomass and polyethylene (PE) was studied in a tandem micro-pyrolyzer using ZSM-5 as the catalyst. Cellulose, xylan and milled wood lignin were co-pyrolyzed with PE in both the presence and absence of catalyst to investigate the interaction between biomass and PE during thermal depolymerization and the following catalytic upgrade of the pyrolysis vapor. Co-pyrolysis with PE was found to increase the yields of furans and double anhydrosugar from cellulose up to 45%. Co-pyrolysis of xylan and PE increased not only the yields of furans and double anhydrosugar, but also the yield of acetic acid by 45%. Depolymerization of lignin was strongly promoted by PE as the yields of various phenolic monomers increased up to 43%. It was also found that the amounts of pyrolysis char and carbon oxides produced from biomass compounds decrease when co-pyrolyzed with PE. The presence of cellulose, xylan or lignin, on the other hand, facilitated depolymerization of PE by increasing the yields of olefins and alkanes with shorter carbon chains. When the pyrolysis vapor was upgraded by HZSM-5 zeolite catalyst, synergy increased the yields of hydrocarbons and suppressed the formation of catalytic coke, compared to when biomass compounds and PE were independently converted. During catalytic co-pyrolysis of cellulose and PE, the increase of the aromatic hydrocarbon yield was accompanied by the decrease in the selectivity of ethylene and propylene and no significant increase of total aliphatic hydrocarbons (i.e., the sum of olefins and alkanes), suggesting Diels–Alder reaction as the dominant reaction. On the other hand, catalytic co-pyrolysis of PE with xylan or lignin increased both the yields of aromatic and aliphatic hydrocarbons. The yield of alkanes decreased most significantly in the mixture of lignin and PE, suggesting that phenolic compounds act as strong hydrogen acceptors when they deoxygenate. In the present study, red oak and PE were also catalytically co-pyrolyzed and the effects of pyrolysis temperature and catalyst temperature on product distribution and the extent of synergy were investigated. Both higher pyrolysis temperature and catalyst temperature were able to reduce the formation of catalytic coke and increase the yield of aromatic hydrocarbons monotonically. However, the maximum yield of aliphatic hydrocarbons was obtained at the intermediate pyrolysis temperature or catalyst temperature. Synergy between biomass and PE was consistent, regardless of changing pyrolysis temperatures. In comparison, the synergy became less significant when catalytic temperature was increased.

1. Introduction

Lignocellulosic biomass is a carbon neutral and renewable substitute for fossil fuels in the production of hydrocarbons and other platform chemicals. Pyrolysis of biomass has been widely studied in different scales due to its simple process and economic advantages [1,2]. When it is fast pyrolyzed and the pyrolysis vapor is rapidly quenched, up to 75% of biomass converts to bio-oil that has higher energy density than biomass and can be easily transported [3]. Bio-oil is a mixture of oxygenated compounds; thus, it has to be catalytically deoxygenated before becoming biofuels. Catalytic pyrolysis is an approach that deoxygenates biomass during pyrolysis, before the vapor condenses. Compared to upgrading condensed bio-oil, catalytic pyrolysis eliminates the secondary reactions of bio-oil during storage and re-heating. Catalytic pyrolysis can be a simple and cost-effective way to produce hydrocarbons in a single process. However, similarly to the problems also found in the catalytic upgrading of bio-oil, catalytic pyrolysis

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Table 1
Elemental composition of feedstock.

Feedstock	Elemental analysis (wt%)			
	C	H	N	O[a]
Red oak	47.16	5.39	0.12	47.24
Cellulose	43.87	5.61	1.95	48.57
Xylan	42.02	5.17	0.11	52.7
Milled wood lignin	58.3	6.01	0.06	35.6
PE	85.71	14.29	0	0

[a] Determined by difference.

of biomass usually produces low yields of hydrocarbons and large amounts of solid residues. Rapid deactivation of catalyst caused by catalyst coke reduces the lifetime of the catalyst and the need for frequent catalyst regeneration could make the process impractical. The aforementioned problems are mostly attributed to the intrinsically high oxygen content and hydrogen deficiency of biomass. Catalytic hydropyrolysis using hydrogen gas at elevated pressures removes oxygen in biomass by forming water and therefore enhances hydrocarbon yields and reduces solid residues [4,5]. However, continuously feeding dry biomass into high-pressure reactors could be challenging. Alternatively, hydrogen can also be supplied externally, by co-pyrolyzing biomass and hydrogen rich materials at atmospheric pressure [6]. Co-pyrolysis with plastics is particularly attractive since waste plastics are abundantly available at low-cost. Many plastic materials are rich in hydrogen and contain less oxygen. For example, polyethylene (PE) is a hydrocarbon-based polymer containing virtually no oxygen, and also accounts for up to 40% of total plastic waste [7]. Although some are recycled, a significant portion of the waste plastics eventually ends up in landfill sites, creating a number of environmental problems. Thus, co-pyrolysis of biomass and plastics also has the additional benefits of promoting a cleaner environment and energy recapture.

While co-pyrolysis of biomass and different forms of plastics were frequently studied, it should be noted that most studies were conducted in fixed reactors [8]. Although slowly pyrolyzing the mixed feedstock for extended reaction time could enhance the decomposition of plastic polymers to smaller molecular units, this pyrolysis method is detrimental to biomass conversion. When slowly pyrolyzed, biomass is preferentially decomposed into less valuable char and light oxygenated gases, as opposed to bio-oil. In recent years, catalytic fast co-pyrolysis of biomass and plastics was studied by a few research groups using micro-pyrolysis reactors [9–13]. The studies showed that positive synergy between biomass and plastics increases hydrocarbon yields and reduces solid residues. It was also suggested that the Diels–Alder reaction among carbohydrate-derived furans and plastic derived olefins in the catalytic site improves hydrocarbon yields during co-pyrolysis. Nevertheless, significantly varied results were observed among the literature. For example, the yields of aromatic hydrocarbons were varied from less than 10% to over 35%, despite that cellulose and PE were co-pyrolyzed using the same catalyst (ZSM-5) [9,11]. The reaction mechanism between biomass compounds and plastics can be very complex [10] and requires further investigation. For example, Diels–Alder reaction does not occur between lignin and plastics. Catalytic co-pyrolysis of biomass and plastics involves two different types of interaction: the interaction among biomass and plastics during thermal decomposition by pyrolysis (i.e., thermal interaction) and the interaction between the decomposition products at the catalyst site (i.e., catalytic interaction). Thermal interaction is often ignored when the synergy of catalytic co-pyrolysis is described, since it is assumed that the reaction time during fast pyrolysis is too short (i.e., within seconds) for biomass and plastics to thermally interact [14]. On the other hand, we recently conducted fast pyrolysis of biomass and plastic in a fluidized bed reactor without catalyst and found that the co-pyrolysis products were not a mixture of the pyrolysis products of biomass and plastics by simple addition [15]. This suggests that catalytic co-pyrolysis could proceed in a much more complex reaction pathway than it was previously proposed by others [9–12].

In the present study, biomass model compounds and PE were co-pyrolyzed using a tandem micropyrolyzer system with and without downstream catalytic bed to determine thermal interaction and catalytic interaction between the different feedstock materials. PE was selected since it is the most abundant plastic in the waste stream and also has been reported to have the strongest synergy with biomass during co-pyrolysis when compared to other types of plastics [9,11]. In this study, red oak and PE were also co-pyrolyzed. Pyrolysis and catalyst temperatures were changed independently and the product distribution and synergy at varied reaction conditions were investigated.

2. Materials and methods

2.1. Materials

Northern red oak (Quercus Rubra) was purchased from Wood Residues Solutions (Montello, WI). The bark free chips were first ground by a mill cut and then sieved to a particle size under 75 μm. Cellulose, xylan, and PE were purchased from Sigma Aldrich. The particle sizes of PE were between 53 and 75 μm. Milled wood lignin was extracted from red oak following the procedure described by Bjorkman [16]. The elemental composition of red oak and its model compounds is given in Table 1.

HZSM-5 zeolite (CBV 3024 E, $SiO_2/Al_2O_3 = 30:1$) was purchased from Zeolyst International. The catalyst was first activated in a muffle furnace at 550 °C for 4 h and then pelletized and screened to 50–70 mesh size before being used.

2.2. Pyrolysis experiment

Fast pyrolysis was conducted in a Tandem micro-pyrolyzer system (Rx-3050 TR, Frontier Laboratories, Japan). The schematic setup of the system can be found elsewhere [17]. The Tandem micro-pyrolyzer consists of two stage reactors; a pyrolysis reactor and a catalytic bed. The temperature of each reactor can be controlled independently and the maximum allowed temperature is 900 °C.

For catalytic pyrolysis, an approximately 0.5 mg sample was placed in a deactivated stainless steel cup, and then dropped into a preheated oven in the first reactor. The pyrolysis vapors were then carried by helium gas to the catalyst bed loaded with 10 mg of catalyst. During co-pyrolysis tests, the mixture of 0.25 mg PE and either 0.25 mg red oak or its model compounds (i.e., cellulose, xylan or milled wood lignin) was placed inside of the cup. For non-catalytic pyrolysis, the catalyst bed was replaced with an empty quartz tube and the above tests were repeated.

2.3. Characterization of pyrolysis products

An Agilent 7890A gas chromatography (GC) with a three-way splitter was used to separate the volatile products from the micro-pyrolyzer. The GC oven temperature was kept at 40 °C for 3 min, then ramped to 250 °C with a heating rate of 10 °C/min, where it stayed for an additional 6 min. The front inlet temperature was kept at 280 °C to prevent the condensation of the products. Two ZB-1701 (60 m × 250 μm × 0.25 μm) capillary columns were connected to mass spectrometer (MS, 5975C, Agilent, USA) and flame ionization detector (FID), respectively. The volatile

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