



Catalytic fast pyrolysis of a wood-plastic composite with metal oxides as catalysts



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ABSTRACT

The catalytic fast pyrolysis of a poplar wood-polypropylene composite (WPP) was investigated using Py-GC/MS in the presence of ZnO, CaO, Fe₂O₃ and MgO. The synergistic effects between wood and plastic components in both non-catalytic and ZnO-catalyzed pyrolysis of WPP were studied. CaO facilitated the removal of oxygen due to its strong basicity, eliminating carboxylic acids and phenols from the products, while slightly increasing cyclopentanones and alkenes. MgO has weaker deoxygenation but stronger chain scission activities versus CaO, and significantly enhanced the alkene yields. Alkene yields were highest using ZnO among the four catalysts. ZnO increased ketone and phenol yields while reducing carboxylic acids. Aromatics were identified in the presence of Fe₂O₃. A synergistic effect between poplar wood and PP in the uncatalyzed pyrolysis of WPP increased the yields of carboxylic acids, phenols and light alkenes, while it reduced carbonyl-containing oxygenates such as aldehydes, ketones and furans. The synergy in the ZnO-catalyzed pyrolysis of WPP further enhanced the formation of monomeric phenols and alkenes.

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1. Introduction

Wood-plastic composites (WPCs) refer to any composites that contain both biomass and plastics (Ashori, 2008). In recent years, WPCs have gained importance in the material market due to their good mechanical strength and durability. The global market for WPCs is expected to increase from nearly 3.1 million metric tons in 2014 to 5.6 million metric tons in 2019, with a compound annual growth rate of 12.7% (Research, 2014). Although WPC wastes can be recycled and reprocessed several times, the mechanical properties progressively decrease because of macromolecular degradation (Beg and Pickering, 2008). These plastic-containing wastes are non-biodegradable and unfriendly in the environment. Recently, the energy recovery technologies such as pyrolysis are receiving more attentions (Chen et al., 2014). Thus, WPC wastes can be removed from environment via fast pyrolysis and converted into biofuels.

The liquid products produced from WPC wastes pyrolysis contain significant fractions of biomass-derived oxygenated compounds and plastic-derived waxy hydrocarbons, which cannot be directly used as transportation fuels and need further upgrading (Li et al., 2014). Several upgrading methods have been developed in recent years including hydrotreating, catalytic cracking, esterification and other processes (Bridgwater, 2012). As known, catalytic pyrolysis is a promising way to improve bio-oil quality by deoxygenation and cracking. A wide variety of zeolites, particularly ZSM-5, have been investigated in catalytic pyrolysis (Custodis et al., 2016; Du et al., 2016; Hu et al., 2017; Wong et al., 2016). ZSM-5 can catalyze the pyrolysis-derived oxygenates into aromatics through a series of reactions (Carlson et al., 2010). Although zeolites are effective in the removal of oxygen, but the liquid yields are found low. Moreover, zeolites deactivate rapidly by coking due to both their surface acidity and pore structure.

Due to their low cost and accessibility, metal oxides have gained attentions in catalytic pyrolysis processes. Metal oxides were also found to be effective on the removal of oxygen (Guda and Toghiani, 2016; Pütün, 2010). Lin et al. (Lin et al., 2010) studied white pine fast pyrolysis in the presence of CaO in a fluidized reactor. The reduction of levoglucosan and acetic acid indicated that

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the glycosidic bond rupture route was transformed to the decomposition and reforming route by CaO. And the side-chain-detachment reaction pathway in lignin was enhanced by CaO, resulting in the increase of phenol and diols. Veses et al. (2014) observed a remarkable decrease of bio-oil acidity and oxygen content during wood catalytic pyrolysis using calcium-based materials in an auger reactor at 450 °C. They suggested that calcium-based materials could not only fix the CO₂-like compounds but also promoted the dehydration reactions. Nokkosmäki et al. (2000) reported that catalyzing biomass pyrolysis with ZnO improved the oil stability without substantial loss of oil yield. Torri et al. (2010) have investigated the catalytic pyrolysis of pine sawdust over various metal oxides (Fe₂O₃, CuO, and ZnO) and found different catalytic effects with these metal oxides. López et al. (2011) studied the catalytic pyrolysis of plastic wastes using red mud, which is a complex mixture based on oxides such as Fe₂O₃, Al₂O₃, TiO₂, MgO, CaO and SiO₂. They found that red mud increased gas yields, decreased liquids viscosity and promoted liquids aromatization. However, no reports have focused on metal oxide-catalyzed pyrolysis of WPCs.

Actually, WPCs pyrolysis has unique advantages compared to the independent pyrolysis of biomass and plastics. The co-pyrolysis oil from wood/plastic mixtures exhibited higher carbon and hydrogen contents, lower oxygen contents, and higher heating values than bio-oil produced from only biomass pyrolysis (Abnisa et al., 2013; Bhattacharya et al., 2009; Yang et al., 2016). Synergistic effects were observed in biomass/plastic co-pyrolysis, which enhanced the liquid quality and quantity (Chen et al., 2016; Dong et al., 2007; Hassan et al., 2016; Kumagai et al., 2016). The upgrading effect was attributed to the interaction between free radical intermediates derived from both biomass and plastics as well as hydrogen transfer reactions in the co-pyrolysis process (Abnisa and Wan Daud, 2014; Xue et al., 2015). The pyrolysis of WPCs reported earlier by our group exhibited advantageous synergistic effects over corresponding co-pyrolyses of wood/plastic mixtures, due to intimate contact between wood fibers and plastic in the feed particles (Lin et al., 2017).

Herein, the upgrading of fast pyrolysis vapors of a poplar wood/polypropylene composite (WPP) over four metal oxide catalysts (ZnO, CaO, Fe₂O₃ and MgO) is reported using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The product compositions of uncatalyzed and catalyzed WPP fast pyrolyses were compared to reveal the catalytic effects of these four metal oxides. The interactions between poplar wood and polypropylene with or without ZnO were also studied in detail.

2. Experimental section

2.1. Materials

Isotactic-polypropylene (PP) (T30S, pellet, melt flow index 3.0) was purchased from Daqing Petrochemical Co., China. Dried 40–80 mesh poplar wood flour was first mixed with PP pellets in a high-speed mixer for 15 min in a 1:1 mass ratio. Then this mixture was extruded through a counter rotating twin-screw extruder to form WPP composite particles. The processing parameters were

reported in previous manuscript (Lin et al., 2015). This WPP composite, poplar wood and PP pellets were milled in a high-speed rotary cutting mill and the resulting particles were sieved to 100–120 μm respectively. The sieved particles were dried at 105 °C overnight before fast pyrolysis. Four metal oxides including ZnO, CaO, α-Fe₂O₃ and MgO (≥98.0%, AR) were purchased from Tianjin ZhiYuan Reagent Co., Ltd. These catalysts were calcined at 600 °C for 2 h and ground to particle size less than 50 μm prior to use.

The elemental analyses of poplar wood, PP and WPP powders were obtained using a EuroVEC-TOR EA3000 elemental analyzer. The oxygen content was calculated by difference. Dibutyl phthalate was added into PP as plasticizer, thus the oxygen was identified as shown in Table 1. Addition of PP significantly increased the carbon and hydrogen contents of WPP, and the oxygen content of this WPP composite (25.9%) was far lower than that of poplar wood (44.5%) (Table 1). The elemental analysis showed that the poplar wood/PP mass ratio in WPP was close to 1, indicating good uniformity was obtained upon extruding the original weighed 1:1 poplar to PP extruder feed.

2.2. Py-GC/MS

Pyrolysis experiments were conducted in a CDS5200 pyroprobe device directly connected to an Agilent 6890N gas chromatograph (GC) mated to an Agilent 5973i mass spectrometer (MS). The sample (0.5 mg) was placed in the middle of the pyrolysis tube and the catalyst was located next to the sample at both ends of the tube as given in previous manuscript (Lin et al., 2015). The sample to catalyst mass ratio was 1:4. WPP pyrolysis experiments were performed at 500, 550, 600 and 650 °C for 60 s at the heating rate of 20 °C/ms. The effect of different temperatures on product distribution of WPP pyrolysis was shown in Fig. S1. It was observed that 600 °C was the optimal pyrolytic temperature. Therefore, the pyrolysis temperature was set at 600 °C and held for 60 s, with a heating rate of 20 °C/ms. Thus, it took about 28 ms to heat samples from ambient temperature to 600 °C. The relative high pyrolysis temperature and long pyrolysis time were mainly attributed to the good thermal stability of PP. Every experiment was replicated at least three times and specific results were averaged. The transfer line was maintained at 285 °C, respectively. The pyrolysis products were separated on an Agilent DB-17 ms capillary column (30 m × 0.25 mm × 0.25 μm film thickness). The split ratio was 50:1 with a helium carrier gas flow of 1 mL/min. The GC oven temperature was held at 40 °C for 4 min and then heated to 230 °C at 5 °C/min. After holding for 2 min at 230 °C, the oven was heated at 10 °C/min to 280 °C and held for 5 min. The mass spectrometer was operated in EI mode at 70 eV over the *m/z* range from 40 to 500 amu. Peak identification was carried out using the NIST 02 mass spectral library. Peak areas were integrated automatically by setting initial threshold of MS signal integration parameter as 18 and setting baselines automatically. All the experiments were done in batches, and the sensitivity of MS detector was constant.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.wasman.2018.07.021>.

Table 1
The ultimate analyses of poplar wood, PP and WPP.

Sample (daf, %)	C	H	O ^a	N	S
Poplar wood	49.10 ± 0.79	6.28 ± 0.16	44.49 ± 0.96	0.13 ± 0.01	–
PP	83.44 ± 0.22	13.26 ± 0.04	3.26 ± 0.18	0.04 ± 0.00	–
WPP	64.79 ± 0.15	9.24 ± 0.63	25.89 ± 0.89	0.08 ± 0.00	–

^a Calculated by difference.

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