Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of waste plastics

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ABSTRACT

In the present study, polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) were pyrolyzed using HZSM-5 zeolite in a tandem micro-pyrolyzer to investigate the effects of plastic type, catalyst and feedstock contact mode, as well as the type of carrier gas on product distribution. Among the four plastics, PS produced highest aromatic yields up to 85% whereas PE and PP mainly produced aliphatic hydrocarbons. In comparison to *ex-situ* pyrolysis, *in-situ* pyrolysis of the plastics produced more solid residue but also promoted the formation of aromatic hydrocarbons, except PS. For PS, *ex-situ* pyrolysis produced a higher yield of aromatics than *in-situ* pyrolysis, mostly contributed by high styrene yield. During *in-situ* pyrolysis, the catalyst reduced the decomposition temperatures of the plastics in the order of PE, PP, PS and PET from high to low. Hydrogen carrier gas reduced solid residue and also increased the selectivity of single ring aromatics in comparison to inert pyrolysis. Hydrogen was more beneficial to PS and PET than PE and PP in terms of reducing coke yield and increasing hydrocarbon yield. The present study also showed that catalytically co-pyrolyzing PS and PE, or PET and PE increases the yield of aromatics and reduces the yield of solid residue due to hydrogen transfer from PE to PS or PET and alkylation reactions among the plastic-derivatives.

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1. Introduction

As one of the most important petroleum-based materials, plastics have significantly contributed to our modern society. Plastic production has been increasing 3–4% annually since 1990s [1]. The plastic consumption is projected to increase dramatically in the developing countries due to the economic expansion [2,3]. On the other hand, the disposal of end-life plastics has become significant environmental and economic issue. Not only is transporting bulky and large quantity of waste plastics to remoted landfills costly, non-biodegradable plastics continue to invade the valuable land resource [4,5]. Waste-to-energy technologies enable converting waste plastics into heat, hydrocarbon fuels and chemicals, therefore reducing the amount of plastics to be landfilled [6]. The common waste plastics include polyethylene (PE, both LDPE and HDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET). Pyrolysis products of plastics include pyrolysis oil, char and light gases. Among them, pyrolysis oil is the main product and usually reaches optimum yield when pyrolysis temperature is around 500 °C [7]. Often, pyrolysis products of plastics need downstream separation and upgrading due to the wide range of carbon numbers among the products. Typically, the carbon chain length of the liquid products from pyrolysis of PE or PP ranging from C_5 to C_{30}. The products with longer chain lengths are waxy materials upon condensation. The wax has low volatility and octane number, thus requiring additional cracking step in order to be used as liquid fuels. Moreover, the formation of waxy materials may also result in clogging and defluidization in pyrolysis reactors [8]. Catalytic pyrolysis of plastics is a method for upgrading the pyrolysis products before the vapor condenses by introducing catalyst during pyrolysis. Upon catalytic pyrolysis, the final products could have a narrower carbon-number distribution and better product selectivity [9,10].

In general, polyolefins (e.g., PE, PP and PS) are more easily cracked with acid catalyst [11]. Zeolite catalyst (e.g., HZSM-5, HY, Hβ) or zeolite based catalysts (e.g., FCC) are frequently chosen to crack polyolefins because these catalysts contain abundant Brønsted and Lewis acid sites [12]. For polyester (e.g., PET) depolymerization, base catalysts, such as calcium oxide and sodium carbonate, are also used [13–15].

The results of catalytic pyrolysis are affected by a number of factors [9,16–19]. For example, Wong et al. [19] pyrolyzed LDPE

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in a fixed bed reactor and found that the yield of pyrolysis oil and its composition depend on the catalyst amount, feeding rate of plastics, carrier-gas flow rate and pyrolysis temperature. Lopez et al. [9,18] converted HDPE in a conical spouted reactor by mixing the plastic with HZSM-5 catalysts with different acidities and reported that zeolite acidity and pore structure affect the product selectivity and coke formation. In addition to the well-studied parameters, the contact mode of the feedstock and catalyst could also affect the product distribution during pyrolysis. During *in-situ* catalytic pyrolysis, catalyst and feedstock are physically mixed during pyrolysis. The examples include pyrolyzing the premixed plastics and catalyst using batch reactors, or feeding plastics into a fluidized reactor or conical spouted bed reactor and allowing the solid plastics to mix with the catalyst and sand inside the reactor [9,20,21]. Alternatively, plastics are thermally pyrolyzed first and the evolving pyrolysis vapors are sent to downstream catalytic bed before the vapor exists the system, which is referred as *ex-situ* catalytic pyrolysis [22,23]. *Ex-situ* catalytic pyrolysis is also denoted as a stage pyrolysis consisting of pyrolysis step and catalysis step. Although the products with improved quality are obtained upon the completion of pyrolysis, advantages and disadvantages of *in-situ* and *ex-situ* pyrolysis are also noted. *In-situ* catalytic pyrolysis is simple and no mechanical modification of existing reactors is required. It also potentially reduces the energy required for pyrolysis by lowering decomposition temperatures. However, recovering used catalyst from its mixture with solid residue is difficult during *in-situ* pyrolysis. The solid residue could also facilitate deactivation of catalyst, especially if the feedstock is high in ash content or metal impurities. Compared to *in-situ* catalytic pyrolysis, *ex-situ* catalytic pyrolysis requires external catalytic bed. The temperatures in the pyrolysis unit have to be moderately high to ensure pyrolysis vapor to be upgraded at the catalyst bed. On the other hand, catalyst regeneration is much simpler with *ex-situ* catalytic pyrolysis. *Ex-situ* catalytic pyrolysis is also particularly attractive in converting high ash content feedstock or the feedstock tends to form char [24,25]. In addition, the overall product distribution and selectivity of the products could be varied between *in-situ* catalytic pyrolysis and *ex-situ* catalytic pyrolysis because of the different contact modes between catalyst and feedstock during pyrolysis. Despite aforementioned differences, few studied *in-situ* and *ex-situ* catalytic pyrolysis of common waste plastics [26].

The type of carrier gas during catalytic pyrolysis could also affect the conversion of the plastics. Although catalytic pyrolysis of plastics was mostly conducted under inert environment, using reactive carrier gas could potentially improve the yields of desired products. It has been reported that catalytic hydropyrolysis of biomass (i.e., H_2 as the carrier gas) reduces coke yield and promotes hydrodeoxygenation of biomass [27]. Hydrogen could quench reactive radicals to inhibit polymerization reactions. Hydrocracking also reduces the formation of high molecular weight products [28]. Sun et al. previously reported that the yields of styrene monomer increases when PS was converted in a fixed bed reactor in the presence of H_2 using Pt-Ce/α-Al$_2$O$_3$ and Rh-Ce/α-Al$_2$O$_3$ as the catalysts [29]. However, catalytic hydropyrolysis was seldom investigated with other plastics.

In the present study, *in-situ* and *ex-situ* catalytic pyrolysis of waste plastics were investigated. The plastics, including PS, PET, PE and PP, were converted in a tandem micro-pyrolyzer using HZSM-5 zeolite as the catalyst and the product distribution was analyzed. HZSM-5 zeolite was selected because it has an excellent cracking and deoxygenation abilities. HZSM-5 is also known for its low deactivation rate and efficient regeneration, in comparison to other types of zeolite catalysts [30]. The *in-situ* and *ex-situ* catalytic pyrolysis of the plastics were also performed using H_2 as the carrier gas. In addition, PE was also catalytically co-pyrolyzed with PS or

PET to investigate possible synergy between the hydrogen rich plastic and the hydrogen deficient plastics.

2. Experimental

2.1. Material

PE was purchased from Sigma-Aldrich. PP, PS and PET were purchased from Yangli Tech Company, China. The purity of all plastics is above 99%. The range of particle size of the PE with ultra-high molecular weight is between 53 and 75 μm. The particle sizes of other plastics are also less than 75 μm. Characterization of the plastics is listed in Table 1. The elemental compositions were calculated based on the molecular formulas of the plastics because of the high purity of the samples.

The standard chemicals of aromatic hydrocarbons were purchased from Sigma Aldrich. The gas standards for calibration, which include CO, CO_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6 and C_5H_{10}, were purchased from Praxair, USA.

HZSM-5 zeolite (CBV 2314, SiO_2/Al_2O_3 = 23:1) was purchased from Zeolyst International. The ammonium form zeolite was calcinated inside a muffle furnace at 550 °C for 5 h with sufficient air flow. The activated catalyst powders were pelletized using a hydraulic pressure pelletizer. The pellets were then crushed and screened to 50–70 mesh size.

2.2. Pyrolysis and analysis

The pyrolysis experiment was carried out in a Tandem micro-pyrolyzer (Frontier Lab, Japan). The reactor system consists of two sequential furnaces and the temperature of each furnace can be adjusted from room temperature to 900 °C. The first furnace is a pyrolysis reactor. A removable quartz tube packed with catalyst is placed inside second furnace. The two furnaces are 5 cm apart and connected by a needle with heat insulation. In the reactor system, sample was loaded to a deactivated stainless cup and then dropped into the preheated first furnace. The heating rate of the sample in the reactor is estimated to be about 250 °C/s [31]. The pyrolysis vapor of the sample was converted in downstream catalyst-bed and the final products exiting the second furnace was directly analyzed by an online Agilent GC/MS-FID-TCD system (Agilent 6890) for chemical composition. During pyrolysis, He or H_2 was used as the carrier gas in both the micro-pyrolyzer and GC/MS. The flow rate of the carrier gas in the micro-pyrolyzer was 156 mL/min. Thus, the residence time of pyrolysis vapor in the reactor is less than a second. The GC oven temperature was initially kept at 40 °C for 3 min, increased to 280 °C with a heating rate of 6 °C/min, and then held at 280 °C for another 3 min. The front-injector temperature was set at 280 °C to prevent product condensation. Two Phenomenex ZB-1701 (60 m × 250 μm × 0.25 μm) capillary columns were separately connected to a mass spectrometer (MS 5975 C, Agilent, USA) and flame ionization detector (FID). A Porous Layer Open Tubular (PLOT) column (60 m × 0.320 mm) (GS-GasPro, Agilent, USA) was connected to a thermal conductivity detector (TCD). The products were first identified by the MS and then quantified by FID. For quantification, five different concentrations of each compound were injected into the GC/MS-FID-TCD to generate a calibration curve with regression coefficient >99%. Non-condensable-gases (NCGs), which includes carbon oxides and light hydrocarbons were quantified by the TCD using the standard gas mixture.

During pyrolysis, the temperatures of both the furnaces were set at 600 °C to ensure the plastics to decompose within the short pyrolysis time. For *ex-situ* catalytic pyrolysis, a 500 μg of plastic sample was pyrolyzed in the first furnace. For catalytic co-