



## In-situ catalytic co-pyrolysis of yellow poplar and high-density polyethylene over mesoporous catalysts



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### ABSTRACT

Catalytic co-pyrolysis of biomass and hydrogen-rich materials is an effective approach for enhancing the production of bio-based hydrocarbons. In this work, mesoporous solid acid materials, such as hierarchical mesoporous MFI (meso MFI), hierarchical mesoporous Y (meso Y) and Al-SBA-15, were used as the catalysts for the catalytic co-pyrolysis of yellow poplar (YP) and high-density polyethylene (HDPE). Among three catalysts, meso MFI revealed the highest catalytic efficiency for the production of aromatic hydrocarbons from catalytic pyrolysis of YP or HDPE due to its effective pore structure, large channels, and high acidity. Moreover, meso MFI showed the highest synergistic formation of aromatic hydrocarbons during the catalytic co-pyrolysis of YP and HDPE as a result of hydrogen donating effect of HDPE and catalytic interactions between YP- and HDPE-derived pyrolyzates. The amounts of solid residue obtained from the catalytic co-pyrolysis of YP and HDPE over meso MFI were also much lower than their theoretical yields.

### 1. Introduction

Rapid depletion of fossil fuels and greenhouse gas emissions caused by their large-scale utilization necessitate the search for sustainable and renewable resources for future supply of energy and chemicals [1–3]. Among various kinds of renewable energy source, lignocellulosic biomass is being considered as a potential option to substitute for fossil fuels since it is abundantly available and a carbon neutral source [4]. Several types of biomass conversion technologies, such as torrefaction, pyrolysis, and gasification, have been suggested. Among them, pyrolysis, as a promising technology for exploitation of biomass, results in the production of large amount of bio-oil. However, highly oxygenated nature of bio-oil obtained from the pyrolysis of biomass limits its direct use as a liquid fuel, and the bio-oil must be upgraded in order to be used as valuable chemicals and fuels [5–10]. Catalytic pyrolysis, carrying out pyrolysis and catalytic upgrading simultaneously in a single unit, is of high potential to be an economically feasible method for the production of biomass-based chemicals. So far, several micro- and mesoporous solid acids such as zeolites and aluminosilicates have been vastly examined as the catalysts for upgrading of biomass-derived oxygenates

[11]. However, the yields of target hydrocarbons obtained from the catalytic pyrolysis is still low level due to the low hydrogen to carbon effective ratio ( $H/C_{eff}$ ), defined in Eq. (1) [11], of biomass materials.

$$H/C_{eff} = \frac{(H-2(O))}{C}$$

H, C, and O: moles of hydrogen, carbons and oxygen (1)

Other drawback of catalytic pyrolysis of biomass is the high rate of coke formation which causes rapid catalyst deactivation and low upgrading efficiency [12]. Coke is carbonaceous deposits generated from pyrolysis vapors via thermal decomposition, i.e., homogeneous reactions in gas phase, and heterogeneous reactions over catalyst [13–15]. High coke yield is also explained with the low  $H/C_{eff}$  of biomass materials leading to the generation of a hydrogen-poor hydrocarbon pool inside catalyst [16]. Low hydrogen content in the hydrocarbon pool causes a high degree of polymerization of pyrolysis-derived compounds and the increased growth rate of coke precursors. To increase the yield of target hydrocarbons such as mono-aromatic hydrocarbons, many researchers investigated catalytic co-pyrolysis of biomass and hydrogen-rich materials over various kinds of catalysts [17–20]. Zhang

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et al. [21] used alcohol as the co-feeding chemical to increase the selectivity to hydrocarbons during the catalytic pyrolysis of pine wood over HZSM-5. Waste plastics are also being considered a promising hydrogen source to be co-pyrolyzed with biomass due to their low price and worldwide abundance [22–25]. Kim et al. [26] studied the effect of catalyst pore size and molecular diameter of co-feeding plastics on the formation of aromatic hydrocarbons during the catalytic copyrolysis of cellulose and thermoplastics (i.e., high density polyethylene (HDPE) and polypropylene (PP)) using HZSM-5 and HY catalysts having different pore size. They found that the diffusion efficiency of plastic molecules into the pore of catalysts can be limited by the catalyst pore size and biomass char, and this limitation can be overcome by applying high reaction temperature and the catalyst having strong acidity. Synergistic formation of aromatic hydrocarbons during the catalytic copyrolysis of biomass and plastics were explained by the effective Diels-Alder type reactions between reaction intermediates of biomass and plastics, such as furans and olefins [27,28]. Increased Diels-Alder type reaction rate between oxygen-containing pyrolysis intermediates and olefins can also decrease the yield of coke, suppressing the oligomerization of oxygen-containing pyrolyzates. As seen above, the aromatics formation efficiency can be influenced not only by the property of co-feeding materials but also by the properties of catalyst such as acid strength and pore size. Recently, Hong et al. [29] compared the aromatic formation efficiencies of microporous and mesoporous HZSM-5 catalysts. They found that the mesoporous HZSM-5, prepared by the desilication of microporous HZSM-5, can provide the higher reaction efficiency than microporous HZSM-5 on the production of aromatic hydrocarbons via the catalytic co-pyrolysis of cellulose and polypropylene, and the increased diffusion efficiency of reaction intermediates through the larger pore of desilicated HZSM-5 was suggested as the main reason for the high activity. In this regard, the use of mesoporous catalysts can be considered as an effective approach to increase a catalytic interaction between the co-pyrolyzed feedstocks. However, the detailed study on the use of mesoporous materials having different mesopore size and acidity for catalytic co-pyrolysis of biomass and plastics is scarce.

Therefore, catalytic co-pyrolysis of yellow poplar (YP) and high-density polyethylene (HDPE) over mesoporous solid catalysts was investigated in this study. For this, three kinds of mesoporous catalysts, hierarchical mesoporous MFI (meso MFI), hierarchical mesoporous Y (meso Y) and Al-SBA-15, were used as the catalysts. Physico-chemical properties of the catalysts was tested by N<sub>2</sub> physisorption, Brunauer–Emmett–Teller (BET) analysis, X-ray fluorescence (XRF) measurement, and temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD). Thermogravimetric (TG) analysis was also performed to know the thermal decomposition temperature profiles of YP and HDPE mixture having different mixing ratio of HDPE (0, 25, 50, 75, and 100%). The production yields of aromatic hydrocarbons obtained from the catalytic co-pyrolysis of the mixtures over the catalysts were compared using a tandem micro reactor-gas chromatography/mass spectrometry (TMR-GC/MS).

## 2. Materials and methods

### 2.1. Samples

YP (*Liriodendron tulipifera*), supplied from Korea Forest Research Institute, was cryo-milled with liquid nitrogen, sieved to make the particle size below 300 μm, and dried at 110 °C for 12 h. HDPE in powder form was obtained from a local company of South Korea, and sieved with 50 mesh screen. To know the physico-chemical properties of YP and HDPE, the proximate and ultimate analysis of YP and HDPE were also performed according to ASTM D 7582 (2015) and ASTM D 5373 (2014) method using an elementary analyzer (Flash EA 1113 series, CE Instruments), respectively.

### 2.2. Catalyst preparation

Meso MFI was synthesized using an amphiphilic organosilane, [(3-trimethoxysilyl)propyl] dodecyltrimethylammonium chloride (TPDAC) ( $[(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{N}(\text{CH}_3)_2\text{C}_n\text{H}_{2n+1}]\text{Cl}$ ,  $n = 12$ ), as a mesopore-directing agent [30]. The synthesis procedure of meso Y was reported elsewhere [20]. Al-SBA-15 was synthesized using the method reported elsewhere [31]. More detailed description of the catalyst preparation procedure was provided in [supplementary information](#) and all catalysts were calcined at 550 °C under air prior to the catalytic co-pyrolysis experiments.

### 2.3. Catalyst characterization

N<sub>2</sub> physisorption using a Micromeritics 3Flex instrument at -196 °C was performed to determine the porosity of catalysts. The surface area and pore size distribution were measured by BET model and Barrett–Joyner–Halenda (BJH) method, respectively. The acid site distribution of catalysts was measured by NH<sub>3</sub>-TPD on a BELCAT-M instrument equipped with a thermal conductivity detector (TCD). For this, 100 mg sample was heated at 500 °C under helium flow (50 ml min<sup>-1</sup>) for 1 h. Then the sample was cooled down to 100 °C, and ammonia adsorption was conducted in a stream of 5% NH<sub>3</sub>/95% He (50 ml min<sup>-1</sup>). Afterwards, the sample was flushed with He gas for the removal of physisorbed NH<sub>3</sub>. The ammonia desorption measurements were performed by heating the sample from 100 to 700 °C at a heating rate of 10 °C min<sup>-1</sup> under He flow (50 ml min<sup>-1</sup>).

### 2.4. Thermogravimetric (TG) analysis

TG analysis was carried out using a thermogravimetric analyzer (Pyris1, PerkinElmer Co.) to study the non-catalytic and catalytic pyrolysis/co-pyrolysis behaviors of YP and HDPE. For catalytic TG analysis, 0.6 ± 0.01 mg of feedstock having different YP/HDPE mixing ratio was physically mixed with 6.0 ± 0.05 mg of catalyst in TG sample cup. The samples were heated from room temperature to 700 °C at a heating rate of 20 °C/min under 60 mL/min of nitrogen flow.

### 2.5. Catalytic pyrolysis

Catalytic pyrolysis was conducted using a TMR (Rx-3050TR, Frontier Laboratories Ltd.)-GC/MS (Agilent 7890A/5795C inert). In each experiment, 0.6 ± 0.01 mg of YP/HDPE mixture and 6.0 ± 0.01 mg of catalyst were mixed physically in a deactivated stainless steel cup. To know the effect of biomass to HDPE mixing ratio, the weight ratio of HDPE in the mixture was changed as 0, 25, 50, 75, and 100%. The sample cup was introduced into a preheated furnace at 600 °C by free-falling to make fast pyrolysis condition. The pyrolysis vapors were carried by helium flow (100 mL min<sup>-1</sup>) through a heated interface (320 °C) to a capillary column (UA-5, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness) in GC. Prior to GC separation, the pyrolysis vapors were cryo-focused for 3 min using liquid nitrogen (-193 °C) provided by MicroJet Cryo Trap (MJT-1030E, Frontier Laboratories Ltd.). After the cryo-focusing time, the pyrolysis products were separated in the column and detected by MSD and FID for qualitative and quantitative analysis of oil products, respectively. The yields of aromatic hydrocarbons were calculated using an external standard (ESTD) calibration method with standard chemical mixture for aromatic hydrocarbons (Supelco). The yields of non-condensable gases (CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbons) were measured by GC-TCD/FID. A 60/80 Carboxen 1000 packed column (15 ft × 1/8 in × 2.1 mm mesh) and HP-AL/KCL capillary column (50 m length × 0.32 mm i.d. × 8 μm film thickness) were used for the separation of carbon oxides and C<sub>1</sub>-C<sub>4</sub> hydrocarbons, respectively. The product quantification was also conducted using the external standard (ESTD) calibration method. The calibration curve for the quantification of target chemicals

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