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Production of aromatic hydrocarbons from catalytic co-pyrolysis of biomass and high density polyethylene: Analytical Py–GC/MS study

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HIGHLIGHTS

- We promote aromatic hydrocarbon production by catalytic co-pyrolysis process.
- Co-pyrolysis temperature of 700 °C is optimal for aromatic hydrocarbon formation.
- The hydrogen to carbon effective ratio of feedstock should be adjusted to >1.0.

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ABSTRACT

In order to promote efficient production of aromatic hydrocarbons, catalytic co-pyrolysis of corn stalk and high density polyethylene (HDPE) over HZSM-5 zeolite catalyst was performed using quantitative Py–GC/MS. For the catalytic fast pyrolysis (CFP) of HDPE, the relative content of aromatic hydrocarbons tended to increase at first and then decreased gradually. For the catalytic co-pyrolysis (co-CFP) of biomass and HDPE, the effects of co-CFP temperature and mass ratio of biomass to HDPE (biomass/HDPE ratio) on the relative content and economic potential of aromatic hydrocarbons were investigated, and the experimental results showed that the highest relative content of aromatic hydrocarbons was obtained at the temperature of 500–600 °C, whereas 700 °C was optimal when the yield of total organic pyrolysis products was taken into account. In addition, the relative contents and value index (VI) of target products remained virtually constant when the biomass/HDPE ratio was >1:1, but then increased with decreasing biomass/HDPE ratio when this mass ratio was <1:1. The hydrogen to carbon effective ratio (H/C_{eff} ratio) of feedstock should be adjusted to be >1.0 so that high relative contents and VI of aromatic hydrocarbons could be achieved.

1. Introduction

Massive consumption of traditional fossil energy resources has caused serious problems and prompted considerable interest in alternative renewable energy [1,2]. As the only renewable resource that can be directly converted to liquid fuels, biomass has attracted increasing attention [3,4]. A wide array of methods has been researched to achieve high-quality liquid fuels (namely bio-oil) from lignocellulosic biomass [5,6], and one of the most promising ways is catalytic fast pyrolysis (CFP) technology that employs fast pyrolysis process and acidic catalysts. Addition of acidic catalysts can de-oxygenate bio-oil and favor the production of hydrocarbon products through catalytic cracking and refining reactions. Among various studied acidic catalysts, HZSM-5 zeolite catalyst has shown an excellent performance [7–9].

However, solid biomass is a hydrogen-deficient feedstock, thus leading to adverse impacts on hydrocarbon production from CFP process. Chen et al. [10] used a parameter called hydrogen to carbon effective ratio (H/C_{eff} ratio) to reflect the relative hydrogen content of different feedstocks. The H/C_{eff} ratio is defined as

$$H/C_{eff} = \frac{\mathrm{H} - 2\mathrm{O} - 3\mathrm{N} - 2\mathrm{S}}{\mathrm{C}} \qquad (1)$$

where H, O, N, S and C are the mole percentages of hydrogen, oxygen, nitrogen, sulfur and carbon in feedstocks, respectively. The H/C_{eff} ratio of biomass and biomass-derived feedstocks is only 0–0.3, which exhibits an extreme lack of hydrogen. Zhang et al. [11] reported the zeolite conversion of 10 biomass-derived feedstocks with different H/C_{eff} ratios, and their experimental results indicated that there was a strong correlation between the H/C_{eff} ratio of feedstock and the content of hydrocarbons. Furthermore, the content of hydrocarbons could be promoted by increasing the H/C_{eff} ratio in feeds. Catalytic co-pyrolysis (co-CFP) of biomass with another additional feedstock that has a high H/C_{eff} ratio is an

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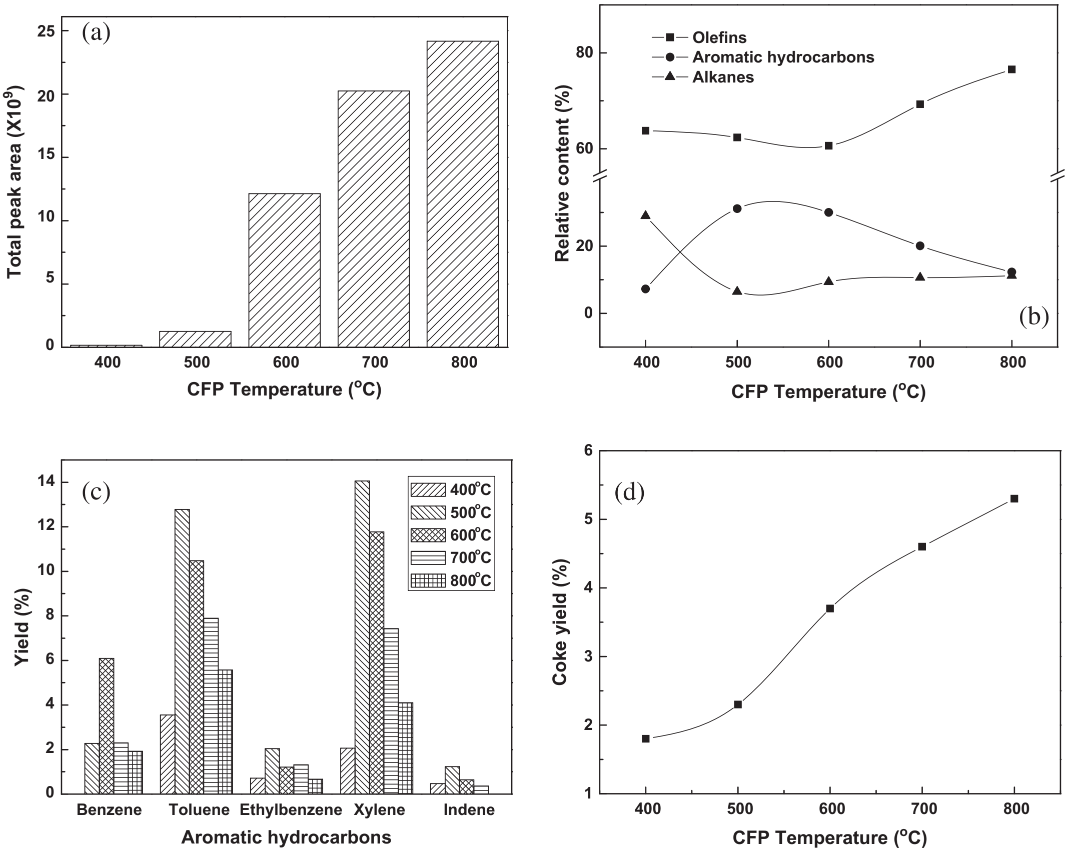

Fig. 1. CFP of HDPE over HZSM-5 catalyst – effect of CFP temperature. (a) Total peak areas. (b) Relative contents of hydrocarbons. (c) Relative contents of several kinds of aromatic hydrocarbons. (d) Coke yields.

attractive approach to increase the content of hydrocarbons. Grease (H/C_{eff} ratio = ~1.5) and saturated monohydric alcohols (H/C_{eff} ratio = 2) can function as hydrogen sources and be co-fed with biomass to improve the overall H/C_{eff} ratio of feedstocks. Zhang et al. [12] found that co-CFP of biomass and methanol could give rise to a high yield of premium products over HZSM-5 catalyst. Unfortunately, the high prices of grease and alcohols seriously limit their practical use, so it is necessary to find other low-cost feedstocks.

As a common municipal solid waste, Polyethylene (PE) can potentially act as the better hydrogen supplier in co-CFP process because of its broad sources, low price and high H/C_{eff} ratio (H/C_{eff} ratio = 2). In this paper, co-CFP of corn stalk and high density polyethylene (HDPE) with HZSM-5 catalyst was carried out, and quantitative pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) was used to analyze the chemical compositions of products. The objective of this work is to evaluate the relative contents and economic potential of aromatic hydrocarbons and determine the optimal conditions during the CFP of corn stalk and PE mixtures.

2. Materials and methods

2.1. Materials

Corn stalk was supplied by a trading center in the city of Zhumadian in Henan Province, China. HDPE was collected from a company in the city of Nanjing in Jiangsu province, China. Prior to the beginning of the experiments, both corn stalk and HDPE were pulverized mechanically and sifted through a 40-mesh sieve. The proximate analysis of the corn stalk (on air-dry basis) was 9.27 wt% moisture, 71.73 wt% volatile, 6.06 wt% ash, and 12.94 wt% fixed carbon (by difference). The elemental composition of the corn stalk (on air-dry, ash-free basis) was 46.73 wt% carbon, 6.11 wt% hydrogen, 0.59 wt% nitrogen, and 46.57 wt% oxygen (by difference). Besides, the H/C_{eff} ratio of corn stalk was 0.04, and the density of HDPE was 0.97 g/cm^3.

HZSM-5 zeolite catalyst (silicon-to-aluminum ratio is 50, particle diameter is 2–5 μm) used in this study was bought from the Catalyst Plant of Nankai University. The porosity and acidity characteristics of the HZSM-5 catalyst are given in Table 1. The porosity characteristic of HZSM-5 catalyst was analyzed by N_2 porosimetry, and the D–R equation was used in the calculation of the surface area. The acidity characteristic of HZSM-5 catalyst was analyzed by Py–FTIR measurement. The FTIR spectrum was recorded using Bruker TENSOR27 infrared spectrometer with a range of 400–4000 cm^{-1} at the resolution of 4 cm^{-1}. HZSM-5 catalyst was dispersed on the thin wafers of KBr and pyridine was used as a probe. The samples were calcined under vacuo at 380 °C for 2 h, and then the adsorption of pyridine vapor was operated at room temperature for 30 min. IR spectrum was recorded and analyzed after subsequent evacuation at 200 °C.

Table 1
Porosity and acidity characteristics of HZSM-5 catalyst.

Porosity characteristics (N_2 porosimetry)	
Specific surface area (m^2/g)	332
Pore volume (cm^3/g)	0.1925
Acidity characteristics (Py–FTIR measurement)	
Brönsted acid sites (μmol/g)	134.3
Lewis acid sites (μmol/g)	32.2