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Short Communication

Optimizing catalysis conditions to decrease aromatic hydrocarbons and increase alkanes for improving jet biofuel quality

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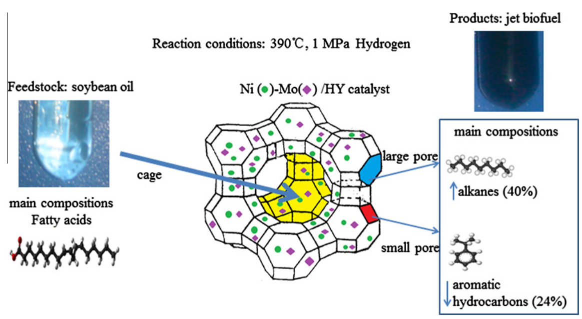
HIGHLIGHTS

- Zeolite HY exhibited higher jet range alkanes selectivity than zeolite HZSM-5.
- Zeolite HY exhibited lower jet range aromatic hydrocarbons selectivity than HZSM-5.
- The reaction temperature was optimized to produce quality jet fuel.
- A high yield of jet fuel was obtained at 1 MPa low hydrogen pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

To produce quality jet biofuel with high amount of alkanes and low amount of aromatic hydrocarbons, two zeolites of HY and HZSM-5 supporting Ni and Mo were used as catalysts to convert soybean oil into jet fuel. Zeolite HY exhibited higher jet range alkane selectivity (40.3%) and lower jet range aromatic hydrocarbon selectivity (23.8%) than zeolite HZSM-5 (13.8% and 58.9%). When reaction temperature increased from 330 to 390 °C, yield of jet fuel over Ni–Mo/HY catalyst at 4 MPa hydrogen pressure increased from 0% to 49.1% due to the shift of reaction pathway from oligomerization to cracking reaction. Further increase of reaction temperature from 390 to 410 °C resulted in increased yield of jet range aromatic hydrocarbons from 18.7% to 30%, which decreased jet fuel quality. A high yield of jet fuel (48.2%) was obtained at 1 MPa low hydrogen pressure over Ni (8 wt.%)–Mo (12 wt.%)/HY catalyst.

1. Introduction

Renewable fuel sources are in demand due to increased crude oil price and environmental concerns (Sinha et al., 2013). Liquid biofuel production from plant oil such as soybean oil, palm oil, algae oil and vegetable oil seems feasible due to its low greenhouse gas emission. Jet fuel has a growing market demand, and its production from plant oil has been eliciting much attention worldwide. Plant oil contains fatty acids and triglycerides, and jet fuel is produced through deoxygenation and carbon chain cracking of plant oil. Jet fuels are required to meet highly stringent international standards. Jet fuel contains C_8–C_{16} alkanes, cycloalkanes, olefins, and aromatic hydrocarbons; aromatic hydrocarbon content in jet fuel is strictly limited. Quality jet fuel has high alkane and low aromatic hydrocarbon content, high energy density, and low freezing point.

Numerous studies have reported on diesel range (C_{16}–C_{22}) hydrocarbon production from plant oil (Peng et al., 2012; Murata et al., 2010; Bezergianni et al., 2009; Kubicka et al., 2010; Snare et al., 2006). However, the freezing point of diesel is too high for air flight. Literature on jet fuel production from plant oil is still rare. Yang reported jet fuel production from pure fatty acids through hydrothermal process, but the carbon chain of jet fuel

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was too long leading to a high freezing point (Yang et al., 2013). Robota reported a multi-step process on cogeneration of diesel and jet fuel from algae lipids, but the yield of jet fuel was very low at 8% (Robota et al., 2013). Verma reported on jet range hydrocarbon production from jatropha oil and algae lipids using hierarchical mesoporous zeolite catalyst at a high hydrogen pressure of 4–10 MPa, but the detailed composition of jet fuel (especially the contents of alkane and aromatic hydrocarbon) was not described (Verma et al., 2011).

In this paper, a low aromatic hydrocarbon and a high alkane selectivity catalyst was reported, namely, Ni and Mo supported on zeolite HY, to convert soybean oil into quality jet fuel. Zeolite HY was found to exhibit higher jet range alkane and lower jet range aromatic hydrocarbon selectivities than zeolite HZSM-5. Influences of reaction temperature and hydrogen pressure were also investigated to improve jet fuel quality.

2. Methods

2.1. Preparation of catalysts

$Ni(NO_3)_2{\cdot}6H_2O$ (⩾98.0% analytical standard) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (⩾99.0% analytical standard) used in the experiments were purchased from Sinopharm Chemical Reagent Co Ltd, Shanghai China. Zeolite HZSM-5 (molar ratio Si/Al = 40, pore size of 0.54 nm) and zeolite HY (molar ratio Si/Al = 5.5, pore size of 0.74 nm) were purchased from the Catalyst Plant of Nankai University. Ni and Mo clusters supported on zeolites HZSM-5 and HY catalysts were prepared using a wetness impregnation method. The procedure used for synthesizing Ni (8 wt.%)–Mo (12 wt.%)/HY and Ni (8 wt.%)–Mo (12 wt.%)/HZSM-5 catalysts were as follows: 2.37 g $Ni(NO_3)_2{\cdot}6H_2O$ and 1.32 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were dissolved in 10 ml deionized water. Then 4.8 g HY or HZSM-5 was added to the solution. The mixture was stirred for 6 h at ambient temperature and then dried in an oven at 70 °C for 8 h. The catalyst was calcined in air at 550 °C (heating rate = 5 °C/min) for 4 h and reduced in hydrogen (flow rate = 300 ml/min) at 500 °C (heating rate = 4 °C/min) for 4 h.

2.2. Catalytic conversion of soybean oil into jet fuel

The soybean oil used in experiments was purchased from Jinlongyu Company, China. The soybean oil conversion experiments were carried out in a 500 ml batch reactor (Parr Instrument Company 4500) equipped with a mechanical stirrer. In a typical run, 100 ml soybean oil and catalysts with a mass ratio of 20:1 were loaded in the reactor. The reactor was sealed and filled with hydrogen to a set pressure at ambient temperature. The reaction was carried out with a stirring speed of 500 rpm at 330 to 410 °C for 8 h. The liquid and solid products were separated by centrifugation after the reaction. Weight of the liquid products was measured on a balance and liquid compositions were analyzed on a GC–MS.

2.3. Analysis method of liquid products

The liquid product samples were diluted at a ratio of 1:10 in chloroform and analyzed by a Thermo-Fisher Polaris-Q GC–MS equipped with a HP-5 capillary column. Injection temperature was set at 320 °C. High injection port temperature was used for reliable and direct quantification of fatty acids and triglycerides without chemical derivatization (Fu et al., 2010; Anand et al., 2012). The column temperature was initially increased from 40 to 80 °C (rate: 2 °C/min), then increased to 300 °C (rate: 10 °C/min) and maintained for 20 min. GC–MS results were quantified using a peak area normalization method based on peak area percentages of the identified components. All measurements were conducted in triplicate. The mean value and standard deviation were reported. Definitions of yield, selectivity and conversion were as follows:

$$\text{Yield} = (\text{mass of the product}/\text{mass of soybean oil}) \times 100\%$$

$$\text{Selectivity} = (\text{mass of the product}/\text{mass of total products}) \times 100\%$$

$$\text{Conversion} = (\text{mass of converted soybean oil}/\text{mass of soybean oil}) \times 100\%$$

3. Results and discussion

3.1. Developing efficient catalysts to improve jet fuel quality

International standards pose a strict limitation on the percentage of aromatic hydrocarbons (⩽20 vol.%) in jet fuel (ASTM D1655-2012, 1994). The chemical compositions of jet fuels converted from soybean oil over Ni (8% wt.)–Mo (12% wt.)/HY catalyst and Ni (8% wt.)–Mo (12% wt.)/HZSM-5 catalyst at 390 °C under 4 MPa hydrogen pressure were compared. As shown in Fig. 1(a), jet fuel converted from soybean oil contained alkanes, aromatic hydrocarbons and cycloalkanes. Zeolite HY exhibited higher alkane selectivity (40.3%) while exhibiting lower aromatic hydrocarbon selectivity (23.8%) than zeolite HZSM-5 (13.8% and 58.9%, respectively). The results indicated that jet fuel quality was noticeably improved by zeolite HY by increasing alkanes and decreasing aromatic hydrocarbons in jet fuel.

The high alkane and low aromatic hydrocarbon selectivity of zeolite HY was attributed to its pore structure. Zeolite HY displayed 12-member ring pores with size of 0.74 nm and cages with size of 1.14 nm (Baerlocher et al., 2000). Large molecules such as fatty acids were initially cracked into long carbon chain alkanes in the cages or on the outer surface. Then, the long carbon chain alkanes were able to diffuse after the crack or be further cracked into short carbon chain alkanes in the pores of zeolite HY. However, zeolite HZSM-5 contained only 10-member ring pores with size of 0.53 × 0.56 nm (Smith and Bailey, 1963). Large molecules had to be pre-cracked into alkanes on the outer surface of zeolite HZSM-5 to gain access to the micropores. Given the small pore size of HZSM-5, the resulting alkanes were not able to diffuse until they were further cracked into aromatic hydrocarbons with shorter carbon chains.

International standards had a stringent requirement regarding high energy density of jet fuels (Rye et al., 2010). The energy density of light hydrocarbons was lower than that of heavy hydrocarbons. As shown in Fig. 1(b), zeolite HY exhibited higher heavy hydrocarbon (C_{12}–C_{16}) selectivity (33%) than zeolite HZSM-5 (19.4%). By contrast, zeolite HY exhibited lower light hydrocarbons (C_8–C_{11}) selectivity (33.5%) than zeolite HZSM-5 (53.3%). The results indicated that jet fuel converted from soybean oil over zeolite HY exhibited higher energy density than that over zeolite HZSM-5, which can be attributed to the smaller pore size of zeolite HZSM-5 (0.54 nm) than zeolite HY (0.74 nm), leading to higher selectivity to light hydrocarbons. The selectivity of jet range hydrocarbons (C_8–C_{16}) was 66.6% at 390 °C, but it increased to 87.4% at 410 °C, which was attributed to severe cracking reactions at higher reaction temperatures.

3.2. Influences of Mo/Ni weight ratios on jet fuel production

Ni or Mo metals supported on zeolite HY were the active sites for deoxygenation of soybean oil. Deoxygenation of plant derived