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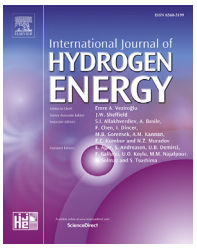

Short Communication

Jet range hydrocarbons converted from microalgal biodiesel over mesoporous zeolite-based catalysts

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ABSTRACT

In order to produce jet biofuel from lipids derived from microalgal biomass, lower-viscosity and smaller-molecular microalgal biodiesel was converted into jet range hydrocarbons over four mesoporous zeolite-based catalysts decorated with nickel. Ni/Meso-Y catalyst exhibited a high selectivity (44.5%) of jet range alkane (C_8–C_{16}) from light microalgal biodiesel. The conversion pathway of light microalgal biodiesel to jet range hydrocarbons was proposed that majority of fatty acids first deoxygenated to C_{15}–C_{16} through decarbonylation and then long chain alkane cracked into short chain alkane. The other fatty acids first cracked into short chain acids and then further deoxygenated through decarbonylation to jet range alkane, in which a part of alkane converted to aromatic hydrocarbons through aromatization. Meso-Y catalyst was suitable for conversion of heavy microalgal biodiesel to jet range hydrocarbons with low selectivity (4.47%) of aromatic hydrocarbons, but the other three catalysts (Meso-HZSM-5, Meso-Hbeta and SAPO-34) gave high aromatic hydrocarbons selectivity.

Introduction

Liquid fuels such as petroleum, diesel and jet fuel mainly derived from crude oil. Combustion of fossil fuels and human activities disturb the environment by the emission of greenhouse gases like nitrous oxide, carbon dioxide, methane [1]. Biomass is a renewable resource and carbon neutral in principle [2]. Microalgae is being considered in context as a promising renewable energy resource, having high triglyceride contents (up to 60%) [3]. Numerous papers have reported biodiesel production from algal lipids [4–7]. However, papers on jet biofuel production from non-edible oil especially algal lipids were still rare.

Jet fuel mainly contained C_8–C_{16} alkane, cycloalkanes, isoalkanes, aromatic hydrocarbons. Jet fuel must meet very stringent international specifications, which makes it much more difficult to develop an alternative fuel for aviation than for automobile applications [8]. The conventional jet fuel was produced from petroleum. Vegetable oils and animal fats would be hydrotreated to produce high cetane number and straight chain alkanes ranging from C_8–C_{16} that can be used in the aviation industry [9]. Li reported jet biofuel production from waste cooking oil catalyzed by mesoporous zeolite Y [10]. However, it is difficult to produce jet biofuel from waste cooking oil in a large scale. Cheng reported jet biofuel production from soybean oil [11]. However, soybean oil is edible. Liu reported jet biofuel production from hydroprocessing

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castor oil [12]. However, castor oil can be used as a medicine. The advantage of microalgae compared to terrestrial biomass is its much higher photosynthetic efficiency which results in higher growth rates and improved CO_2 mitigation [13]. Biller reported the upgrading of algal lipids through hydrothermal process [14]. However, the products mainly contained fatty acids. The content of alkane was very low.

Mesoporous materials, such as mesoporous zeolite and aluminum incorporated mesoporous silica SBA-15, have been recently reported to facilitate the diffusion of reactants into pores [15]. Mesoporous zeolite is a crystalline zeolite with intercrystalline and intracrystal-line mesoporous systems. The synthesis, characterization, and catalytic application of mesoporous zeolite are among the most active areas of research on porous catalytic materials and significant success has been achieved.

Hydrotreating of plant lipids seemed to be a possible way for jet biofuel production. We put forward jet biofuel production from algal biodiesel in this paper. Two grades of algal biodiesel were tested for quality jet biofuel production.

Materials and methods

Preparation of catalysts

The analytical standard Ni(NO3) 2·6H2O (≥98.0%) was purchased from Sinopharm Chemical Reagent Co Ltd, (Shanghai, China). Zeolite SAPO-34 was purchased from the Nankai University catalyst company. Mesoporous zeolites were purchased from the Fengxiang Company, (Hang Zhou, China). Ni/zeolite bifunctional catalysts were prepared using wetness impregnation method, and a similar procedure was used to synthesize Ni/zeolite catalysts. For example, Ni (10 wt%)/Meso-Y was synthesized as follows: 2.97 g of Ni(NO3)2·6H2O was dissolved in 10 mL of hyperpure water. 5.4 g of mesoporous zeolite Y was added to the solution. The mixture was stirred for 4 h at room temperature. Then the mixture was 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 then reduced in hydrogen (flow rate = 350 mL/min) at 500 °C (heating rate = 4 °C/min) for 4 h.

Characterization of catalysts

X-ray diffraction (XRD) patterns of the catalysts were obtained using an X'Pert PRO MPD diffractometer (PANalyti-cal) operated at 40 kV and 40 mA with Cu Kα radiation. Nitrogen sorption isotherms were measured at −196 °C using a Micrometrics ASAP 2020 M system. Surface areas of catalysts were determined using the Brunauer-Emmett-Teller model. The micropore volumes of catalysts were determined using t-plot method. Mesopore volumes were determined using the Barrett-Joyner-Halenda (BJH) model. Micropore size distributions were determined using the Horvath-Kawazoe method. Mesopore size distributions were determined using the BJH model.

Preparation of jet biofuel

The jet range hydrocarbons was prepared in a 500 ml batch reactor (Parr Instrument Company 4500) equipped with a mechanical stirrer. Four types of catalysts including Ni/Meso-HZSM-5, Ni/Meso-Hbeta, Ni/Meso-Y, and Ni/SAPO-34 were tested. Taking Ni/Meso-Y catalyst as an example, 100 ml of microalgal biodiesel and Ni/Meso-Y catalyst at a 20:1 mass ratio was loaded in the reactor. The reactor was then sealed and filled with hydrogen to control the pressure and temperature. The reaction was triggered by stirring speed at 500 rpm at 370°C-410°Cfor 8 h. The liquid and solid products were separated by centrifugation. The weight of the liquid products was measured with a balance. The liquid composition was analyzed using gas chromatography mass spectrometry (GC-MS).

Analysis of liquid products

The liquid product samples were diluted to a ratio of 1:10 in chloroform and analyzed using an Agilent 6890 N GC/5975B MSD equipped with an HP-5 capillary column. The injection temperature was set to 320 °C. A high injection port temperature was used to ensure the reliable and direct quantification of the fatty acids and triglycerides without chemical derivatization [16]. The column temperature was initially increased from 30 °C to 80 °C at 2 °C/min, then increased to 300 °C at 10 °C/min, and finally maintained at 300 °C for 20 min. The GC-MS results were quantified using the peak area normalization method based on the peak area percentages of the identified components. All measurements were taken in triplicate. The mean and standard deviation were recorded. Yield and selectivity, were defined as follows:

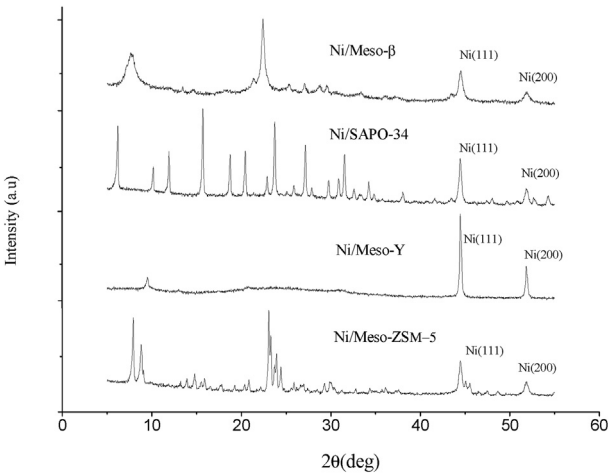

Fig. 1 – XRD patterns of different Ni-loaded zeolite catalysts.

Table 1 – Nitrogen adsorption of Ni/Meso-HZSM-5, Ni/SAPO-34, Ni/Meso-Y, Ni/Meso-β catalysts.

Catalysts	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	Pore size (nm)
Ni/Meso-ZSM-5	320.6	0.1	0.13	2.8
Ni/Meso-Y	517.6	0.26	0.03	3.9
Ni/SAPO-34	89.2	0.05	0.05	0.57
Ni/Meso-β	368.4	0.15	0.1	3.7

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