



Full Length Article

Production of jet fuel range biofuels by catalytic transformation of triglycerides based oils



Xiaoping Wu^a, Peiwen Jiang^a, Feng Jin^a, Junxu Liu^a, Yiheng Zhang^a, Lijuan Zhu^a, Tongyan Xia^a, Kuanliang Shao^a, Tiejun Wang^b, Quanxin Li^{a,*}

^a Department of Chemical Physics, Key Laboratory of Urban Pollutant Conversion, Chinese Academy of Sciences, Anhui Key Laboratory of Biomass Clean Energy, University of Science & Technology of China, Hefei 230026, PR China

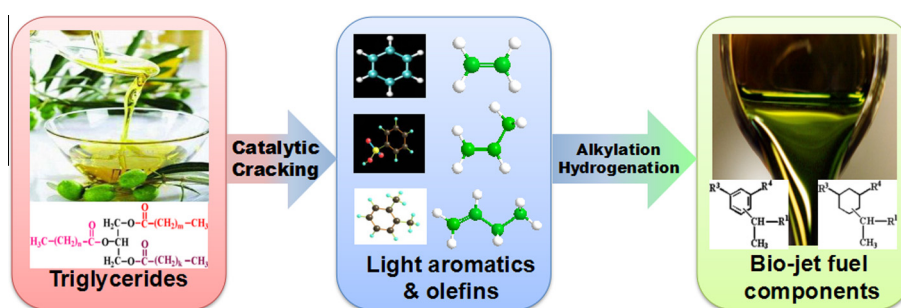
^b Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China

HIGHLIGHTS

- A proposed transformation of vegetable oils into bio-jet fuels was demonstrated.
- C₆–C₉ aromatics were obtained by catalytic cracking of vegetable oil over HZSM-5 (80).
- Aromatic biofuel was achieved by the alkylation reactions using [bmim]Cl-2AlCl₃.
- Cycloparaffinic biofuel was produced by hydrogenation of aromatics over Pd/AC.

GRAPHICAL ABSTRACT

A proposed catalytic strategy for the production of cycloparaffinic and aromatic components in jet fuels from triglycerides based oils via the catalytic cracking of vegetable oils to light aromatics followed by the alkylation of light aromatics and the hydrogenation.



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ABSTRACT

This work demonstrated that triglycerides based vegetable oils were directly converted into cycloparaffinic and aromatic components in jet fuel by a three-step process. This process involved the catalytic cracking of vegetable oils into light aromatics over the zeolite catalyst (HZSM-5(80)), followed by the aromatic alkylation of light aromatics using the ionic liquid of [bmim]Cl-2AlCl₃ and the hydrogenation of aromatics over the Pd/AC catalyst. The production of C₈–C₁₅ aromatics with an 86.2 wt% in the aromatic biofuel was achieved by the room temperature alkylation at 25 °C for 30 min. The carbon number distribution in the resulting biofuels was readily adjustable to the desired range by varying the reaction time. The aromatic and cycloparaffinic biofuels obtained basically meet the requirements of jet fuels based on the combustion heat, the H/C mol ratio and the average molecular formulation.

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1. Introduction

Concerns about declining fossil fuel reserves and the increasing levels of carbon dioxide in the atmosphere have accelerated

advances in alternative jet fuels researches [1–10]. Several promising approaches, including the hydrotreating of animal and vegetable oils [3,5,11–14], FischerTropsch synthesis with bio-syngas [1,4,8,15,16], catalytic conversion of soluble sugars in aqueous phase [17,18] and other synthesis routes [19–21], have been developed to produce bio-jet fuels from various biomass feedstocks.

* Corresponding author.

E-mail address: liqx@ustc.edu.cn (Q. Li).

Catalytic cracking of vegetable oils and animal fats composed predominantly of triglycerides represents a useful method for producing biofuels which are particularly suitable for use in automotive applications [22]. Generally, the catalytic cracking of oleaginous feedstocks is conducted in a fixed-bed reactor at middle temperature and atmospheric pressure over an acid catalyst. The major catalysts used include protonated zeolites, aluminum-containing mesostructured materials and amorphous materials [23–28]. The products derived from the catalytic cracking of oleaginous feedstocks consist of organic liquid products (OLPs), gaseous compounds, water and coke. OLPs are gasoline or diesel range hydrocarbons together with a smaller fraction of kerosene range hydrocarbons [23–28]. The properties of hydrocarbons depend on the catalysts used, reaction conditions and oleaginous feedstocks. Generally, the cracking of vegetable oils over an acid catalyst like zeolite exhibited a higher yield of aromatics, which involves the cleavage of C–C and C–O bonds together with the decarboxylation, decarbonylation, dehydration, hydrogen transfer, isomerization, cyclization, aromatization and polymerization [27,28]. On the contrary, the catalytic cracking of oleaginous feedstocks over metal oxide catalysts or noble metal catalysts generally forms more alkane and olefin hydrocarbons in OLPs [29–31].

Alternatively, the hydrogenation of vegetable oils and animal fats can produce liquid alkanes which are suitable for use in gasoline, diesel or jet fuels applications [3,5,11–14]. This hydrogenation process was typically conducted in a batch reactor under high hydrogen pressure and temperatures from 300 to 450 °C. Noble metal catalysts (like Pd, Pt, and Rh catalysts) and sulfided metal catalysts (like sulfided NiMo/Al₂O₃ and CoMo/Al₂O₃) exhibits high activity in the hydrogenation of oleaginous feedstocks [3,5,11–14]. Low temperature hydrogenation (below 350 °C) usually results in straight-chain alkanes in the diesel like fuel ranging from C₁₅ to C₁₈. The subsequent cracking of long chain alkanes and isomerization can increase the yield of kerosene range iso-alkanes [3,14]. Now, the synthetic paraffinic kerosenes (SPKs) obtained from oleaginous feedstocks have been approved for use as a blend oil in commercial aviation fuels [5,32,33].

Generally, commercial or military jet fuel is a mixture of three main components including alkanes, cycloparaffins and aromatics which typically range from C₈ to C₁₅ [34,35]. As mentioned above, SPKs produced by the hydrogenation of triglycerides are currently being utilized as the blending component of alkanes in conventional jet fuels. However, another two chemical compositions (kerosene range cycloparaffins and aromatics) are difficult to be obtained from the developed hydrogenation of oleaginous feedstocks [3,12,34]. Alternatively, Fischer–Tropsch synthesis (FTS) is a highly developed route to convert biomass into liquid alkanes used as transportation fuels [1,8,15,16,36]. Since most of the liquid hydrocarbons produced by FTS are paraffins and olefins, naphthenes and aromatics should be increased in the FTS-derived fractions to meet the specific requirement of jet fuels [1,8]. On the other hand, the catalytic cracking of triglycerides based oils over an acid catalyst mainly produces light aromatics with smaller amount of kerosene fraction. Therefore, the development of new technology for producing cycloparaffinic and aromatic components of jet fuels is still needed.

The purpose of this work is to convert vegetable oils into cycloparaffinic and aromatic biofuels in jet fuel range. Concerning that the catalytic cracking of oleaginous feedstocks over an acid catalyst could result in a high yield of aromatics [28], we selected the zeolite catalysts like HZSM-5 (80) for producing C₆–C₉ light aromatics by the catalytic cracking of vegetable oil. Owing to the unique properties of ionic liquids (ILs) like low vapor pressure, high stability, nonflammability and Bronsted and Lewis acidity, ILs have attracted wide interest in separation, extraction and catalysis processes [37,38]. Present work also demonstrated that the

production of C₈–C₁₅ aromatics from vegetable oil was obtained by the alkylation of aromatics using the [bmim]Cl-2AlCl₃ ionic liquid. Moreover, it has been shown that noble metal catalysts (like Pd/AC) had high activity for complete hydrogenation saturation of aromatic compounds [39,40]. To produce C₈–C₁₅ cycloparaffins, the subsequent hydrogenation of C₈–C₁₅ aromatics was conducted using the Pd/AC catalyst.

2. Materials and methods

2.1. Materials

The vegetable oil was purchased from Anhui Yineng Bio-energy Co. Ltd. (Hefei, China). The chemical and elemental compositions of the vegetable oil are shown in Table 1.

2.2. Catalysts preparation and characterization

The zeolite catalysts (HZSM-5, HY and HMCM-41) used for the catalytic cracking of the vegetable oil were supplied by Nankai University catalyst Co., Ltd. (Tianjin, China). Prior to use, the zeolite catalysts were calcined at 550 °C for 4 h at nitrogen atmosphere. As a contrast, SiO₂ was also tested for the pyrolysis process of vegetable oil.

The ionic liquid catalyst of 1-butyl-3-methylimidazolium chloroaluminate ([bmim]Cl-2AlCl₃) used in the alkylation of aromatics was prepared as the following procedures. The dried *N*-methylimidazolium and 1-chlorobutane were placed into a dry round-bottomed flask equipped with a reflux cooler and a magnetic agitator. The mixture was heated and reacted at 85 °C for 24 h. The imidazolium salt of 1-butyl-3-methylimidazolium chloride ([bmim]Cl) obtained was washed by acetonitrile, and dried in a vacuum drying box to remove the residual solvent and water. Finally, the [bmim]Cl-2AlCl₃ ionic liquid was prepared by adding the dried aluminum chloride (AlCl₃) to the imidazolium salt with a 2.0 molar ratio between AlCl₃ and [bmim]Cl, and stirring overnight at 25 °C. Moreover, the Pd/AC catalyst used in the hydrogenation of aromatics was prepared by the incipient wetness impregnation of the HNO₃-treated active carbon (AC) with the H₂PdCl₄ solution. The impregnated product was dried at 120 °C for 24 h, and finally reduced by hydrogen with a flowing speed of 50 cm³/min at 280 °C for 8 h.

The metallic element contents in the catalysts were determined by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The zeolite catalysts were further characterized by the nitrogen adsorption-desorption isotherms and ammonia temperature-programmed desorption analyses [41]. Main properties of the zeolite catalysts and SiO₂ were summarized in Table 2. The acid features of the ionic liquid catalyst were determined by the Bruker Tensor 27 FT-IR spectrometer using pyridine as a probe molecule of Lewis and Bronsted acid at room temperature [40]. The FT-IR spectrum was acquired at 1 cm⁻¹ resolution using 16 scans for each sample.

Table 1
Properties of the vegetable oil used.

Composition analysis	Content (wt%)	Ultimate analysis	Content (wt%)
Palmitic acid	4.8	C	77.32
Stearic acid	1.5	H	10.91
Oleic acid	51.5	O	11.62
Linoleic acid	21.2	N	0.74
Linolenic acid	5.8	S	–
Others	15.2		

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