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Improvement of selectivity from lipid to jet fuel by rational integration of feedstock properties and catalytic strategy

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ABSTRACT

A high yield jet fuel production process by integration of rational feedstock selection and selective hydro-isomerization was proposed and reported in this paper. A Pt/ZSM-12 catalyst was found to be an effective catalyst for the conversion of *n*-C15 paraffin into multi-branched isomers and mono-branched isomers which satisfied the jet fuel specification. Based on this finding, by integration of feedstock selection, oxygen removing mechanism control and selective hydro-isomerization, a very high weight yield (60%) of algal lipid to jet fuel can be obtained. The obtained jet fuel satisfied the specification of ASTM 7566 standard. Such high jet fuel yield can obviously improve the economics of jet fuel production technology.

1. Introduction

The double threats of energy shortage and environment issue have accelerated the research of renewable jet fuel [1]. Up to now, there are three renewable jet fuel production pathways have been approved by ASTM committee. These routes include F-T synthesis, hydro-processed ester and fatty acid (HEFA) and direct synthesis of hydrocarbon (farnesane) by fermentation from sugar (DSHC) [2]. Some other processing routes from lipid or lignocellulosic biomass are also in the ASTM approving process.

Among above mentioned jet fuel production technologies, HEFA route is the most studied route and already commercialized [3–14]. The lipid based oil can be converted into jet fuel through mainly two steps including *n*-paraffin production and *n*-paraffin hydrocracking/hydro-isomerization. Two mechanisms including hydrodeoxygenation and decarboxylation are utilized in *n*-paraffin production from lipid oil [3,4]. The number of carbon chain can be used to judge the mechanism involved during the *n*-paraffin formation. The necessary of mild-hydrocracking or hydro-isomerization is then determined by the difference between feedstock and jet fuel products. Through the different integration of unit-technologies, different jet fuel production technologies from lipid based oil have been developed. NESTE Company is a lead company who developed lipid oil hydro-processing technology for green diesel and jet fuel production, and it is now operated in commercial scale. Other oil companies like UOP and Topsoe also developed similar technologies as declared in open publication or patents [13]. Researchers in University of North Carolina developed a technology named "Centia™" for low quality lipid oil conversion. This three-step technology includes hydrolysis of lipid into fatty acid, decarboxylation of fatty acid into alkane, and hydro-cracking/hydro-isomerization of alkane into jet fuel range *iso*-paraffin [14]. In open literature, researchers also reported the one-step conversion of lipid into jet fuel range paraffin using different metal/acid bi-functional catalyst to integrate the two processes together [10].

However, though a lot of studies have been conducted, there are still several challenges in HEFA process. The yield of jet fuel from typical lipid based oil, in which fatty acid chain has 18 carbons, is quite low (about 35–40%). One major reason of such low overall jet fuel yield from lipid is the necessity of hydrocracking step for converting the C18 or C16 alkane into jet fuel range paraffin (C9–C15). The carbonations involved hydro-cracking mechanism resulted in low jet fuel range paraffin selectivities of C16 and C18 alkane. Another challenge is that the typical hydro-processing system is unable to process low quality lipid such as lipid with high polar lipid (the case of algal oil and microbial oil) and high free fatty acid (cooking oil) content [15,16]. These challenges should be overcome for an economic jet fuel production technology from lipid

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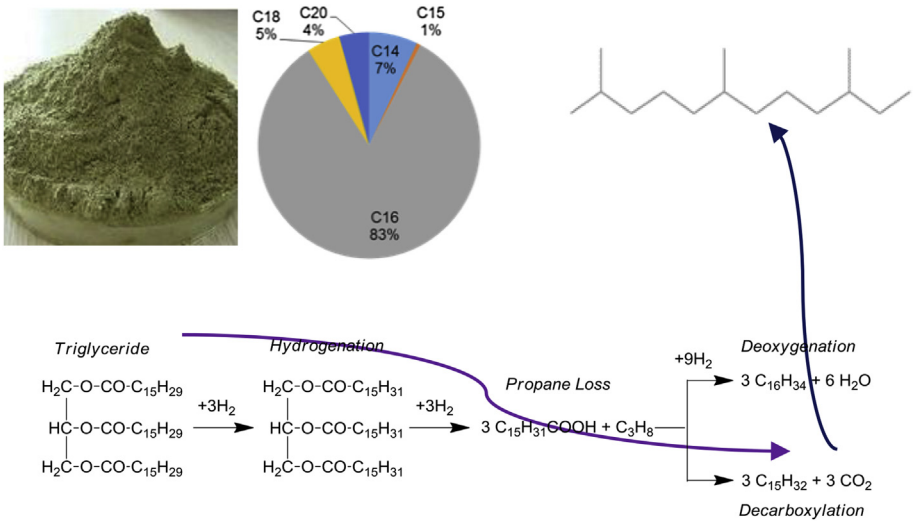

Fig. 1. Schematically exhibition of the proposed jet fuel production technology.

based oil.

Here in this paper an integrated process schematically shown in Fig. 1 was proposed for high yield jet fuel production from lipid. High yield (>60%) could be obtained from suitable lipid through the following progresses: 1) selected or produced lipid oil rich in C16 fatty acid either from algae or oil-bearing crops; 2) all fatty acid in neutral lipid, polar lipid and fatty acid was released into fatty acid; 3) the fatty acid was decarboxylated into C15 rich *n*-paraffin, and finally the n-paraffin was selectively converted into multi-branched C15 molecules which can be used as jet fuel blend through hydro-isomerization.

2. Materials and experiment

2.1. Materials

ZSM-22 and ZSM-12 were synthesized according to the pervious publication [17,18]. USY zeolite from Nankai Catalyst Company was used as reference. Chloroplatinic acid hydrate ($H_2Cl_6Pt{\cdot}xH_2O$, ≥99.9% trace metals basis, Aldrich) was used as the source of the platinum. Polyvinylpyrrolidone (PVP, average molecular weights of 29,000, Aldrich) was used as a standard protective polymer for the Pt nanoparticles. All chemicals were used as received without further purification. Algal oil was extracted from outdoor culverted algae (*Tribonema minus*) and their properties are shown in Table 1.

2.2. Pt nanoparticle synthesis

Polyvinylpyrrolidone (PVP) capped Pt nanoparticles with an average particle size of 2.6 nm were synthesized and supported on H-ZSM-22 according to previously reported methods [19]. Briefly, PVP (133 mg) was dissolved in a mixture of 20 mL of 49.6 mg $H_2PtCl_6{\cdot}xH_2O$ aqueous solution and 180 mL of ethanol. The mixture was heated at 75 °C for 3 h accompanied by N_2 bubbling to synthesize the PVP-protected Pt NPs. The solvent was evaporated and the residue was re-dispersed in 25 mL of water.

2.3. Preparation of Pt/zeolite bifunctional catalyst

Pt colloidal aqueous solution (16 mL, 4.84 mM) was mixed with 84 mL of water and 100 mL of ethanol. Then 2 g of ZSM-22 was quickly added to the mixture, and the slurry was sonicated for 3 h at room temperature. The brown precipitates were separated by centrifugation, thoroughly washed with water and ethanol. The final slurry was dried in an oven at 90 °C, and calcined at 420 °C for 4 h for removing the PVP completely.

2.4. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advanced X-ray diffractometer, using Cu Kα radiation at room temperature and instrumental settings of 40 kV and 40 mA. Data was recorded in the 2θ range 5–50° with a 0.02° step size.

Scanning electron microscopy (SEM) images were recorded with a Hitachi S4800 instrument. Samples were prepared by dusting the zeolite powder onto double sided carbon tape, mounted on a copper stub. The samples were subsequently sputter coated with a thin gold film to reduce charging effects.

Table 1
The algal oil properties and fatty acid profile.

Fatty acid profile						Lipid class			
Fatty acid	C20	C18	C16	C15	C14	Lipid	Neutral lipid	Polar lipid	Free fatty acid
Content (wt.%)	4	5	83	1	7	Content (wt.%)	67	27	6

Table 2
Experiment conditions of algal oil hydrolysis and decarboxylation steps.

Process step	Process condition and scale
Hydrolysis step	5 kg/h unit, Colgate-Emery Process, 250 °C, 5 MPa, 60% oil, Oil/Water ratio: 0.5
Decarboxylation	3 L autoclave, Catalyst: 10% Pd/C to oil, 300 °C, 1.5 MPa, 72% yield respect to fatty acid