



## Research Paper

# From medium chain fatty alcohol to jet fuel: Rational integration of selective dehydration and hydro-processing

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## ABSTRACT

Middle chain fatty alcohols, which can be easily obtained from bio-synthesis and fatty acid hydro-treatment, were used as a renewable resource to produce alternative jet fuels by rational integration of selective dehydration and hydro-processing. Various catalysts such as ZSM-22, Al-MCF and ZSM-5 with different textural and acidic properties were tested in the dehydration step. It was found that the structural and acidic properties have significant influences on the dehydration performance and product distribution. After Pt introduction, the fatty alcohols can be converted into paraffins with different isomerization degrees. The different integrations of dehydration and hydro-processing steps resulted in different medium chain fatty alcohol to jet fuel production processes. Three different production processes, one-step hydro-isomerization over Pt/ZSM-22, dehydration (Al-MCF)/hydro-isomerization (Pt/ZSM-22) and dehydration (ZSM-22)/hydro-processing (Pt/MCF) were developed and tested. The dehydration (Al-MCF)/hydro-isomerization (Pt/ZSM-22) process, which provides the highest iso-paraffin yield, was used for conversion of a commercially available alcohol mixture in a pilot scale reactor. The product obtained from such pilot scale experiment had a freezing point of  $< -60$  °C and met the requirements of ASTM 7566 specification except for density.

## 1. Introduction

The exploration of alternative jet fuel, which is a complex mixture of primarily *n*-iso-paraffins, cycloparaffins, and alkylbenzenes with a carbon number range of 9–15, has been drawing worldwide attention because of the double threats of petroleum shortage and environmental concerns [1,2]. The levy of carbon tax further accelerates the development of jet fuel from renewable resources [3]. A lot of studies has been carried out to produce jet fuel from lipids, sugars and lingo-cellulosic biomass. Among several proposed renewable jet fuel production technologies [4–13], Hydrotreated Esters and Fatty Acids (HEFA) was the most studied route and already commercialized. Using a 50/50 (v/v) blend of petroleum-based and lipid-based jet fuels for flight was already approved by American Society for Testing Material (ASTM) committee. However, lack of raw materials and relatively low jet fuel yield of this process limit its application.

Medium chain fatty alcohols (MCFAs), with straight hydrocarbon chains ranging from C9 to C15, can be produced either through processing natural fats and oils (e.g., coconut oil, palm kernel oil, cottonseed oil, rice bran oil, etc.) or from petrochemicals (e.g., crude oil and natural gas). MCFAs can also be synthesized by microorganisms from glucose or even CO<sub>2</sub> [14–17]. For example, Tan et al. successfully

produced pentadecanol by overexpressing acetyl-CoA carboxylase in cyanobacteria [16]. Furthermore, fatty alcohol is a potential intermediate in other biofuel production processes. For instance, Anbarasan et al. reported the integration of biological and chemo-catalytic routes to efficiently convert ABE fermentation products into ketones with carbon numbers in the range of jet fuel or gasoline by a palladium-catalyzed alkylation. During further hydro-deoxygenation of these ketones, fatty alcohol is formed as an intermediate [18–20].

The *n*-iso-paraffin, which has a higher energy density because of a high ratio of H/C in comparison to other composition, accounts for up to 50–70 vol% in typical jet fuels. Compared with *n*-paraffin, iso-paraffin with the same carbon number has a lower freezing point. Thus, the percentage of iso-paraffin in jet fuel is an important factor to evaluate the property of jet fuel [10,11].

A lot of researches have been conducted on the hydro-isomerization of *n*-paraffin to the corresponding iso-paraffin, of which the catalyst is always bi-functional metal/acid catalyst with porous materials such as ZSM-22 and mesoporous materials as support [21–24]. However, few studies have focused on the hydro-isomerization of fatty alcohol to iso-paraffin. During the conversion of fatty alcohol to iso-paraffin, dehydration and sketch isomerization is necessary. Such a conversion can be realized by selective dehydration and hydro-processing. In this paper,

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the catalytic performances of different catalysts in dehydration (ZSM-22, Al-MCF and ZSM-5) and hydro-isomerization (Pt/ZSM-22 and Pt/MCF) reactions were firstly studied. Based on the relationship between structure and performance, flexible integrated processes from medium fatty alcohol to jet fuel were proposed. Finally, the dehydration (Al-MCF)/hydro-isomerization (Pt/ZSM-22) process, which provides the highest iso-paraffin yield, was used for conversion of a commercially available alcohol mixture in a pilot scale reactor.

## 2. Experimental section

### 2.1. Materials

The materials used in this study including *n*-decanol and 1-octene were purchased from Sigma-Aldrich. The n-C12-based mixture of n-C8 to n-C18 fatty alcohols was purchased from Zhejiang Lanxi Chemical Works. ZSM-22 and aluminum incorporated mesocellulose silica foams (Al-MCF) were synthesized in our lab and ZSM-5 (CBV8014) was purchased from Zeolyst International.

### 2.2. Synthesis of catalyst

Proton form of the commercial ZSM-5 (CBV8014) was obtained by ammonium ion exchange (three times) with  $\text{NH}_4\text{NO}_3$  (1 mol/L) under reflux conditions at 80 °C for 2 h followed by calcination at 550 °C for 4 h.

Al-MCF and ZSM-22 were synthesized according to previous publications [23–25]. The synthetic method of Al-MCF was briefly shown here as an example. 5 g of 1,3,5-trimethylbenzene was added into a solution containing 4 g of P123, 10 mL of HCl (37 wt.%), and 65 mL of water. After the solution was heated to 40 °C under reflux conditions for 2 h, 9.2 mL of tetraethoxysilane was then added and kept at 40 °C for 20 h. The resulting solution was then transferred into an autoclave and 46 mg of  $\text{NH}_4\text{F}$  was added. Then, the autoclave was placed at 140 °C for 24 h. The precipitate was subjected to a sequence of filtration, washing with water and ethanol, drying at 80 °C for 1 h, and calcining at 550 °C for 4 h to form MCF. A certain amount of MCF was added to a mixture of  $\text{AlCl}_3$ -ethanol and stirred at room temperature for 12 h. The Si/Al ratio was controlled to be 10. Al-MCF was thus obtained by drying the resulting solid at 130 °C for 1 h and calcination at 550 °C for 4 h. Ammonium ion exchanges (three times) were also conducted for Al-MCF with  $\text{NH}_4\text{NO}_3$  (1 mol/L) at room temperature for 4 h followed by calcination at 550 °C for 4 h.

In order to obtain the bi-functional catalyst for hydro-isomerization reaction, Pt was introduced by the incipient wetness impregnation method [26]. Following the impregnation step, the solid was calcined at 420 °C for 4 h to form Pt/ZSM-22 and Pt/Al-MCF, respectively. All of the catalysts used in this study were shaped and subsequently crushed to 20–40 mesh.

### 2.3. Characterization of the catalysts

X-ray diffraction (XRD) measurements were carried out in a Bruker diffractometer with  $\text{CuK}\alpha$  radiation (45 kV, 200 mA), data was recorded in the 2 Theta range of 5–50° with an angular step size of 0.05 and a counting time of 8 s per step.

Transmission electron microscopy (TEM) was obtained with a FEI Tecnai G2 20 S Twin microscope operated at 200 kV. High resolution TEM analysis was carried out with a JEOL 3010F micro-scope. Before TEM investigation, samples were dispersed in ethanol, and then deposited on a holey film supported of a lacey support films. During TEM analysis, large specimen was investigated and representative TEM images were recorded.

Nitrogen adsorption-desorption measurements were performed on a Micromeritics ASAP 2020 HD 88 surface area and porosity analyzer. The calcined samples were degassed at 350 °C in a vacuum of

$1.33 \times 10^{-3}$  Pa for 10 h and then switched to the analysis station for adsorption-desorption analysis at –196 °C.

Temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) was carried out in an Micromeritics Autochem 2910 II instrument. During analysis, 0.1 g catalyst was pretreated at 400 °C in He flow (20 mL/min) for 2 h. Afterward, 10 vol%  $\text{NH}_3$  in He (20 mL/min) was adsorbed at 200 °C for 30 min followed by He purging at the same temperature for 1 h.  $\text{NH}_3$  was desorbed in range 100–600 °C at a heating rate of 10 °C/min.

$^{27}\text{Al}$  nuclear magnetic resonance measurements with the magic angle sample spinning ( $^{27}\text{Al}$  MAS NMR) were performed on a Bruker Advanced 300 spectrometer. The spectra were measured at 78.2 MHz using a 4 mm MAS probe at 8 kHz MAS spinning frequency under the room temperature. The parameters were as following: the pulse length of the selective 10° pulse was 0.5  $\mu\text{s}$ , the repetition time to complete the spin lattice relaxation was 4 s; 64 scans were accumulated. The  $^{27}\text{Al}$  chemical shifts were referenced using the narrow  $\text{AlO}_6$  signal of YAG set to  $\delta$  ( $^{27}\text{Al}$ ) = 0.6 ppm calibrated against a 1 M Al ( $\text{NO}_3$ )<sub>3</sub> aqueous solution.

Fourier transform infrared measurements were performed on a Nicolet Magna-IR 750 spectrometer in KBr pellets. 10 mg of sample was pressed into a self-supporting wafer, which was then evacuated in situ at 500 °C for 2 h in an IR cell. When the temperature was cooled to about 25 °C, Pyridine was then introduced into the cell until the saturated adsorption was reached. Finally, adsorbed pyridine was desorbed at 150 °C, 350 °C and 450 °C in vacuum respectively, and the FT-IR spectra were then recorded. Spectra at 150 °C and 350 °C was chosen for giving the total acid amount and middle-strong acid amount, respectively. Peak areas at 1540–1548 and 1445–1460  $\text{cm}^{-1}$  were integrated to measure Brønsted acid and Lewis acid sites with coefficient being 1.88 and 1.42, respectively.

### 2.4. Dehydration of fatty alcohol

Catalysts used in dehydration process included Al-MCF, ZSM-22, and ZSM-5 (CBV8014). Dehydration of fatty alcohol was conducted in a down-flow fixed bed reactor under ambient pressure using 1 g of catalyst, which was settled in the middle of reactor with proper amount of ceramic rings capped with silica wool in the lower part of the reactor. Before reaction, the catalyst was pretreated at 400 °C for 3 h under a 200 mL/min  $\text{N}_2$  flow. Then the reactor was cooled to reaction temperature, and *n*-decanol was pumped into a preheater at 280 °C, heated into steam and purged into reactor with 200 mL/min  $\text{N}_2$  flow. The dehydration performance over three catalysts at different temperatures were tested. The resulting product was fed into a high pressure fixed bed reactor for hydro-isomerization using metal/acid bifunctional catalyst as described in the section 2.5. The liquid hourly space velocity (LHSV) in dehydration reaction was 6  $\text{h}^{-1}$ . During the dehydration experiments, the liquid product yield is between 90 wt% and 95 wt%, depending on the catalyst. The content of organic phase in the liquid product is about 84 wt%, and the rest is water phase.

In the downstream of the reactor, a condenser at –7 °C were employed for collecting condensable products, which was sampled per hour and analyzed by GC/MS (Agilent-7890A/5975C) equipped with a capillary column (HP-5, 30 m  $\times$  0.25 mm).

### 2.5. Hydro-processing of fatty alcohol and the dehydration products

A down-flow fixed bed reactor similar to dehydration reaction was used in the fatty alcohol hydro-processing. 1 g of Pt/ZSM-22 or Pt/Al-MCF, was firstly introduced into the middle part of the reactor and pretreated at 400 °C for 3 h with  $\text{H}_2$  flow. After the temperature decreased to the settled reaction temperature, reactant was continuously pumped into the reactor with a rate of 0.1 mL/min. The liquid hourly space velocity (LHSV) in dehydration reaction was 6  $\text{h}^{-1}$ , which was determined by a series of screening experiments shown in supporting

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