



# Bio-aviation fuel production from hydroprocessing castor oil promoted by the nickel-based bifunctional catalysts



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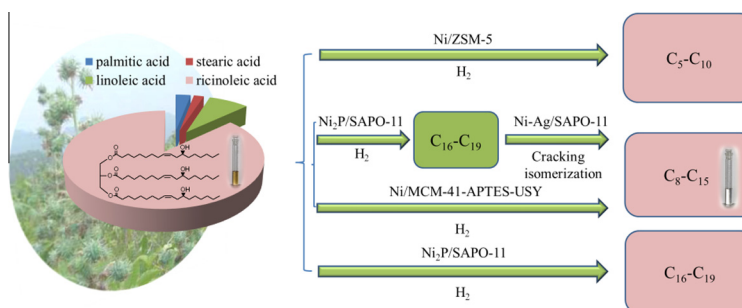
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## HIGHLIGHTS

- Bio-aviation fuel was firstly synthesized by hydroprocessing castor oil.
- Castor oil was converted into aviation fuel by the two-step process and a one-pot process respectively.
- The degree of hydrodeoxygenation and hydrocracking could be adjusted by Ni supported on moderate acidic zeolites.

## GRAPHICAL ABSTRACT

Different fuel range alkanes can be synthesized from hydroprocessing castor oil by Ni supported on different acidic zeolites, and bio-aviation fuel can be obtained by Ni supported on moderate acidic strength zeolites.



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## ABSTRACT

Bio-aviation fuel was firstly synthesized by hydroprocessing castor oil in a continuous-flow fixed-bed microreactor with the main objective to obtain the high yield of aviation fuel and determine the elemental compositions of the product phases as well as the reaction mechanism. Highest aviation range alkane yields (91.6 wt%) were achieved with high *isomer/n-alkane ratio (i/n)* 4.4–7.2 over Ni supported on acidic zeolites. In addition, different fuel range alkanes can be obtained by adjusting the degree of hydrodeoxygenation (HDO) and hydrocracking. And the observations are rationalized by a set of reaction pathways for the various product phases.

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## 1. Introduction

One of the world's most serious problems is the depletion of petroleum-based resources because of increased industrialization and motorization. It has been reported that the transport sector

uses 40% of the primary energy consumed in the world (Mohan et al., 2006). Furthermore, the combustion of transportation fuels, especially in the aviation industry, contributes to the greenhouse effect due to the carbon emission. Therefore, it is necessary to find renewable, sustainable and efficient energy sources with lower emissions. Biofuels from vegetable oils show promising potential in the manufacture of liquid fuels. Hydrocarbons has been produced by HDO technology (Hancsó, 2014; Kumar et al., 2010;

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Verma et al., 2011; Warner et al., 2014; Mu, 2014; Bu et al., 2012; Sukrutha, 2014; Ren, 2014; Mascarelli, 2009), and there are some reports in the literature on using vegetable oils, such as palm, soybean, sunflower and coconut (Bykova et al., 2012). Castor is a kind of widely cultivated, inexpensive, environmentally friendly and industrial oil plant, meanwhile, castor oil, as an important and special feed, has long been known as the medicinal oil and an ingredient in the oleochemical industry (Mutlu, 2010; Horvath et al., 2008; Brown et al., 2010; Huang et al., 2014; Elliott, 2007; Antal et al., 1991; Ambekar, 1957), which has not been studied for bio-aviation fuel by HDO technology so far.

Aviation turbine fuels are a complex hydrocarbon mixture consisting of different classes, such as paraffin ( $C_8$ – $C_{15}$ ), naphthene and aromatics. Bio-aviation fuels are mainly composed of alkanes that are used as mixing components in aviation turbine fuels, with the largest proportion being less than 50% according to ASTM D7566. Therefore, high  $C_8$ – $C_{15}$  selectivity and the degree of isomerization become the key points for meeting the mixing standards of ASTM D7566. The properties of biofuels, such as freezing point, flash point and viscosity can be influenced by the components and the degree of isomerization.

Vegetable oils are composed of triglycerides, long-chain carbon (16–18) fatty acids; therefore, diesel range carbon chains ( $C_{16}$ – $C_{18}$ ) can be produced by the reaction pathways including dehydration, decarbonylation and decarboxylation (Bezergianni and Dimitriadis, 2013; Peng et al., 2012; Li et al., 2013; Berenblyum et al., 2012). In this context, there have been numerous studies on biodiesel production through HDO technology. Šimáček (2009) studied the hydroprocessing of rapeseed oil over Ni–Mo/alumina hydrotreating catalysts at various temperatures (260–340 °C) under a pressure of 7 MPa in a laboratory flow reactor to produce biodiesel fuels. The obtained organic liquid product (mostly  $C_{17}$  and  $C_{18}$ ) does not contain basically any intermediates nor any remaining raw material at a sufficiently high reaction temperature (above about 310 °C). Sotelo-Boy (2010) investigated the hydrocracking of rapeseed oil over three different types of bifunctional catalysts: Pt/HY, Pt/H–ZSM-5 and sulfided NiMo/ $\gamma$ - $Al_2O_3$ . Pt/zeolite-supported catalysts were found to give a strong cracking activity, producing gasoline range alkanes for the most part due to the strong acid sites. However, the less acidic sulfided NiMo/ $\gamma$ - $Al_2O_3$  produced more  $C_{17}$  and  $C_{18}$  (diesel range). Therefore, the selectivity of HDO production is influenced by the acid strength. However,  $C_8$ – $C_{15}$  hydrocarbons and moderate isomerization selectivity are ideally suited for jet fuels also because of the stringent international specifications. Thus, adjusting the degree of HDO

and hydrocracking plays a vital role in production of bio-aviation fuel.

In this work, we focused on the effects of nonsulfided nickel-based bifunctional catalysts on HDO and hydrocracking. In general, transition metals are mainly responsible for the hydrogenation of unsaturated triglyceride and the acidic zeolite contributes to the degree of hydrocracking. More importantly, moderate cracking, adjusted by the acidity of catalysts, can convert  $C_{16}$ – $C_{18}$  straight chain alkanes into  $C_8$ – $C_{15}$  or directly obtain  $C_8$ – $C_{15}$  hydrocarbons with high isomerization selectivity from castor oil using a one-pot process (as shown in Fig. 1 and Table 1). Bio-aviation fuel can be attained through a two-step process and a one-pot process. The two-step process focuses on the hydrocracking of  $C_{16}$ – $C_{19}$  to  $C_8$ – $C_{15}$ , which mainly studies the addition of Ag into Ni/SAPO-11 to adjust the degree of hydrocracking. However, the  $C_8$ – $C_{15}$  can be produced via the one-pot process over (3-aminopropyl)-triethoxysilane (APTES) modified MCM-41/USY composite-supported Ni. In this composite system, MCM-41 and USY are covalently bound together by the addition of APTES. The strong acid site of USY can be moderately covered by adjusting the ratio of MCM-41 and USY being supported by  $NH_3$ -TPD to lessen cracking, and the addition of APTES contributes to the homogeneous mixing of MCM-41 and USY. Furthermore, the mesoporous–microporous system improves the mass transfer ability of triglyceride molecule leading to excellent catalytic efficiency.

## 2. Methods

### 2.1. Materials

The castor oil was commercially available from Tianjin Guangfu Technology Co. Ltd. MCM-41 ( $S_{BET}$ : 842  $m^2/g$ ), SAPO-11 ( $S_{BET}$ : 240.3  $m^2/g$ ), USY ( $S_{BET}$ : 655  $m^2/g$ ), ZSM-5 ( $S_{BET}$ : 262.5  $m^2/g$ ) and H-Beta ( $S_{BET}$ : 650  $m^2/g$ ) were purchased from the catalyst plant of Nankai University.

### 2.2. Catalyst preparation and characterization

#### 2.2.1. Catalyst preparation

We applied the decomposition of hypophosphite precursors method to synthesize  $Ni_2P$ /SAPO-11 as we previously reported (Guan et al., 2009), and metal phosphides would not be easily influenced by Al–O of SAPO-11 in the case of high temperature calcination.  $Ni_2P$ /SAPO-11 was prepared with P:Ni mole ratio of 1.5.

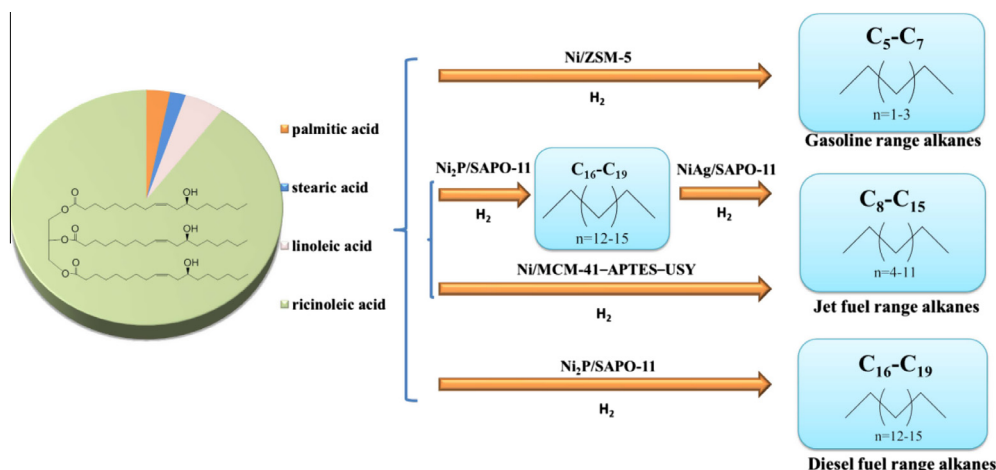


Fig. 1. Hydroprocessing castor oil by Ni-based bifunctional catalysts with variable acidity.

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