One-step preparation of biological aviation kerosene by catalytic hydrogenation of waste lard over Pt/SAPO-11

X Zhang1, Y B Chen1,3, X Y Li1, D Souliyathai1, S P Zhang1, Q Wang1, Q Liu2, J C Du2 and A M Zhang2

1School of Energy and Environment Science, Yunnan Normal University, Kunming, Yunnan, China
2Kunming Institute of Precious Metals, Kunming, Yunnan, China
E-mail: c20072007@163.com

Abstract. Biological aviation kerosene was produced by one-step catalytic hydrotreatment of waste lard oil over Pt/SAPO-11 in a high-pressure fixed bed micro reactor. The influence of reaction conditions such as temperature, pressure, hydrogen oil ratio, and space velocity on the deoxygenation rate, the selectivity of C\textsubscript{8}-C\textsubscript{16} hydrocarbons and the isomerization rate of C\textsubscript{8}-C\textsubscript{16} hydrocarbons have been investigated. The experimental results showed that the temperature of 400{\textdegree}C, pressure of 5 MPa, hydrogen oil ratio of 1000 and space velocity of 1.2 h\textsuperscript{-1} were the best experimental reaction conditions. Under these conditions, the conversion rate is 96.62\%, the selectivity of C\textsubscript{8}-C\textsubscript{16} hydrocarbons is 50.25\%, and the isomerization rate of C\textsubscript{8}-C\textsubscript{16} hydrocarbons is 35.68\%.

1. Introduction
With the rapid development of economy and the improvement of people's living standard, the air transportation industry is playing an important role in the process of economic globalization [1]. As far as civil aviation concerned, the number of people and goods transported by air increased by 4.9\% and 5.3\%, respectively [2]. In 2005-2010, the total diesel fuel and jet fuel consumed 500-600 million barrels per day [3], and the global air transport industry consumes 15-17×10\textsuperscript{8} barrels of aviation kerosene a year [4,5]. Conventional aviation kerosene burns on the aircraft's turbine engines, generating CO\textsubscript{2} directly into the atmosphere of the stratosphere, causing severe greenhouse effects; At the same time, it also affects the global climate change. As a result, the airline industry faces severe challenges in reducing greenhouse gas emissions. In the face of pressure reduction, IATA made three promises: from 2009-2020, the combustion efficiency of aviation kerosene average annual increase by 1.5\%; by 2020, reach zero emissions targets; compared with the year 2050, emissions fell to 50\% [6,7]. In addition to environmental problems, aviation kerosene prices soared, from jet fuel $320/t average cost in 2004 increased to $1005/t in 2011, it also forced the airline industry to pursue a clean, low price alternative fuel. In addition to environmental and cost considerations should also be considered such as aerospace safety work [8]. In addition, the air transport sector requires high energy density liquid hydrocarbon fuels [9]. Alternative fuels for aviation kerosene must have some special properties, for example, good cold flow, thermal stability and low freezing point [10], and fuel must be suitable for the currently designed aircraft engines. Biomass as the only carbon resource other than
petrochemical energy [11] has a bright future in the production of clean energy. The biomass is converted into C₈-C₁₆ isomeric alkanes, naphthenic hydrocarbons, olefins and aromatic hydrocarbons. It is the best way to substitute biochemical aviation kerosene for the replacement of petrochemical aviation kerosene by converting biomass into C₈-C₁₆ isomeric alkanes, naphthenic hydrocarbons, olefins and aromatic hydrocarbons to prepare bio aviation kerosene [12]. Studies have shown that in the full life cycle, bio-aviation kerosene greenhouse gas emissions than Petrochemical aviation kerosene reduced by 50%-90% [13]. At present, many kinds of biological aviation kerosene have been developed, including Fischer Tropsch synthesis (F-T synthesis) method, biotransformation, thermochemical conversion, hydrogenation method, etc. In this paper, bio-fuel aviation kerosene was prepared by using one-step hydrogenation of the waste lard as raw material over Pt/SAPO-11 as catalyst. The effects of temperature, pressure, hydrogen oil ratio and space velocity on the deoxygenation rate, selectivity of C₈-C₁₆ hydrocarbons and the isomerization rate of C₈-C₁₆ hydrocarbons were investigated by one-step preparation of biological aviation kerosene.

2. Experimental

2.1. Materials and reagents

Waste lard: the main fatty acids were made up their fatty glyceride, as shown in table 1 and figure 1.

| Retention time | Fatty acid name    | Molecular formula | Relative percentage content/% |
|---------------|-------------------|-------------------|------------------------------|
| 7.04          | myristic acid     | C₁₄H₂₈O₂          | 1.2                          |
| 8.84          | hexadecenoic acid | C₁₆H₃₀O₂          | 1.88                         |
| 9.05          | cetylic acid      | C₁₆H₃₂O₂          | 17.89                        |
| 10.63         | linoleic acid     | C₁₈H₃₂O₂          | 15.59                        |
| 10.69         | oleic acid        | C₁₈H₃₄O₂          | 50.38                        |

| Time (min) | Relative content (%) |
|------------|----------------------|
| 0          | 0                    |
| 5          | 40                   |
| 10         | 50                   |
| 15         | 50                   |

Figure 1. GC diagram of the main fatty acid composition of lard.

The chemical reagents are analytical pure (AR), Main: anhydrous sodium sulfate, methanol, concentrated sulfuric acid (Xilong Chemical Co., Ltd.). Petroleum ether, dichloromethane, anhydrous ethanol (Tianjin wind boat chemical reagent Technology Co., Ltd.)
Pt/SAPO-11 catalyst: the research group made the preparation by dipping method [14]. The functionalized SAPO-11 carrier was impregnated in H₃PtCl₆ solution with equal volume of 6 h, dried at room temperature for 15 h, dried at 110°C for 4 h, calcined at 500°C for 6 h, then cooled and ground to make 2%(WT) Pt/SAPO-11 catalyst [15,16]. The catalyst under 320°C/1MPa of hydrogen pressure was activated 6 h before using.

2.2. Main instruments
MRT-H00521JB type high-pressure micro fixed bed catalytic reaction evaluation equipment (research group design, commissioned by Beijing Aerospace century star laboratory equipment Co., Ltd.), Clarus 680-Clarus SQ8T GC-MS (American PerkinElmer Corporation), DHG-9203A electric blower drying box (Shanghai constant Scientific Instrument Co., Ltd.), HZQ-C double layer air bath constant temperature oscillator (Jintan Dadi automatic instrument factory), Analytical balance (Shanghai Hengping Scientific Instrument Co., Ltd.), Rectifying column (Tianjin friend Technology Co., Ltd.).

2.3. Method

2.3.1. Characterization of catalyst structure

- **X ray diffraction (XRD)**
  The XRD test was carried out on the D/MAX-2000 type fully automatic X ray diffractometer. The test conditions: source of radiation was CuKα, the wavelength was 0.15406 nm, the tube current was 40 mA, the tube voltage was 40 kV [17]. The X ray diffraction of the result are given in figure 2.

![Figure 2. Pt/SAPO-11 catalyst.](image)

Pt/SAPO-11 catalysts exhibit characteristic peaks of SAPO-11 molecular sieves at 9.82, 16.03, 21.84, 23.46, etc, and the peaks are sharp and high in intensity. Modification did not change the skeletal structure of the molecular sieve.

- **N₂-Physisorption**

| sample       | specific area (m²/g) | pore volume (cm³/g) | mean pore size (nm) |
|--------------|----------------------|---------------------|---------------------|
| Pt/SPAO-11   | 223.17               | 0.2121              | 3.6                 |
The surface area of the catalyst, pore capacity, the average aperture was detected in the United States Contador Company NOVA2000e surface area and porosity analyzer. The adsorption temperature of N\textsubscript{2} was 77 K [17]. The specific surface area, pore capacity and mean pore size were calculated by BET method. The catalyst BET analysis of the Pt/SPAO-11 molecular sieve is shown in table 2.

3. Results and discussion

3.1. Influence of temperature
At the space velocity of 1h\textsuperscript{-1}, the hydrogen-oil ratio was 1200, and the pressure was 4 MPa, the temperature was heated to 360, 380, 400, 420 and 440 respectively, prepare aviation kerosene, in high pressure fixed bed micro evaluation device on one-step catalytic hydrogenation of waste lard. Figure 3 shows the influence of the temperature on conversion rate of the waste lard, the selectivity of C\textsubscript{8}-C\textsubscript{16} hydrocarbons, and the isomerization rate of C\textsubscript{8}-C\textsubscript{16} hydrocarbons under different reaction temperatures.

Figure 3. Effect of temperature on one step hydrogenation of waste lard.

Figure 3 shows that with the increase in temperature from 360 to 440°C, lard conversion rate obviously increased firstly and then decreased, and the 400°C of temperature conversion rate reached 97.01%, for the selectivity of C\textsubscript{8}-C\textsubscript{16} hydrocarbons increases gradually. When the temperature was greater than 400, the selectivity of hydrocarbons was 41.02%, and then decreased by about 28%. It may be that the higher temperature causes the cracking reaction to increase and long chain heavy hydrocarbon are converted into short chain hydrocarbons, resulting in the selectivity of C\textsubscript{8}-C\textsubscript{16} hydrocarbons decreased. The isomerization rate of C\textsubscript{8}-C\textsubscript{16} hydrocarbons increases gradually with the increase of temperature, and the isomerization rate of C\textsubscript{8}-C\textsubscript{16} hydrocarbons decreases gradually when the temperature reaches 380°C. This is because the alkane isomerization reaction was exothermic reaction, the temperature was too high, which was not conducive to isomerization reaction, at 400°C the selectivity of C8-C16 hydrocarbons was 20.02%. Above all, 400°C was the best reaction temperature. The GC spectra of the catalytic products of waste lard under the optimum reaction temperature are shown in figure 4.
Figure 4. GC spectra of catalytic products of waste lard hydrogenation at the optimum reaction temperature.

3.2. Effect of space velocity

Figure 5 is the influence of space velocity on conversion, the selectivity of $C_8$-$C_{16}$ hydrocarbons and the isomerization rate of $C_8$-$C_{16}$ hydrocarbons.

![Graph showing effect of space velocity](image)

**Figure 5.** Effect of space velocity on one step hydrogenation of waste lard.

Figure 5 shows that the conversion rate is small, and all of them remain above 95%. When the space velocity was $1.2h^{-1}$, the selectivity of $C_8$-$C_{16}$ hydrocarbons and the isomerization rate of $C_8$-$C_{16}$ hydrocarbons increase gradually with the increase of space velocity, and reached the maximum of 43.24% and 24.14% respectively. In a certain range of space velocity, increasing the space velocity can make the raw oil more fully contact with the catalyst and increase the reaction speed, which is beneficial to the reaction. When the speed reaches a certain level, then increase the space velocity of raw oil attached to the catalyst surface hindered hydrogen and catalyst contact, which is not conducive to $C_8$-$C_{16}$ hydrocarbons and $C_8$-$C_{16}$ isoparaffin conversion, resulting in the selectivity of $C_8$-$C_{16}$ hydrocarbons and the isomerization rate of $C_8$-$C_{16}$ hydrocarbons are decreased. Therefore, the optimum space velocity was $1.2h^{-1}$. The GC spectra of the catalytic products of waste lard under the optimum reaction space velocity are shown in figure 6.
Figure 6. GC spectra of catalytic products of waste lard hydrogenation at the optimum reaction space velocity.

3.3. Effect of hydrogen oil ratio

Figure 7 is the influence of hydrogen oil ratio on conversion, the selectivity of C₈-C₁₆ hydrocarbons and the isomerization rate of C₈-C₁₆ hydrocarbons.

Figure 7. Effect of hydrogen oil ratio on one step hydrogenation of waste lard.

Figure 7 shows that the hydrocarbon content in liquid products, the selectivity of C₈-C₁₆ hydrocarbons and the isomerization rate of C₈-C₁₆ hydrocarbons tend to increase firstly and then decrease with the increase of hydrogen oil ratio. When the hydrogen oil ratio was 1000, the conversion rate, the selectivity of C₈-C₁₆ hydrocarbon and the isomerization rate of C₈-C₁₆ hydrocarbons reached the maximum values of 95.52%, 49.63%, 25.02% respectively. It may be because hydrogen oil ratio is relatively low in the entire reaction system, hydrogen, raw materials and catalysts are not fully exposed, resulting in slower reaction rate. Appropriately increasing the hydrogen oil ratio is beneficial to the conversion of hydrocarbons and isomerization of alkanes. But when the hydrogen oil ratio is too large, hydrogen surrounds the catalyst, so that the raw oil and catalyst can not be effectively contacted, leading to the rate of deoxygenation, the selectivity of C₈-C₁₆ hydrocarbons and the isomerization rate of C₈-C₁₆ hydrocarbons are decreased. So, the optimum hydrogen oil ratio was 1000. The GC spectra
of the catalytic products of waste lard under the optimum reaction hydrogen oil ratio are shown in figure 8.

![Figure 8. GC spectra of catalytic products of waste lard hydrogenation at the optimum reaction hydrogen oil ratio.](image)

3.4. Effect of pressure

Figure 9 is the influence of pressure on conversion, the selectivity of C₈-C₁₆ hydrocarbons and the isomerization rate of C₈-C₁₆ hydrocarbons.

![Figure 9. Effect of pressure on one step hydrogenation of waste lard.](image)

Figure 9 shows that the conversion rate, the selectivity of C₈-C₁₆ hydrocarbons and the isomerization rate of C₈-C₁₆ hydrocarbons tend to increase firstly and then decrease with the increase of pressure. When the pressure was 5 MPa, the conversion rate, the selectivity of C₈-C₁₆ hydrocarbon and the isomerization rate of C₈-C₁₆ hydrocarbons reached the maximum values of 96.62%, 50.25%, 35.02% respectively. It may be due to the beginning of the reaction, as the pressure continues to rise, the reactant partial pressure increases, the reaction speed increases, resulting in deoxygenation rate, C₈-C₁₆ hydrocarbon selectivity, and the isomerization rate of C₈-C₁₆ hydrocarbons increases. When the pressure reaches a certain level, increasing the pressure is beneficial to the coke production, blocking the catalyst channel, resulting in deoxygenation rate, the selectivity of C₈-C₁₆ hydrocarbons, and the isomerization rate of C₈-C₁₆ hydrocarbons decreased. Therefore, the optimum reaction pressure was 5
MPa. The GC spectra of the catalytic products of waste lard under the optimum reaction pressure are shown in figure 10.

![Figure 10. GC spectra of catalytic products of waste lard hydrogenation at the optimum reaction pressure.](image)

4. Conclusions

- Temperature is the key factor affecting the conversion rate of waste lard. When the temperature is certain, other factors have little influence on the conversion rate of waste lard.
- The temperature and space velocity have great influence on the selectivity of C₈-C₁₆ hydrocarbon. In the suitable range, increasing the temperature and increasing the space velocity are beneficial to the selectivity of C₈-C₁₆ hydrocarbon; Space velocity and pressure have a great influence on the isomerization rate of C₈-C₁₆ hydrocarbons. In a suitable range, increasing the space velocity and pressure is beneficial to the isomerization rate of C₈-C₁₆ hydrocarbons.
- The optimum reaction conditions for the preparation of aviation kerosene by one-step hydrogenation of waste lard were: temperature of 400°C, space velocity of 1.2h⁻¹, hydrogen oil ratio of 1000, and pressure of 5 MPa. Under these conditions, the conversion rate of waste lard, the selectivity of C₈-C₁₆ hydrocarbon and the isomerization rate of C₈-C₁₆ hydrocarbons were 96.62%, 50.25% and 35.68%, respectively.

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