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Catalytic cracking of triglycerides with a base catalyst and modification of pyrolytic oils for production of aviation fuels†

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Molecular structure transformation is a critical step for synthesis of aviation biofuels from triglycerides, to yield alkanes, aromatics and cycloalkanes. To this end, triglycerides were treated by catalytic cracking coupled with rectification to obtain hydrocarbon fuels, and the molecular weight of the liquid product was adjusted to the desirable boiling range of aviation fuel. To further modify the molecular structures, the pyrolytic hydrocarbons were partially converted into aromatics and cycloalkanes by a two-step process. Different raw materials including soybean oil, rubber seed oil, waste cooking oil and acidified oil were cracked with a 5 wt% base catalyst at 350–450 °C (under the atmospheric pressure) in a benchtop reactor. Afterwards, the linear hydrocarbons of C8–C15 size were transformed into aromatics by HZSM-5 at 350 °C for 6 h. Then, a portion of the aromatics were converted into cycloalkanes catalyzed by Pd/AC at 200 °C and 6 MPa (H_2) for 6 h. As a result, a desirable mixture of linear hydrocarbons, aromatics and cycloalkanes was obtained with a similar composition and properties to traditional fossil aviation fuels.

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1. Introduction

In recent years, increased attention has been paid to the development of alternative aviation fuels. Thermal chemical conversion of biomass is an efficient pathway to mass produce liquid fuels in a relatively short period with minimal CO_2 emissions.[1–4] Pyrolysis of triglycerides and related feedstocks has been extensively used to obtain alternative hydrocarbon fuels similar to those obtained from petroleum.[5–7] Triglycerides are the major components of vegetable oils and animal fats, being comprised of three long fatty acid chains connected with a glycerol moiety. The cracking of triglycerides occurs at about 330–450 °C in the presence of various heterogeneous catalysts or without a catalyst.[8–12] In the process of decomposition, the scission of C–C bonds and cleavage of the C–O bonds are two main kinds of reactions.[13]

Vegetable oils and animal fats can be directly decomposed into liquid phase hydrocarbons in the absence of a catalyst *via* a high temperature process. Studies of non-catalytic cracking have been previously reported.[14–16] The mixture of paraffins, olefins, aromatics, ketones, and carboxylic acids were obtained during thermal conversion. Kozliak *et al.*[14] cracked jojoba oil without a catalyst to produce fuels with the main product size distributions C6–C22. The average GC content of alkanes and alkenes was 76.5% and only 5.5% aromatics were obtained. However, only mostly acyclic hydrocarbons can be generated from high temperature reactions without a catalyst, which cannot meet the requirements of high grade transportation fuels. Furthermore, the liquid fuel obtained from non-catalytic cracking had a high carboxylic acid content, 25–30% (ref. 16) and the acid number ranged from 116 mg KOH g^{-1} to 207 mg KOH g^{-1}.[12]

An important methodology for improving the properties of liquid fuels obtained from triglycerides is catalytic cracking. Various catalysts have been used in thermal cracking depending on the desired final products. As for the thermal conversion of triglycerides, many microporous and mesoporous molecular sieves have been applied, such as ZSM-5,[17–20] MCM-41 (ref. 21–24) and composite catalysts.[25–27]

It has been reported that catalytic cracking of vegetable oils over HZSM-5 gave a high yield of aromatics (84.8 wt%) in the organic liquid products, which mainly consisted of C6–C9 aromatic hydrocarbons (69.5 wt%).[17] Zhao *et al.*[18] investigated the optimization of camelina oil cracking with Zn/ZSM-5 as a catalyst. The yield of the hydrocarbon bio-fuel ranged between 46–60%. Zandonai *et al.*[13] transformed vegetable oils by hydrocracking performed over ZSM-5 and obtained less than 50% yields of organic liquid products, which consisted of 43%

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aromatics, 46% acids and 9% aliphatics. In general, due to the high acidity and activity of the catalyst, cracking of triglycerides over HZSM-5 is suitable to produce smaller molecular size gasoline components, which are not in the range of aviation fuel.[20] The mesoporous catalyst MCM-41 also has been reported as a catalyst for cracking vegetable oils and waste cooking oils.[21,22] Comparing the performance of MCM-41 to ZSM-5, it has been found that the MCM-41 is more selective for alkanes and alkenes with C15–C18 size, which are in the diesel fuel range because of relatively large pores sizes.[21–23] Simultaneously, the fatty acid content was not significantly decreased over most catalysts based on MCM-41. Kubička *et al.*[21] investigated the conversion of triglycerides over CoMo/MCM-41 and the content of the fatty acids ranged from 10% to 60%. Li *et al.*[11,23] prepared K_2O/Ba-MCM-41 for cracking of soybean oil and waste cooking oil, and the acid values of the products were 33.2 mg KOH g^{-1} and 43 mg KOH g^{-1}, respectively. Despite good catalytic performance, the production of those alkaline zeolites, prepared under hydrothermal conditions, was highly expensive.[24]

According to the above results, all of the products of non-catalytic and catalytic triglyceride cracking have low viscosity and high calorific value. However, with respect to the molecular weight distribution, neither microporous nor mesoporous molecular sieves can provide a suitable length of carbon–carbon chain in the products. On the other hand, with regards to molecular structure, a high acid value limits the application of the obtained products, particularly those obtained without catalysts.

In our previous work, basic catalysts were used to produce pyrolytic oils with relatively low acid values. The catalytic cracking of soybean oil using Na_2CO_3 or K_2CO_3 as catalysts could decrease the acid value at 21–28 mg KOH g^{-1} and the yield of liquid products could be as high as 75.6%.[28] The analysis by GC-MS showed that the components of liquid products obtained from different woody oils were mostly alkanes, alkenes and carboxylic acids, and the carbon–carbon chain length was mostly C8–C19.[29]

Although a high yield of products with a low acid value can be obtained, we believe that the transformation of molecular structure needs further improvement to meet the requirements of aviation fuel. In particular, some methods have been developed for the production of various hydrocarbons from triglycerides. Benson *et al.*[30,31] elucidated the cracking pathway of model fatty acid and acylglyceride compounds at 400 °C on HZSM-5, a shape-selective zeolite catalyst. The process included the cracking of the unsaturated fatty acid side chains outside the catalyst pores and cyclization and aromatization of linear alkanes and alkenes inside the catalyst pores to form aromatic compounds. Fegade *et al.*[32] produced aromatics from triglycerides with a two-step process. A distilled organic liquid product produced by non-catalytic cracking of soybean oil was converted into a mixture of aromatics (58 wt%) and cyclic hydrocarbons (13 wt%) using HZSM-5 as a catalyst. It is important to note that high yields of aromatics were observed in a two-step process compared with one step process.[13,18]

In this work we report a new method to produce aviation biofuels that have similar compounds and properties to petroleum-derived jet fuels. The investigation includes: (1) base catalyzed cracking, production of C8–C15 linear hydrocarbons; (2) aromatization, partial transformation of linear hydrocarbons (C8–C15) into aromatics; (3) hydrogenation, conversion of some aromatics into cycloalkanes. Through the control of molecular weight and modification of molecular structures, three main hydrocarbon types in jet fuel were obtained from triglycerides, and the properties of the final product were up to standard of traditional petroleum-based jet fuel. Moreover, the organic products on the surface of the coke residue were analyzed and the mechanism of the coke formation in the process of basic catalytic cracking was proposed.

2. Experimental

2.1 General

Refined soybean oil and waste cooking oil were obtained from an industrial source and used without further purification. Rubber seed oil was obtained in Yunnan, China. The acidified oil was obtained from soysoap stock produced with sulfuric acid as the catalyst. The main physical and chemical characteristics of these raw oils are summarized in Table 1. The fatty acid composition of each oil was analyzed by GC-MS according to the content of methyl esters produced by either transesterification or esterification.

The sodium carbonate catalyst (Na_2CO_3) was of technical grade with a purity of 98.0 wt%. The HZSM-5 ($SiO_2/Al_2O_3 = 25$) was produced by Nankai University Catalyst Co., Ltd. and the Pd/AC (10% Pd) was provided by Aladdin in Shanghai, China. Gas chromatographic (GC) grade standards for *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, *n*-pentadecane, *o*-xylene, methyl dodecanoate (internal standard) and tetrahydrofuran (solvent) were purchased from Aladdin in Shanghai, China.

2.2 Description of the experimental apparatus

The experimental methodology is illustrated in Fig. 1. First, the triglycerides of plant oils or waste oils were subjected to catalytic cracking with the Na_2CO_3 catalyst. The products from the cracking process were distilled to obtain the aviation range fuel. The results of analysis of the remaining diesel fraction is available in the ESI.† To meet the requirements of jet fuel, the aromatization was processed to modify the composition of aviation fuel fraction with HZSM-5. Then, the content of cycloalkanes in the aromatized fuel was enhanced by a partial hydrogenation of the aromatics produced, catalyzed by Pd/AC.

2.2.1 Catalytic cracking of plant oils and waste oils. A benchtop, home-made 3 L stainless still batch unit equipped with a temperature controlled rectification column and two thermocouples was employed for catalytic cracking (Fig. 2a). Two thermocouples were used to detect the temperature of the vessel and rectification column, respectively. 1500 g of feedstock (W_1) and 5% (wt) Na_2CO_3 (W_2) were loaded into the reactor, and the pyrolysis reaction occurred at 350–450 °C at the atmospheric pressure. When the reactor was heated to 350 °C,

Table 1 Basic properties of the feedstocks

Properties	Soybean oil	Rubber seed oil	Waste cooking oil	Acidified oil
Density[a] (kg m^{-3})	0.92	0.92	0.84	0.94
Heat value (MJ kg^{-1})	38.95	38.50	37.89	31.78
Viscosity[a] (mm^2 s^{-1})	64.82	76.68	149.06	—[b]
Acid value (mg KOH g^{-1})	0.31	19.72	104.65	114.00
Elemental analysis (wt%)				
C	77.43	77.36	76.06	64.22
H	11.53	11.75	12.04	10.47
O	10.70	10.53	11.27	24.29
N	0.33	0.36	0.63	1.02
Composition of fatty acids (%)				
Palmitic acid (16 : 0)	16.3 ± 1.0	8.3 ± 1.6	14.5 ± 2.0	19.6 ± 2.4
Stearic acid (18 : 0)	7.5 ± 0.3	5.7 ± 2.4	2.4 ± 1.6	None
Oleic acid (18 : 1)	22.0 ± 1.5	47.6 ± 3.3	67.1 ± 2.2	34.8 ± 1.8
Linoleic acid (18 : 2)	51.1 ± 3.0	38.4 ± 0.8	13.5 ± 2.1	45.6 ± 4.2

[a] Measured at 20 °C. [b] The acidified oil had a paste-like consistency at 20 °C and so its viscosity could not be measured.

the pyrolyzed vapor left the reactor by the upper side rectification column at a temperature of 300 °C. Meanwhile, compounds with high boiling points, >300 °C, were expected to be retained on the rectification column and returned to the reactor for additional cracking. The flow of gas-phase feed entered the water-cooled condenser. The non-condensable gas came out from the top control valve and the condensate was separated and stored in the liquid collector. The liquid product obtained in the collector was layered in an aqueous phase (water, W_3) and organic phase (liquid fuel, W_4), which were separated by decantation. A further distillation of the organic phase was carried out using standard laboratory techniques. The distillates were separated into three fractions with different distillation parameters: distillation temperature (DT) < 270 °C, atmospheric pressure (aviation fuel fraction, W_5); DT < 340 °C, vacuum (diesel fraction, see ESI†); DT > 340 °C, vacuum (residual oil). The first two fractions were weighed and analyzed by GC-MS and GC.

Moreover, some coke (W_6) remained in the reactor. In order to detect the compounds occurring in coke, the coked fraction was ground to reduce the particle size, washed with water to remove the rest of the catalysts, and dried in an oven for elemental analysis and XRD analysis. The organic components of the dried powder were dissolved with 50 mL of tetrahydrofuran, which was evaporated to remove half of the solvent and the liquid phase was analyzed by GC-MS.

The yields for different products are defined as follows:

$$\text{Yield (liquid fuel)} = \frac{W_4}{W_1} \times 100\%$$

$$\text{Yield (aviation fuel fraction)} = \frac{W_5}{W_1} \times 100\%$$

$$\text{Yield (water)} = \frac{W_3}{W_1} \times 100\%$$

$$\text{Yield (coke)} = \frac{W_6 - W_2}{W_1} \times 100\%$$

$$\text{Yield (gas)} = \frac{W_1 - W_3 - W_4 - W_6}{W_1} \times 100\%$$

2.2.2 Aromatization and hydrogenation of the aviation fuel fraction.

Before the next step, the distilled aviation fuel fraction was washed to remove a portion of the acids, and so the acid value was decreased. The distilled aviation fuel fraction with a low acid value was weighed to 80 g and introduced to a 250 mL semi-continuous stainless autoclave equipped with a mechanical stirrer (Fig. 2b), with 5 wt% ZSM-5 as a catalyst. The

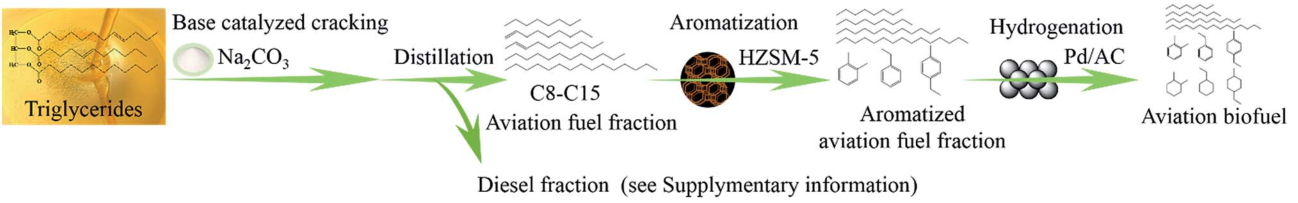

Fig. 1 Experimental technical route for the chemical transformation of triglycerides to aviation biofuel.

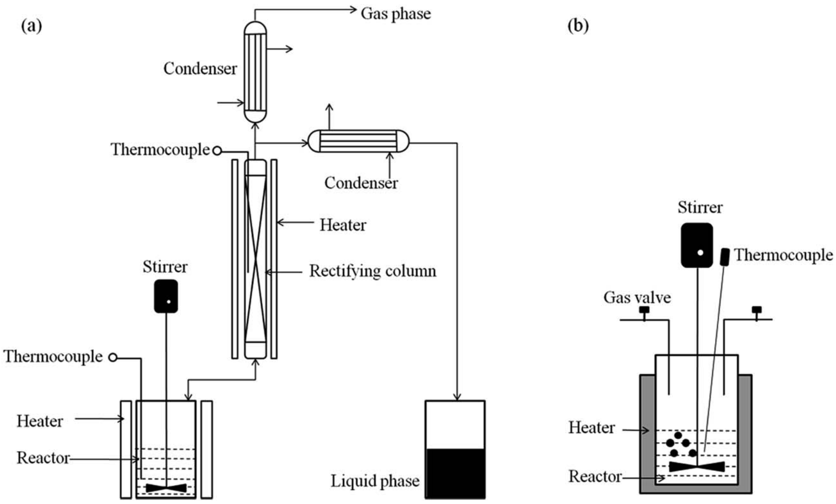

Fig. 2 Schematic diagram of the experiment setup for the catalytic cracking coupled rectification (a) and the aromatization of linear hydrocarbons and hydrogenation reaction of aromatics (b).

autoclave was heated to 350 °C with a stirring speed at 500 rpm. The reaction was kept at the final temperature for 6 h before cooling to room temperature with tap water. Gaseous products were removed from the controlled gas valve, and the aromatized products were separated from the catalyst by centrifugal process for GC-MS and GC analyses and the next stage of hydrogenation.

Further, 30 g of the aromatized products and 5 wt% Pd/AC were charged into a 100 mL stainless autoclave similar to the reactor for hydrogenation. After purging the air thrice with hydrogen, the reactor was pressurized with 6 MPa H_2 and the sealed system was heated to 200 °C. The reaction temperature was maintained for 6 h with a stirring speed of 500 rpm. Following the completion of hydrogenation reaction, liquid fuel was separated from the solid catalyst by vacuum filtration. The liquid products were identified by GC-MS for a detailed distribution of components. FT-IR was also applied for quantification of the main functional groups. Moreover, the basic properties of the liquid hydrogenated products were measured and compared with the petroleum products. All the above experiments were carried out in duplicate, and standard deviations were calculated and provided.

2.3 Analytical methods

To identify the composition of liquid products, gas chromatography-mass spectrometry (GC-MS) was carried out on an Agilent 6890N/5973N instrument, equipped with a FID detector and a capillary column of HP-5 (30 m × 0.25 mm × 0.25 μm). The oven was heated from the initial temperature of 50 °C (held for 2 min) to 280 °C (held for 20 min) at a heating rate of 5 °C min^{-1}. The EI voltage used in the MS ion source was 70 eV. The mass spectral scans were taken from 50 Da to 550 Da. Chromatographic peaks were identified according to the GC-MS library. Products were quantitated using gas chromatography (GC-FID). The tests were performed on a column of RTX-5 (30 m × 0.32 mm × 0.25 μm) and with the following program: an initial temperature of 50 °C for 2 min, followed by a heating rate of 5 °C min^{-1} until a final temperature of 280 °C, maintained for 20 min. IR spectra (iS10 Nicolet USA) were used to determine the main functional groups of the liquid fuels. Properties of the liquid products were characterized by several tests. The density of raw materials and liquid products were measured with a pycnometer. The viscosity was measured with capillary viscometers (GB/T265-1988). The heat value was measured with an IKA-C200 calorimetric bomb (ASTM D4809). The acid value was measured in terms of GB/T 5530-2005 and GB/T 12574. The elemental content was determined by a PE-2004 elemental analyzer (JY/T 017-1996). The freezing points were measured according to GB/T2430. X-ray diffraction (XRD) was used to detect the internal structure of the coke.

3. Results and discussion

3.1 Catalytic cracking of different feedstocks with a base catalyst

The process of catalytic cracking of soybean oil was investigated, and the results are presented in Fig. 3. Liquid products were initially obtained at around 350 °C, and the main product was water. With an increase of reaction temperature the yield of the liquid product increased. When the reaction temperature reached 450 °C, no liquid was formed anymore, which indicated the end of the reaction. In the process of catalytic cracking, 67% liquid production was obtained at 370–430 °C, and the yield of 390–400 °C fraction was about 25%. As a result, high yields of liquid pyrolytic oil were obtained and the total yield reached 74% based on the initial weight of soybean oil. Moreover, the composition of the liquid products at different temperatures was evaluated and the results are shown in Fig. 3b. It can be concluded that the two main components of the products are alkanes and alkenes. We also found that the yield of aromatics was increased, which can be attributed to the conversion of linear hydrocarbons to aromatics through cyclization and aromatization reaction at higher reaction temperature.

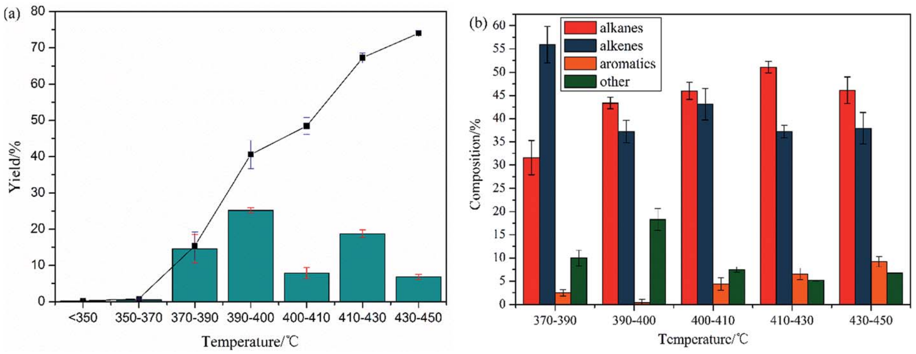

Fig. 3 The yield (a) and composition (b) of the liquid products at different temperatures in the process of soybean oil cracking.

Table 2 Catalytic cracking of different feedstocks over 5 wt% Na_2CO_3

	Aviation fuel fraction		Liquid fuel	Water	Coke	Gas
Feedstock	Yield/%	Acid value/mg KOH g^{-1}	Yield/%	Yield/%	Yield/%	Yield/%
Soybean oil	40 ± 2.1	41.7 ± 0.6	69.6 ± 0.5	4.4 ± 0.4	12.4 ± 1.4	13.6 ± 0.8
Rubber seed oil	17.2 ± 3.1	35.5 ± 1.2	61 ± 0.5	5.2 ± 0.7	2.1 ± 0.1	32 ± 0.9
Waste cooking oil	29.5 ± 1.9	55.9 ± 1.6	76 ± 1.0	4.6 ± 0.1	9.8 ± 0.5	9.6 ± 1.6
Acidified oil	26.3 ± 2.5	53.6 ± 2.8	63.7 ± 1.5	6.4 ± 0.3	6.5 ± 0.9	21.9 ± 0.4

The performance of different feedstocks were investigated for cracking with 5 wt% base catalyst of Na_2CO_3 at the rectification temperature of 300 °C. Afterwards, the yield of liquid fuels, water, coke, and gas were evaluated. The liquid fuels were distilled into the aviation fuel fraction and diesel fraction (see Table S1 in ESI†) and the acid value was analyzed. The results are shown in Table 2. The method of catalytic cracking has good applicability with different materials, and the high yield (61–76%) of liquid fuel can be obtained from cracking with a base catalyst. Meanwhile, the acid value of the aviation fuel fraction distilled from the liquid product ranges from 34 mg KOH g^{-1} to 56 mg KOH g^{-1}.

Furthermore, the main components in the aviation fuel fraction obtained from different feedstocks were detected and quantified with GC-MS and GC-FID, respectively (Table 3). The main components of the aviation fuel fraction are alkanes and alkenes whose total content is more than 70%. However, the content of aromatics (*i.e.*, 9.9–14.4%) was low. The content of the detected carboxylic acids in the aviation fuel fraction ranges from 2.5% to 7.9%, and there were also some undetected compounds. It is important to note that the distribution of the carbon number of the aviation fuel fraction is C8–C15 (Fig. 4).

Different molecular structures of the compounds present different ignition and emission characteristics, which are important factors for the properties of fuels.[33] Previous researchers[33,34] have shown that alkanes, cycloalkanes, and aromatics are important components in jet fuel. Alkanes are dominant components in jet fuels, which greatly affect the heat of combustion values.[35] Cycloalkanes are important because this kind of compounds present high thermal stability for the jet fuel.[35] Aromatics are relatively less than 25 volume% in conventional jet fuel, but strongly influence physical properties such as density, energy density and smoke point.[35] Therefore molecules in the obtained aviation fuel fraction needed further modification to meet the requirements of currently used jet fuel.

3.2 Aromatization and hydrogenation of the aviation fuel fraction

In order to obtain aviation range fuel containing different kinds of compositions and at the same time to decrease the content of

Table 3 Distribution (wt%) in the aviation fuel fraction obtained from different feedstocks

	Alkanes					
Feedstock	Paraffins	Cycloalkanes	Total	Alkenes	Aromatics	Carboxylic acids
Soybean oil	16.5	14.4	30.9	39.8	14.4	3.5
Rubber seed oil	18.6	17	35.6	37.2	9.9	2.8
Waste cooking oil	22.9	9.5	32.3	37.5	10.6	7.9
Acidified oil	25.9	10.1	35.9	33.6	13.7	2.5

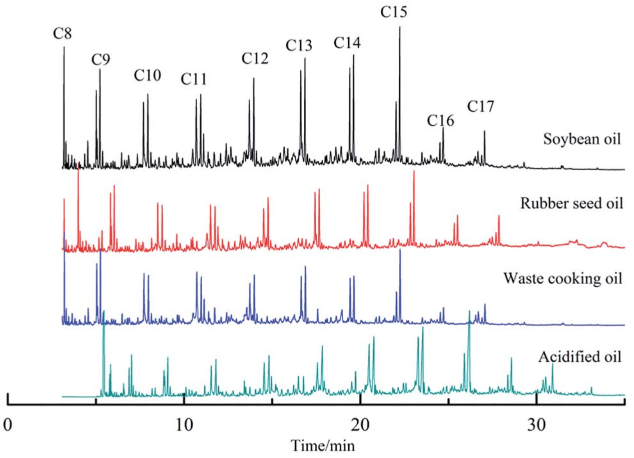

Fig. 4 GC-MS chromatograms of the aviation fuel fraction obtained from different feedstocks.

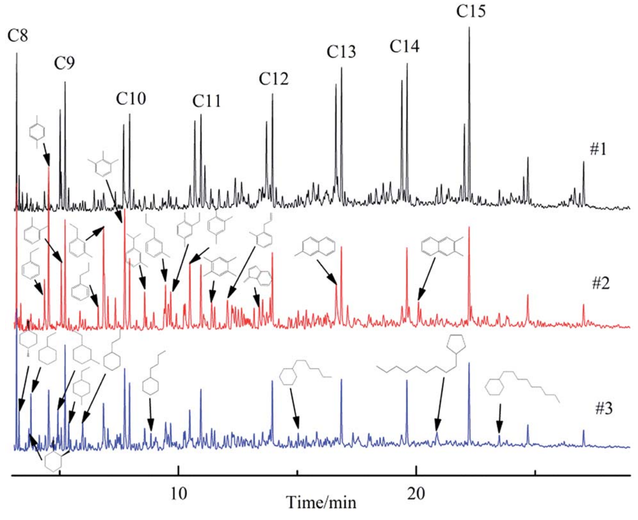

Fig. 5 GC-MS chromatograms for different compounds of the aviation fuel fraction obtained from soybean oil. (#1) The pyrolytic aviation fuel fraction; (#2) the aromatized aviation fuel fraction; (#3) the hydrogenated aviation fuel fraction.

olefins, which would reduce the stability of fuel, HZSM-5 was selected as the catalyst for aromatization. The composition of the aviation fuel fraction was significantly changed as a result of this treatment, as can be seen from the results presented in Table 4 (products #1 and #2). Under the influence of HZSM-5, the relative content of aromatics in the aviation fuel fraction increased from 14.4% to 26.7%. Meanwhile, a sharp decline in the content of alkenes and an increase in the content of paraffins were also detected. Therefore, we can conclude that in the process of aromatization, the olefins are dehydrogenated and cyclized by HZSM-5, and some undetected organics, such as carboxylic acids, are also transformed into paraffins through decarboxylation.

The treatment by hydrogenation on the third step was selected to increase the content of cycloalkanes. The results are presented in Table 4 (#3). About 80.1% of aromatics were hydrogenated to cycloalkanes and its content in the obtained products increased from 14.8% to 29.1%. Most of the remaining olefins were hydrogenated into paraffins.

Fig. 5 shows the results of GC-MS for the products obtained in the pyrolytic aviation fuel fraction (#1) along with its corresponding products from aromatization (#2) and hydrogenation (#3). In the pyrolytic aviation fuel fraction, most compounds identified by GC-MS were linear hydrocarbons. It is noteworthy that the alkenes disappeared and more aromatics were identified after aromatization. Cycloalkanes were formed by hydrogenation. These results suggest that the composition of pyrolytic products can be efficiently changed by the aromatization and hydrogenation reaction catalyzed by HZSM-5 and Pd/AC, respectively.

Fig. 6 shows the FT-IR spectra of the pyrolytic, aromatized and hydrogenated aviation fuel fraction. It can be seen that the spectra featured the strongest band centered at 2920 cm^{-1}, indicating the aliphatic C–H stretching. The narrow shape of the peaks indicates that the bulk of aliphatic acids are mostly decomposed in the process of catalytic cracking. The significant difference between aromatized and pyrolytic products is the intensity of the band reflecting stretching of the carbonyl group (1710 cm^{-1}). After aromatization, the band at 1710 cm^{-1} disappeared, which is consistent with our findings in the GC-MS analysis that the carbonyls can be removed by aromatization. The band at 1450–1370 cm^{-1} (CH, aliphatic) was also detected.

3.3 Properties of the aviation fuel fraction

Significant properties of the aviation fuel fraction are summarized in Table 5. The standard requirements of the RP-3 jet fuel are also presented. The acid value of the pyrolytic aviation fuel fraction is 20 mg KOH g^{-1}. After aromatization and hydrogenation, the acid value of the product decreased virtually to zero, consistent with the previous results shown in Table 4 and Fig. 6.

Table 4 Distribution (wt%) in the aviation fuel fraction from soybean oil[a]

	Alkanes					
Product	Paraffins	Cycloalkanes	Total	Alkenes	Aromatics	Carboxylic acids
#1	16.5	14.4	30.9	39.8	14.4	3.5
#2	21.7	14.8	36.6	15.2	26.7	0.0
#3	43.2	29.1	71.4	4.6	5.3	0.0

[a] #1: the pyrolytic aviation fuel fraction; #2: the aromatized aviation fuel fraction; #3: the hydrogenated aviation fuel fraction.

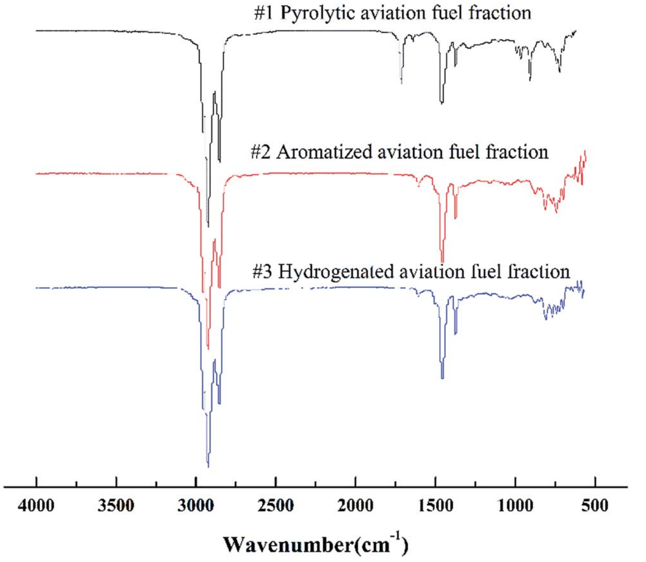

Fig. 6 FT-IR spectra of aviation fuel fraction obtained from soybean oil.

Table 5 Basic properties of the products obtained from soybean oil

Physical and chemical properties	Pyrolytic product	Aromatized-hydrogenated product	RP-3[c]
Density[a] (kg m^{-3})	799	808	775–830
Heat value (MJ kg^{-1})	43.6	44.4	>42.8
Viscosity[a] (mm^2 s^{-1})	1.82	2.11	>1.25
Acid value (mg KOH g^{-1})	20[b]	None	<0.015
Freezing point (°C)	−37	−48	−47

[a] Measured at 20 °C. [b] The distilled aviation fuel fraction was washed with water to remove a portion of acids. [c] Refers GB/T 6537-2006 in China.

The density and viscosity were, respectively, 808 kg m^{-3} and 2.11 mm^2 s^{-1}, which meet the requirements of RP-3. The heat value of the aviation biofuel was 44.4 MJ kg^{-1} conforming to the requirement of RP-3. Due to the utilization in low temperature environment, aviation fuels need to have a good low temperature fluidity. In addition to low viscosity, the freezing point (−48 °C) of the modified aviation fuel fraction is also up to the standard according to the GB/T 6537-2006.

3.4 Coke

To understand the mechanism of coke formation during the basic catalytic cracking, elemental and GC-MS analyses of the solid fraction were performed. According to the results of element analysis, the content of the carbon was 90.4 ± 1.3%, the hydrogen was 3.9 ± 0.4%, and the ratio of H/C was 0.04. No sulfur or nitrogen were detected. Besides, the XRD data (see Fig. S2 in ESI†) indicates that the coke is a highly carbonized product. According to the information obtained from GC-MS analysis in Fig. 7, the main compositions of the organics extracted from coke are polycyclic aromatic hydrocarbons, which is about 77% of the total analyzed organics. The long-chain hydrocarbons were also observed as apparent precursors of coke, which can be dehydrogenated and then cyclized to aromatics, polycyclic aromatic hydrocarbons and elemental carbon at the high temperature. Overall, the results of GC-MS are consistent with those of elemental analysis.

3.5 Coke formation mechanism

Although many investigations on coke formation in fluid catalytic cracking process have been reported,[36,37] there are only few reports about the mechanism of coking in basic catalytic cracking. As reported, the formation of coke from different kinds of reactants would go through the process of aromatization at high cracking temperature.[38] In the thermal cracking of triglycerides, the ester bond is cleaved, and furthermore,

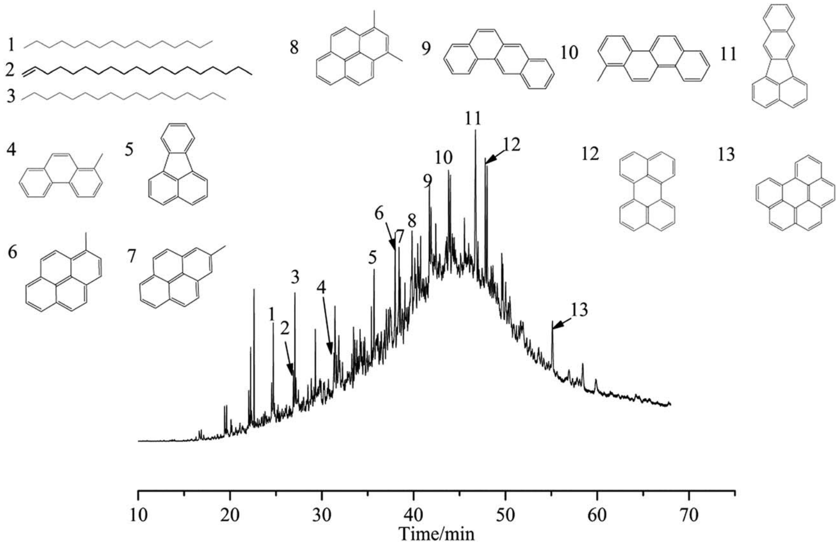

Fig. 7 GC-MS analysis of the organic compounds extracted from coke.

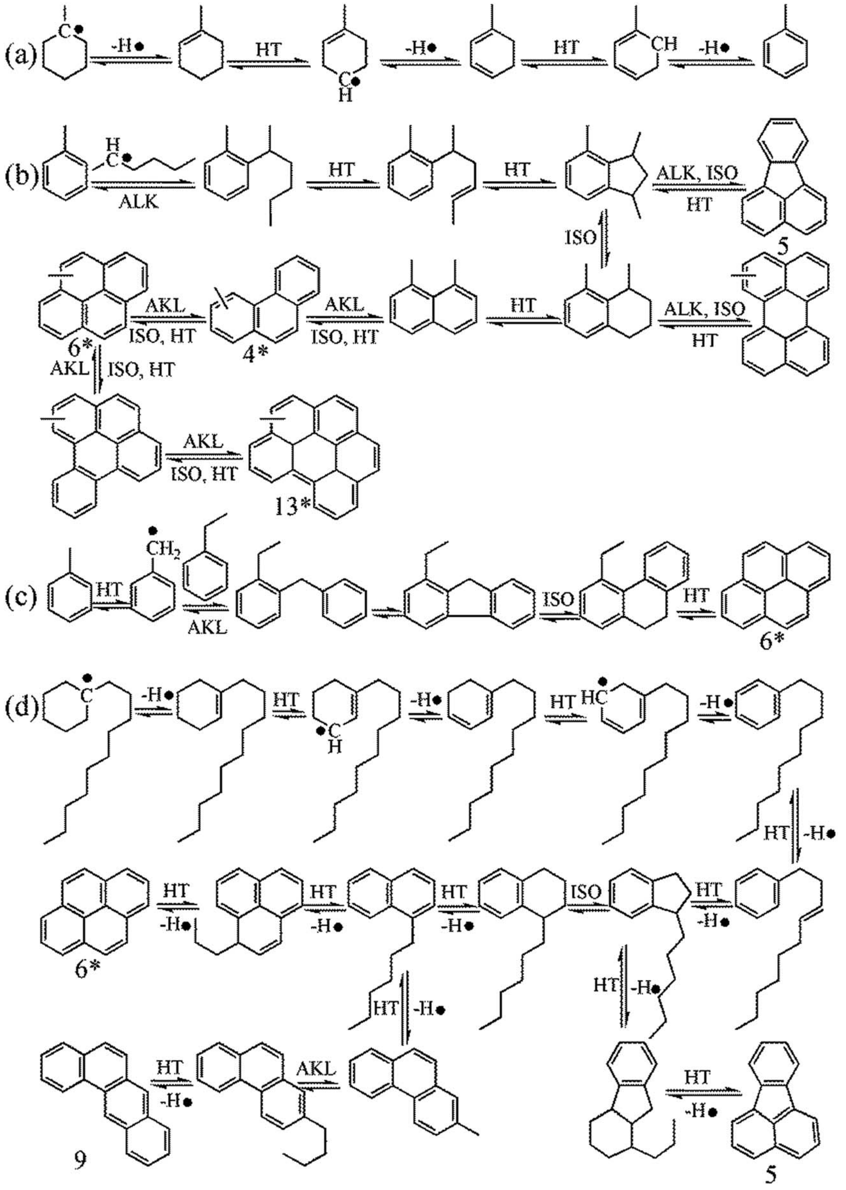

Fig. 8 Potential mechanism of coke formation in the process of basic catalytic cracking. (a) The formation of aromatics from small molecule hydrocarbons; (b) aromatics and olefins react to form polycyclic aromatic hydrocarbons; (c) aromatic hydrocarbons react to form polycyclic aromatic hydrocarbons; (d) long chain hydrocarbons react to form polycyclic aromatic hydrocarbons.

deoxygenation (including decarbonylation and decarboxylation) and cracking can bring in different sizes of radicals, which can form aromatic hydrocarbons with Diels–Alder reactions and hydrogen abstraction.[30,31,39] In addition, when triglycerides are cracked, many alkanes and alkenes are also formed, and collectively they are the primary precursors of coke.

According to the analysis of organics extracted from coke, we put forward the free radical mechanism of coke formation, which can be seen in Fig. 8. It can be seen that the organics in coke are generally polyaromatic hydrocarbons, which are the most important precursors to coke (Fig. 7). Alkanes would undergo cracking to produce olefins, which in turn take part into hydrogen transfer (HT) reaction, forming dienes and then aromatic structures (Fig. 8a and d). The formation of coke will be much easier if abundant olefins and aromatics occurred in the liquid phase.[38] As shown in Fig. 8b, aromatics and olefins may react to form alkylbenzenes through a series of alkylation (ALK), hydrogen transfer (HT), and isomerization (ISO) steps to form polycyclic aromatic hydrocarbons. The formation of coke from aromatic molecules (Fig. 8c) is also relatively easy and the formation of polycyclic aromatics process is similar to the reaction between aromatics and olefins. The formation of polycyclic aromatic hydrocarbons from the long chain hydrocarbons is also put forward (Fig. 8d). In fact, the precursor molecules would repeat the reactions such as ALK, HT, and ISO and with the increase of the molecular weight the coke was formed finally.

4. Conclusions

The thermal chemical conversion of triglycerides from different plant oils or waste oils seems to provide an efficient pathway to obtain aviation biofuels. Large quantities of liquid fuel (60–77%) were obtained by catalytic cracking in a benchtop reactor. The aviation fuel fraction (C8–C15) could be separated from the pyrolytic product by distillation. Upgrading of the pyrolytic aviation fuel fraction over HZSM-5 and Pd/AC was carried out in a high-pressure autoclave in sequence. After the subsequent aromatization over HZSM-5, the alkenes were transformed into aromatics and the content of carboxylic acids was decreased by the decarboxylation reaction. Then, a portion of the aromatics was converted into cycloalkanes catalyzed by Pd/AC. As a result, a desirable mixture of linear hydrocarbons (43.2 wt%), aromatics (6.3 wt%), and cycloalkanes (28.1 wt%) within the aviation fuel range (C8–C15) was obtained. In addition to the similar composition to aviation fuel based on petroleum, with a density of 808 kg m^{-3} and viscosity of 2.11 mm^2 s^{-1}, the properties of aviation biofuel also satisfied the requirements of RP-3 jet fuel. The heat value of the aviation biofuel was 44.4 MJ kg^{-1}. The freezing point of the aviation biofuel was −48 °C, indicating good low temperature fluidity.

This methodology also provides an alternative diesel product, with up to 21–41% of yield during the catalytic cracking process (see ESI†). Multiple end products enhance the application prospect of the pyrolytic oils and decrease the risk of price turbulence in the oil market.

Conflicts of interest

There are no conflicts to declare.

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