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Thermochemical conversion of waste acidic oil into hydrocarbon products over basic composite catalysts

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ABSTRACT

Removal of oxygen atoms from triglycerides is the most important step in their conversion into hydrocarbons. Basic catalysts have proven to be highly efficient in deoxygenation, whereby the oxygen atoms are removed in the form of CO and CO₂, yielding pyrolytic oil with acid number below 10 mg KOH·g⁻¹. We have now investigated the deoxygenation abilities of composite basic catalysts during the thermochemical conversion process. The dynamics of the catalytic cracking reaction using metal oxides, such as calcium oxide, in the presence of sodium carbonate, has been tested. According to thermogravimetric analysis (TGA) data, the activation energy for catalytic cracking was influenced by cations. By using calcium oxide as a catalyst, the activation energy was reduced from 260 kJ/mol to 185 kJ/mol, leading to a reduction in the reaction temperature of approximately 20–40 °C. The yield of the cracked liquid fraction was of the order of 66-70%, more than 90% of which could be recovered as liquid hydrocarbons. The results presented herein indicate an alternative reaction pathway, allowing thermochemical conversion to be conducted at a lower operational temperature, which would be beneficial for industrial production with lower energy consumption.

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1. Introduction

Biomass is a renewable resource that can be transformed into a variety of chemicals (Dodds and Gross, 2007), biofuels (Dupont et al., 2009a,b), and solid carbon (Simona et al., 2016) through physical and chemical techniques (Liu et al., 2017). The global biomass potential amount is about 200 EJ (up to 600 EJ), accounting for about one-third of the world's total energy consumption (Rong and Tao, 2016). Making full use of this resource is attractive for addressing resource shortages (Zhang et al., 2018) and environmental pollution problems (Taromi and Kaliaguine, 2018). However, there are economic obstacles to making full use of biomass energy; to obtain the full environmental benefit, green production

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routes need to be ensured by considering technical conditions, which means green supply chain management (Oliveira, and Rébula, 2018). Compared with other research, many cases of biomass production are significantly favorable from an environmental point of view, but government subsidies are needed to fully realize the economic benefits (Hašková, et al., 2016). So, it is important for economic and environmental friendly production when utilization the biomass energy.

Triglycerides are important biomass materials, occurring widely in plant oils and animal fats, and have been used as biofuels for transportation in place of petroleum-based fuels (Lin et al., 2018). Many such oils are used as edible oils in China. As such, considering the economic benefit and resource efficiency, they are not suitable raw materials for hydrocarbon fuels. Nevertheless, abundant waste oil is produced in the refining and consumption of edible oils (Xu et al., 2016). Therefore, non-edible (Maroušek et al., 2013) and waste cooking oils (Dizge N et al., 2009) are primarily used as raw materials. These feedstocks have no competition from human consumption or agriculture, and their use can also solve







Cleane Production environmental issues associated with the disposal of waste organic materials. The structure of the liquid fuel component of cracked waste oil has high potential for conversion into high-quality liquid fuels (Tingting L et al., 2018).

Thermochemical conversion of vegetable oil and animal fat is considered as an important reaction pathway, and has been much studied since 1947 (Chang and Wan, 1947). Non-catalytic cracking of vegetable oil and animal fat is an attractive option for the production of renewable fuels (Palanisamy and Gevert, 2016; Kozliak et al., 2013). The main products are alkanes, olefins, aldehydes, ketones, and carboxylic acids. However, liquids obtained from noncatalytic cracking usually have a high acid number in excess of 100 mg KOH·g⁻¹ due to low deoxygenation efficiency (Xu et al., 2016). Although non-catalytic cracking can also produce hydrocarbons, the high acid value product does not meet the requirements for fuel production.

At present, there are two alternative approaches for treating waste oil, hydrocracking (Bezergianni et al., 2009) and thermochemical conversion (Xu and Jiang, 2010). A great deal of research has indicated that direct hydrogenation of plant oil and animal fat can yield substitutes for petroleum diesel (Srifa et al., 2014) and jet fuel (Kim et al., 2017; AuthorAnonymous et al., 2018 Ramesh et al., 2019). For example, Kim et al. used a catalyst of Pt supported on nanocrystalline large-pore BEA zeolite to hydrocrack triglycerides, and thereby obtained biojet fuel with the highest iso-paraffin content. However, pretreatment is usually required to improve feedstock purity prior to hydrogenation, and removal of the O atoms with H₂ consumption is not an economically viable or safe process. Compared with hydrocracking, thermochemical conversion is an important alternative process for converting waste oil into hydrocarbon products. It has broader scope in terms of raw materials, requires no pretreatment, and the compositions of the products are similar to those of petrochemical fuels. Moreover, by controlling the reaction temperature, the lengths of the molecular chains in the pyrolysis oil component can be adjusted to obtain different fuel products, including aviation biofuel (Fanglin et al., 2018) and second-generation biodiesel (Yigezu and Muthukumar, 2014; Dupont et al., 2009a,b).

Many types of catalysts are used for the catalytic cracking of vegetable oil and animal fat, which are modeled on those used in petroleum catalytic cracking technology. Commonly used catalysts include ZSM-5 (Chen et al., 2014; Wu et al., 2017; Ramos et al., 2016), MCM-41 (Ramya et al., 2012; Li et al., 2013), and SBA-15 (Zhang et al., 2015). Many studies have indicated that ZSM-5 can be used to catalyze the cracking of triglycerides to obtain more aromatized hydrocarbons, due to the ZSM-5 is performing well aromatization active than the other two microporous zeolites. Both MCM-41 and SBA-15 show good selectivity for particular liquid hydrocarbons. However, the obtained pyrolysis oil has a high carboxylic acid content, leading to a high acid value. Many studies have indicated that the use of a basic catalyst, such as CaO or Na₂CO₃, can significantly reduce the acid value and favor the production of liquid fuels (Xu and Jiang, 2010; Xu et al., 2009).

In this study, with the aim of reducing costs in the process of high-efficiency deoxygenation, the synergistic effects of combined catalysts have been studied, along with the kinetics of the reaction. By using two model compounds, sodium stearate and calcium stearate, activation energies have been studied. We have further explored whether the activation energy is related to pyrolysis reaction temperature when using sodium carbonate and calcium oxide as co-catalysts and other composite catalysts. The removal of O atoms has been studied through the pyrolysis of model compounds, and a deoxygenation mechanism is proposed. Finally, the physical and chemical properties of the hydrocarbon fuel products have been investigated.

2. Experimental

2.1. General

The acidic waste oil was obtained from an industrial source. Specifically, it was the oil obtained by acidifying the by-product soap of an oil refinery. The acidified waste oil was a black oily liquid at room temperature. The acid value and density of the raw material were determined as 106.4 mg KOH•g⁻¹ and 0.908 kg m⁻³, respectively. Sodium carbonate (Na₂CO₃) with a purity of 99.8 wt% was procured from China Sun Speciality Products Co., Ltd. Calcium oxide (AR) and alumina (AR) were obtained from Xilong Scientific Co., Ltd. ZSM-5 (SiO₂/Al₂O₃ = 27) was purchased from Nankai University Catalyst Co., Ltd. SBA-15 (SiO₂/Al₂O₃ \geq 500) was obtained from Nanjing XFNANO Materials Tech Co., Ltd. Composite catalysts were prepared simply by mixing the respective components.

2.2. Experimental procedure

2.2.1. Cracking process

As shown in Fig. 1, the process of converting acidic waste oil into organic liquid involved two steps. The first step was thermochemical conversion of acidic waste oil over basic composite catalysts to obtain the pyrolysis oil. Catalytic cracking was performed in a homemade 5L stainless steel distillation unit (Fig. S1a). The feedstock (800 g) and the catalyst were introduced into the reactor, which was equipped with a rotor, spun at a stirring speed of 350 rpm. The reaction temperature was then increased with an electrical heater operated at 200 V under atmospheric pressure. The acidic waste oil was decomposed in the temperature range 300-450 °C. The distillation column temperature was maintained in the range 280-330 °C, and the heavy fraction was returned to the reactor. Six liquid fractions were obtained during the cracking process, in temperature intervals of <350 °C, 350-370 °C, 370–390 °C, 390–410 °C, 410–430 °C, and 430–450 °C. The yields of liquid fractions in these temperature ranges were calculated. Water was removed by the static liquid separation method, and samples were analyzed by gas chromatography-mass spectrometry (GC-MS) in order to investigate the changes in the compositions of the pyrolysis oils. The six liquid fractions were then mixed to obtain the whole pyrolysis oil, which was also analyzed by GC-MS. The yield (calculation formulae for the different products are given in the Supporting Information) and the physical and chemical properties of the pyrolysis oil were recorded.

2.2.2. Distillation process

The cracking process was followed by distillation. A threenecked flask (1 L) containing the raw material was placed on a SZCI-2 digital intelligent temperature-controlled magnetic stirrer for stirring and heating. A thermometer was inserted into the flask to measure the temperature of the distilled fraction. The mercury bulb of the thermometer was parallel to the condensation tube. The fraction was collected at the end of the condenser and the yield was calculated (Fig. S1b).

Two liquid products were obtained from the distillation: an aviation biofuel fraction at a distillation temperature lower than 280 °C, with a carbon chain distribution from C8 to C15, and a biodiesel fraction with carbon chains > C15 at a distillation temperature of 280–340 °C. The two fractions correspond to the boiling points of pentadecane and hexadecane of 268 °C and 287 °C, respectively. The yields of the two liquid fractions and coke were referenced to the original weight of the acidic waste oil. We also investigated the changes in the acid value by using different basic composite catalysts.



Fig. 1. Flow chart for the catalytic cracking of the acidic waste oil.

2.3. Pyrolysis of the model compounds

In order to investigate the deoxygenation mechanism of the pyrolysis of acidic waste oil over a basic catalyst, thermal cracking experiments on model compounds such as sodium stearate and calcium stearate were carried out. The model compound (10 g) was placed in a three-necked flask, which was purged three times with N₂. The mixture was then electrically heated, and the gas evolved was collected in an air bag. The components of the gaseous products were tested by GC and the results are listed in Table S1.

2.4. Analytical methods

GC-MS analysis was performed on an Agilent 6890N/5973N instrument equipped with an HP-5 capillary column $(30 \text{ m} \times 250 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m})$, and a flame-ionization detector (FID) was used to determine the composition of the liquid products. The initial GC-MS temperature was set at 50 °C (held for 2 min), and was then programmed to increase from 50 °C to 280 °C at a rate of 5 °C/min, and held at 280 °C for 20 min. The EI voltage of the MS ion source was 70 eV, and the mass spectral scanning range was 50-550 Da. The composition of the gaseous products was analyzed by means of a Tsushima GC-2104 gas chromatograph, which was equipped with two detectors, a thermal conductivity detector (TCD) to detect the components H₂, CO, CO₂, N₂, and O₂, and a hydrogen FID to detect the components C₂H₂, C₂H₆, C₂H₄, and CH₄. The gas was quantitatively and qualitatively analyzed by a standard gas control method and a peak-area single-point external standard method. The carrier gas was argon, the oven temperature was set at 50 °C, and the TCD and FID temperatures were both 100 °C. The densities of the acidic waste oil and liquid product were measured

Table 1

Products from cracking of acidic waste oil over different composite catalysts.

by means of a temperature-programmed pycnometer. A capillary viscometer was used to measure the viscosity according to GB/ T265-1988. The calorific value was measured with an IKA-C200 calorimeter (ASTM D4809). Acid value was determined according to GB/T-5530-2005 and GB/T-12574. TG analyses were performed using a Netzsch 409 PC synchronous analyzer. Changes in the masses of the stearate salts with temperature were measured during their thermal decomposition. The temperature was increased at a rate of 10 °C/min from ambient to 800 °C, with nitrogen as the carrier gas. Freezing points were measured by means of a freezing-point-of-petroleum-products tester according to GB/ T2430. Elemental analyses of the solids produced and the acidic waste oil were carried out using a PE-2004 elemental analyzer according to JY/T 017-1996, and the obtained data are shown in Table S2. In order to identify the crystalline phase of the catalysts, X-ray diffraction (XRD) analysis was performed on a D8 Focus diffractometer employing Cu- K_{α} radiation and operated at 40 kV.

3. Results and discussion

3.1. Catalytic cracking of acidic waste oil using different composite basic catalysts

The aim of this study was to investigate the influence of different composite basic catalysts in the thermochemical conversion process. As can be seen in Table 1, the acidic waste oil was cracked over basic catalysts to afford liquid hydrocarbons in yields of about 66–70%, lower than the yield of the uncatalyzed cracking process. This was mainly because fatty acids still persisted in the liquid in the latter case, due to low deoxygenation efficiency. In contrast, basic catalysts greatly improved the deoxygenation

Entry	Catalyst	Liquid fuel		Water	Coke	Gas
		Yield/%	Acid value /mg KOH∙g ⁻¹	Yield/%	Yield/%	Yield/%
None ^a		78.20 ± 1.2	77.13	3.96 ± 0.5	8.05 ± 0.2	9.79 ± 1.0
Na ₂ CO ₃ ^b	1	69.80 ± 0.3	8.90	2.31 ± 0.2	2.36 ± 0.1	25.53 ± 0.4
CaO ^b	2	65.30 ± 0.4	7.27	4.20 ± 0.3	5.68 ± 0.2	24.82 ± 0.1
CaO—Na ₂ CO ₃ ^b	3	68.12 ± 0.6	3.86	2.94 ± 0.5	4.78 ± 0.4	24.14 ± 0.3
CaO-Na ₂ CO ₃ -Al ₂ O ₃ ^b	4	66.87 ± 0.9	2.69	3.55 ± 0.4	6.92 ± 0.5	22.66 ± 0.2
CaO-Na ₂ CO ₃ -ZSM-5 ^{b c}	5	66.64 ± 1.0	3.66	4.89 ± 0.7	0.90 ± 0.3	27.57 ± 0.3
CaO-Na ₂ CO ₃ -SBA-15 ^b	6	67.35 ± 0.5	3.30	4.61 ± 0.3	5.91 ± 0.4	22.13 ± 0.4

Reaction conditions: yields quoted were calculated relative to the weight of feedstock oil (800 g).

^a : cracking of the acidic waste oil without a catalyst.

^b : catalyst 1: 15 wt% Na₂CO₃; catalyst 2: 15 wt% CaO; catalyst 3: 7.5 wt% CaO and 7.5 wt% Na₂CO₃; catalyst 4: 7.5 wt% CaO, 7.5 wt% Na₂CO₃, and 7.5 wt% Al₂O₃; catalyst 5: 7.5 wt% CaO, 7.5 wt% Na₂CO₃, and 7.5 wt% ZSM-5; catalyst 6: 7.5 wt% CaO, 7.5 wt% Na₂CO₃, and 7.5 wt% SBA-15.

^c : ZSM-5 (SiO₂/Al₂O₃ = 27).

Table 2
Distribution of liquid product yields over different catalysts in various temperature ranges.

Entry	Catalyst	Temperature range					
		<350 °C	350−370 °C	370-390°C	390-410 °C	410-430°C	430–450 °C
		Yield/%	Yield/%	Yield/%	Yield/%	Yield/%	Yield/%
None		1.27 ± 0.4	8.19 ± 0.6	12.30 ± 0.3	38.43 ± 0.2	17.73 ± 0.4	4.25 ± 0.1
Na ₂ CO ₃	1	1.99 ± 1.2	2.98 ± 0.3	5.24 ± 0.4	15.37 ± 0.4	21.03 ± 0.3	25.50 ± 0.7
CaO	2	5.61 ± 0.5	6.99 ± 0.2	23.10 ± 0.2	17.58 ± 0.2	10.46 ± 0.3	5.76 ± 1.0
CaO-Na ₂ CO ₃	3	4.35 ± 0.9	2.36 ± 0.4	10.13 ± 0.6	25.56 ± 0.8	23.59 ± 0.4	5.07 ± 1.2
CaO-Na ₂ CO ₃ -Al ₂ O ₃	4	3.50 ± 1.1	2.00 ± 0.1	15.54 ± 0.2	28.36 ± 0.2	18.53 ± 0.5	2.49 ± 0.9
CaO-Na ₂ CO ₃ -ZSM-5	5	3.67 ± 0.8	3.68 ± 0.5	11.23 ± 0.2	27.66 ± 0.4	21.57 ± 0.1	3.73 ± 1.6
CaO-Na ₂ CO ₃ -SBA-15	6	5.74 ± 1.3	10.96 ± 0.3	33.68 ± 0.7	12.56 ± 0.3	5.64 ± 0.8	3.40 ± 1.5

Notes: All yields were calculated relative to the weight of feedstock oil (800 g). The reaction temperature is divided into six ranges.

efficiency, and the O atoms of fatty acids were removed in the form of CO and CO₂. The reduced carboxyl group content led to a low acid value of the pyrolysis oil, decreasing from 77 mg KOH·g⁻¹ to less than 10 mg KOH·g⁻¹. Moreover, the long fatty acid chains were fragmented, leading to more gaseous products. Specifically, the gas content was increased from 10% (uncatalyzed cracking) to more than 20% (basic catalyst cracking). The use of ZSM-5 as the catalyst, as commonly used for aromatization, produces more gaseous products. During the cracking process, long chains are first dehydrogenated to form olefins, which then condense to form aromatic hydrocarbons. The process of dehydrogenation to form short-chain olefins increases the content of gas molecules.

Table 2 shows the yields of liquid products collected in different temperature ranges by using different basic composite catalysts. Water was the main product at reaction temperatures below 350 °C, albeit only in a very small proportion of about 2–5%. The acidic waste oil was pyrolyzed in the temperature range 350-450 °C. In comparison, the pyrolysis of acidic waste oil without a catalyst yielded a liquid mainly in the temperature range 390-430 °C, composed of aldehydes, alkenes, ketones, and carboxylic acids because of the low deoxygenation efficiency. However, different basic catalysts exert an influence on the reaction temperature. For example, using sodium carbonate as the cracking catalyst, liquid fuel was mainly obtained in the temperature range 390-450 °C. Adding calcium oxide as a co-catalyst, the temperature range was lowered by approximately 20-40 °C, suppressing thermal cracking reactions and thus leading to more of the desired C8-C16 jet fuel fraction. In the presence of ZSM-5 and SBA-15 as co-catalysts, the temperature ranges were lowered to 390–430 $^\circ\text{C}$ and 370–410 $^\circ\text{C}$, respectively.

Different molecular sieve catalysts were also studied in composite catalyst systems. The ZSM-5 ($SiO_2/Al_2O_3 = 27$) molecular sieves used in this work had a pore size of about 2.2 nm, smaller than that of SBA-15 ($SiO_2/Al_2O_3 \ge 500$; 5–11 nm). Triglycerides can more easily access the channels of SBA-15, thereby increasing the contact area between the feedstock oil and catalyst, allowing bonds to be cleaved more readily. Hence, the temperature of the cracking is further reduced. The XRD patterns of ZSM-5, SBA-15, and Al_2O_3 are shown in Figs. S2–S4.

3.2. Dynamic analysis

It is well known that the catalytic cracking of triglycerides involves the following steps: triglycerides are first decomposed to fatty acids, neutralization of which by the catalyst yields an intermediate fatty acid metal salt; deoxygenation of this intermediate then yields the hydrocarbon products (Xu and Feng, 2019). In order to investigate the influence on activation energy of using different basic catalysts, two model compounds, sodium stearate and calcium stearate, were tested by TGA. The results are shown in Fig. 2, and detailed calculations of the processes are shown in Tables S3–S6. As can be seen in Fig. 2A, calcium stearate and sodium stearate gave disparate average activation energies of around 185 kJ/mol and 260 kJ/mol, respectively. Calcium stearate was decomposed prior to sodium stearate at the same heating rate (Fig. 2B). Hence, adding calcium oxide to form a composite catalyst



Fig. 2. Dynamic analysis of sodium stearate and calcium stearate.



Fig. 3. Compositions of different pyrolysis oil components.

lowered the reaction temperature, suppressing unpredictable C–C bond cleavage, and thus leading to an improved yield of the C8–C16 biojet fuel fraction.

3.3. Compositional analysis of the pyrolysis oil

The liquid fuels collected in the different temperature ranges were analyzed by GC-MS, and the results are shown in Fig. 4A–F. The components of the pyrolysis oil included linear alkanes, cycloalkanes, alkenes, aromatics, alkynes, and other products (alcohols, ketones, acids, aldehydes, etc.). The main products were alkanes (chain alkanes and cyclo-alkanes) and alkenes, with contents of about 30% and 30–40%, respectively (Fig. 3F). From the changes in the product compositions, it was clear that the catalyst had an effect on the decomposition of the fatty acid salts. Compared to the use of sodium carbonate, the use of calcium oxide as a co-catalyst furnished more hydrocarbons in the temperature range 350–410 °C because of the lower activation energy of calcium stearate (Fig. 3A–C). With aromatizing ZSM-5 as a co-catalyst, more aromatic hydrocarbons were produced (Fig. 3F). With SBA-15 as cocatalyst, more alkanes were obtained in the temperature range 350-370 °C. We envisage that the basic catalyst became attached to the pores of SBA-15, increasing the catalytic reaction area and thereby facilitating the cleavage reaction.

3.4. Proposed catalytic cracking mechanism

In order to investigate the deoxygenation mechanism, the gaseous products collected from pyrolyses of the model compounds were tested by GC. As shown in Table S1, mostly gaseous products (CH₄, C₂H₄, C₂H₆, CO, and CO₂) were obtained from the pyrolysis experiments. During the thermochemical conversion using sodium carbonate and calcium oxide as catalysts, O atoms were mainly removed as the form of CO along with some CO₂. At same time, long carbon chains were fragmented, so that CH₄, C₂H₄, and C₂H₆ were detected. GC-MS analysis of the liquid product indicated that O atoms had been efficiently removed.

Our proposed deoxygenation mechanism for the thermochemical conversion of triglycerides over a basic catalyst is illustrated in Fig. 4. The fatty acid is converted into a metal salt, and O atoms are removed as the form of CO or CO₂. At the same time, the long carbon chains are cleaved to form short-chain hydrocarbons. Carbon chain cleavage is a disordered reaction process, occurring in the temperature range 350-450 °C. Free radicals (R•) are either dehydrogenated or hydrogenated to form alkenes or alkanes. Dehydrogenation and cyclization of alkenes can then lead to cycloalkanes, which can be further dehydrogenated to produce aromatic hydrocarbons. The thermochemical conversion method can thus provide an alternative pathway for the deoxygenation of triglycerides to form hydrocarbon liquid fuels, and further adjustment of the molecular structure can yield products meeting the requirements of different fuel types.

3.5. Property analysis of distillation products

As shown in Table 3, the yields of the aviation biofuel and diesel fractions were about 40% and 20–30%, respectively. These fractions had low acid numbers in the range 1.5–2.5 mg KOH·g⁻¹, lower than those of fractions obtained from the uncatalyzed cracking process. These fuels were further washed with aqueous sodium hydroxide solution (0.375 mol/L), and the oil layer in the stratified zone constituted a fuel with a lower acid value. Although the distillation fractions still contained some fatty acids, these were saponified by treatment with sodium hydroxide solution, providing low acid value fuels. The acid number of the aviation fuel component was about 0.01 mg KOH·g⁻¹, both meeting the requirements for RP-3 and 0# diesel.

The physical and chemical properties of the distillation products are shown in Table 4, along with those of RP-3 and 0# diesel fuels. The listed properties of the aviation biofuel fraction meet the requirements of RP-3, except for freezing point, and those of the biodiesel fraction almost conform to those of 0# diesel. The results show that the liquid hydrocarbons obtained from the pyrolysis of acidic waste oil are viable alternatives to hydrocarbon fuels (aviation biofuels and biodiesel).

4. Conclusions

The utilization of waste triglycerides is an important issue in resource reuse. Thermochemical conversion of these low-quality triglycerides into hydrocarbon fuels provides an alternative pathway for the sustainable development of renewable liquid fuels. In this study, catalytic cracking of triglycerides has been carried out with different combinations of basic catalysts, whereby 66–70% of liquid fuel product was optimally obtained. Adding ZSM-5 to the composite catalyst produced more aromatic hydrocarbons, whereas the use of SBA-15 led to a lowering of the reaction



C6-C17 Hydrocarbons



C6-C17 Hydrocarbons

Fig. 4. Proposed thermal cracking mechanism of triglycerides with sodium carbonate and calcium oxide.

Table	3
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Acid values and yields of product fractions from pyrolysis oil distillation in the presence of different composite catalysts.

Entry	Catalyst	Aviation fuel fraction		Diesel fraction	Coke	
		Yield/%	Acid value	Yield/%	Acid value	Yield/%
			/mg KOH \cdot g ⁻¹		/mg KOH \cdot g $^{-1}$	
None		37.97	81.13	32.83	117.03	7.34
Na ₂ CO ₃	1	37.76	2.45	26.07	3.28	5.97
CaO	3	39.30	1.89	23.57	1.95	2.43
CaO-Na2CO3	2	35.16	2.45	28.86	2.65	4.10
CaO-Na ₂ CO ₃ -Al ₂ O ₃	3	40.30	1.89	24.43	1.95	2.13
CaO-Na ₂ CO ₃ -ZSM-5 ^a	4	42.59	1.80	21.23	2.80	2.81
CaO-Na ₂ CO ₃ -SBA-15	5	39.32	1.72	23.36	2.93	4.67

Note: All yields were calculated relative to the weight of feedstock oil (800 g); all data are average values.

^a ZSM-5 (SiO₂/Al₂O₃ = 27).

Table 4

Physical and chemical properties of the aviation biofuel and biodiesel fractions, along with those of standards.

Basic properties	Aviation fuel fraction	RP-3 ^b	Diesel fraction	0# diesel ^c
Density ^a (kg⋅m ⁻³)	800.9	775–830	869.5	820-860
Heat value (MJ·kg ⁻¹)	43.40	>42.8	45.18	43.5
Viscosity ^a (mm ² · s ⁻¹)	1.685	>1.25	13.32	3.0-8.0
Acid value (mg KOH \cdot g ⁻¹)	0.01	<0.015	0.1	0
Freezing point (°C)	-44	-47	-13	0

Distillation with CaO as co-catalyst.

^a Measured at 20 °C.

^b Refers to GB/6537-2006 in China.

^c Refers to GB/T 19147-2003 in China.

temperature. However, considering the economic benefit, the use of inexpensive CaO as the cracking catalyst was most effective.

Indeed, we found that CaO showed great catalytic cracking performance. The pyrolysis kinetics of sodium stearate and calcium stearate were analyzed, yielding activation energies of 260 kJ/mol and 185 kJ/mol, respectively. Thus, the use of CaO as a catalyst can reduce the pyrolysis temperature by about 20-40 °C, suppressing excessive thermal cracking reactions, and hence leading to more of the C8–C16 jet fuel fraction. Oxygen atoms were removed in the form of CO and CO₂ during the pyrolysis process, leading to low acid value products with improved chemical properties. Nevertheless, further investigations are still needed in this field, aimed at regulation of the molecular structure of the liquid product to obtain the final fuel products, and improved utilization of the solid carbon residue.

As regards the economics of the process, waste triglycerides (about 2500 RMB/t in China), such as waste acidic oil, constitute a low-cost feedstock. Catalytic cracking of waste triglycerides converts them into value-added liquid hydrocarbons (about 8000 RMB/t in China), achieved here with the inexpensive catalyst CaO at a conversion rate of about 63%. There are also two by-products, flammable gas and solid carbon. The heating value of the flammable gas is sufficient to provide the energy used in the cracking process, realizing closed-loop energy recovery. The solid carbon residue has a high carbon content of 90%, and thus has potential for carbon material production. No waste water, gas, or solid is produced during the whole process. Moreover, because the use of CaO lowers the catalytic cracking temperature by approximately 20-40 °C, energy consumption is reduced. Overall, this thermochemical conversion of waste triglycerides to hydrocarbon fuels can be regarded as an economically viable process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.06.109.

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