

Biofuel Production from Catalytic Cracking of Triglyceride Materials Followed by an Esterification Reaction in a Scale-up Reactor

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ABSTRACT: Thermochemical conversion of vegetable oils has become an attractive and alternative method for the production of high-grade biofuels. In the present work, thermal and catalytic cracking reactions were studied in a 60 L scale-up reactor using soybean oil and high acid value waste oil under the catalysis of a basic catalyst. A bio-oil yield of approximately 70% was obtained at a reaction temperature of 450 °C with a heating rate of 5 °C/min. After the thermal and catalytic cracking reactions, upgrading of bio-oils in a continuous pilot reactor was investigated. It was found that those undesired products (carboxylic acids) were changed into their corresponding fatty acid esters efficiently by a continuous esterification operation. The upgraded oils were further fractionated into gasoline and diesel fractions via distillation processing according to the requirements of the boiling range in the China specification for petroleum fuels. The results showed that the obtained biofuels have excellent cold-flow properties superior to those of conventional petroleum-based liquid fuels.

1. INTRODUCTION

Animal fats and plant oils are mainly composed of triglycerides, which can be converted through a thermochemical reaction to produce high-grade biofuels. As an important thermochemical method, thermal and catalytic cracking are considered as a important route by converting triglyceride feedstock to lighter fractions that mostly fall in the boiling range of petroleum-based fuel.^{1,2} Since the first oil crisis in 1974–1975, many studies on the thermochemical conversion of triglyceride materials have been reported, and the results indicate the technical viability to produce liquid fuels comparable to fossil fuels.

Several reviews^{1,3} have been reported for the production of biofuels via thermochemical cracking of triglyceride materials. The method is characterized by a reactor operation temperature of around 500 °C, low residence time, and high heating rates. Many natural triglycerides, such as plant oils (palm, rapeseed, and soybean) and animal fats (lard and tallow), can be used to produce biofuels that are suitable for gasoline engines^{4,5} by the catalytic cracking process. Although these triglycerides showed potential prospect for the production of high-grade liquid fuels, it is worthwhile mentioning that use of edible oil as a biofuel feedstock has negative impacts, such as competing with the supply of food. As a result, the use of recycled cooking greases (used vegetable oil) and non-edible oil (castor, tall, and *Jatropha*) is one of the solutions of this problem.^{2,6–8}

During the thermal and catalytic cracking reactions, the catalysts have great effect on the molecular distribution of the product. Catalysts used in the cracking reaction of triglycerides are mostly microporous molecular sieves and mesoporous materials. The medium pore zeolite catalysts (ZSM-5) gave the best performance in terms of conversion, with gasoline,

benzene, toluene, and xylene as the aromatic yield.⁹ These studies mainly focus on the production of gasoline fractions with the carbon chain C₆–C₁₂. The yield of the gasoline fractions usually falls in the 30–50% range.^{9,10} The yield of liquid product (mostly diesel fractions) could be significantly improved to 70% using mesoporous materials, such as MCM-41.¹⁰ Overall, the performance of catalytic cracking of the mesoporous materials gave a lower gaseous yield and higher coke formation because of their lower acidity, and they are selective to the formation of diesel fractions.¹

In our previous research, we have investigated different types of catalysts, including solid acidic catalyst (Al₂O₃), neutral catalysts (mesoporous silica molecular sieve and MCM-41), and basic catalysts. A high content of fatty acids was observed in the bio-oil product using most of the acidic catalyst and neutral catalysts. On the contrary, the product obtained from the basic catalyst gave a relatively low acid value, with the molecules mostly falling in the boiling range of diesel fuels. It is likely that the basic catalyst reacts first with fatty acids to produce metal salts, which are then further decomposed into hydrocarbons. On the basis of this investigation, further experiments were performed, such as using different kinds of feedstocks and fractionations of bio-oil products.

Besides, other studies have been reported on the upgrading of the triglycerides to high-grade liquid fuels, including catalytic cracking, esterification, and hydrogenation.^{11–13} Although many studies regarding thermal and catalytic cracking of triglycerides and their upgrading processes have been reported, most of the studies were carried out in batch systems or on a

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laboratory scale. A few researchers have reported a pilot plant for thermal and catalytic cracking of triglycerides.^{2,14} However, there are many operation parameters that should be suitably addressed in a scale-up reactor, such as the reaction temperature for different feedstocks and the upgrading method for pyrolytic products. Therefore, we believe that the product upgrading and scale-up strategies are opportunity study areas.

Thus, in this study, a scale-up batch reactor (60 L) was used to investigate thermal and catalytic cracking reactions of soybean and waste oils. A combination of thermal and catalytic cracking reactions and fractionation processing was realized in this scale-up reactor. Upgrading of pyrolytic products through the esterification reaction was also tested in a scale-up continuous reactor. After esterification, the pyrolytic product was distilled according to the boiling ranges of gasoline and diesel. Following ASTM specifications for liquid fuels, these two products were physically and chemically tested. The results showed that their properties are comparable to gasoline and diesel fuels obtained from petroleum.

2. EXPERIMENTAL SECTION

2.1. General. Soybean and waste oils were purchased from a local market. The important properties are given in Table 1. This solid

Table 1. Physical and Chemical Properties of Raw Materials

properties	waste oil	soybean oil
density (g/cm ³)	0.95	0.923
viscosity at 40 °C (mm ² /s)	42.8	60.2
heating value (kJ/g)	39.0	39.7
moisture (wt %)	3.38	
acid number (mg of KOH/g)	159.6	0.5
elemental analysis (wt %)	C	77.56
	H	12.09
	O ^a	11.69
	N	8.25
	P	2.1
		not detected
		not detected

^aThe oxygen content was calculated by mass difference. ^bPhosphorus was measured by inductively coupled plasma–optical emission spectroscopy (ICP–OES).

acidic catalyst used in the esterification reaction was prepared according to the literature.¹⁵ The main properties are listed in Table 2. All other reagents are of analytical grade. Gas chromatography–

Table 2. Physicochemical Properties of the Solid Acid Catalyst

sample	M–S ₂ O ₈ ^{2–} /ZrO ₂
BET surface area (m ² /g)	32.7
average pore size (nm)	216
pore volume (cm ³ /g)	0.17

mass spectrometry (GC–MS, Agilent 6890N/5973N) measurements were used to characterize the components in bio-oils. The analysis was performed on a column of HP-5 (30 m × 0.25 mm, 0.25 μm film thickness). The oven working temperature was between 50 and 250 °C at a heating rate of 5 °C/min. Infrared (IR) spectra were obtained on a MAGNA-IR 550 spectrophotometer. The moisture was determined on a KF-412A Titrino by the Karl Fischer titration method (ASTM D1744). The dynamic viscosity was measured with SYP-IA viscometers (GB/T265-88), and the gross calorific value was measured using an IKA-C200 calorimetric bomb (ASTM D4809).

2.2. Production of Biofuels. **2.2.1. Thermal and Catalytic Cracking of High Acid Value Waste Oil.** The thermal and catalytic

cracking of triglyceride feedstock were carried out in a scale-up batch reactor. Figure 1 shows the conceptual design of the process comprising the reactor, where the thermal and catalytic cracking occur, a rectification column (height of 1000 mm with an internal diameter of 150 mm), where the light fraction vaporized (it also catches the heavier products and returns them back into the cracking reaction), a condensation section composed of one heat exchanger, a collection section, and a control section.

In the beginning of the thermal and catalytic cracking reactions, the triglycerides were charged in an elevated bunker (1 of Figure 1) by a centrifugal pump. After that, the raw materials flowed into the reactor through a flow meter (2 of Figure 1) and a preheater (3 of Figure 1) in sequence. The reactor (4 of Figure 1) is made of carbon steel, with a height of 450 mm and internal diameter of 495 mm, comprising 4 kW/h electrical resistances. The instrumentation of the reactor is composed of two thermocouples, one in the reactor for measuring the temperature of the reaction and the other measuring the temperature of the vapor at the top of the column. The temperature of the rectification column (5 of Figure 1) with a conventional metallic packing was maintained at a range of 330–340 °C using electrical resistance with 1 kW/h. The condenser (6 of Figure 1), made of stainless steel, is cooled with tap water, and the condensate is separated and stored in the liquid collector (7 of Figure 1).

In a typical experiment, the catalyst (Na₂CO₃) was charged directly into the reactor. The experimental procedure to carry out the thermal and catalytic cracking experiments consisted of about a 1.5 h time period for the start-up of the electrical resistances, reaching the temperature for thermal and catalytic cracking reactions (400–500 °C). Then, the vapor left the reactor through the rectification column at temperatures ranging from 330 to 340 °C (including gasoline and diesel fractions). The vapor feed then enters a water-cooled heat exchanger. As a result, the liquid product was collected in a collector. The distribution of pyrolytic products was recorded by weighting the pyrolytic product in intervals during the thermal and catalytic cracking reactions.

The yield of bio-oil from each experiment was calculated in terms of its mass over the initial soybean oil mass. The residue in the reactor was weighed to give the coke yield. The yield of biogas is the difference to give 100%.

2.2.2. Esterification of the Product from the Catalytic Reaction. Upgrading of bio-oils was carried out in a continuous scale-up reactor. Figure 2 shows the conceptual design of the process comprising the reactor, where the esterification reaction occurs (height of the reactor is 600 mm with an internal diameter of 133 mm), a preheater, where methanol is vaporized (the temperature can be varied from room temperature to 400 °C by electronic resistance), two containers for bio-oil and methanol storage, a rectification column for methanol recovery (a height of 1500 mm with an internal diameter of 40 mm), a collection section, and a control section.

The experimental procedure to carry out the esterification reactions consisted of a 1 h time period for the start-up of the oil bath (2 of Figure 2), reaching the programmed temperature conditions (80–100 °C). After this operation, 4 kg of bio-oil and 200 g of catalyst (5 of Figure 2) were fed into the reactor (4 of Figure 2). Methanol was then fed through a preheater (3 of Figure 2) at the rate of 0.3 kg/h and vaporized. When the acid value of the mixtures in the reactor decreased to 10 mg of KOH/g, the bio-oil from the container (1 of Figure 2) was fed into the reactor at a rate of 1 kg/h. Thereafter, the esterified bio-oils were continuously produced and collected in a liquid collector (8 of Figure 2). The methanol vaporized from the reactor was fed into the rectification column (9 of Figure 2) for methanol recovery.

2.2.3. Fractionation of Esterified Bio-oils. The liquid products collected from the esterification process were submitted to a simple distillation. A reduced simple distillation process was carried out to obtain products in the boiling range of gasoline/diesel fuels. The condensate under the temperature of 190 °C was separated and named the gasoline fraction. After that, the product was further distilled to give the diesel fraction by reduced distillation (5 KPa) under the temperature of 300 °C.

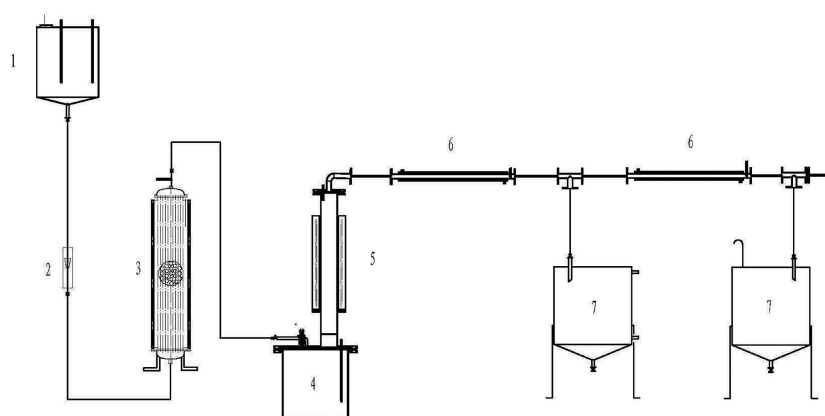


Figure 1. Apparatus (60 L) used for the catalytic cracking reaction: (1) elevated bunker, (2) flow meter, (3) preheater, (4) cracking reactor, (5) rectification column, (6) heat exchanger, and (7) liquid collector.

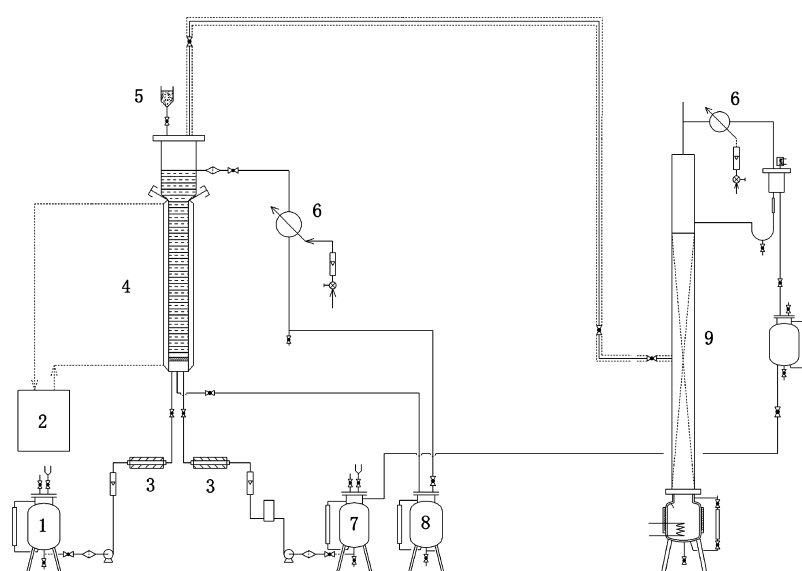


Figure 2. Continuous scale-up reactor (5 L) for upgrading of bio-oil: (1) pyrolytic product container, (2) oil bath, (3) preheater, (4) fluidized-bed reactor, (5) catalyst container, (6) heat exchanger, (7) methanol container, (8) liquid collector, and (9) rectification system.

3. RESULTS AND DISCUSSION

3.1. Catalytic Cracking of Triglyceride Materials in a Scale-up Reactor Using a Basic Catalyst. The optimum reaction conditions for the production of bio-oils have been studied previously in our research group. The results showed that the basic catalyst generated products with a relatively low acid number and excellent cold-flow properties. According to these results, we tried to operate the thermal and catalytic cracking reactions using a basic catalyst in a scale-up reactor. The detailed results are shown in Table 3.

Table 3. Scale-up Experiments for Thermal and Catalytic Cracking of Soybean Oil Using a Basic Catalyst

	yield of bio-oil (%)	yield of gas (%)	carbon residue (%)	acid value (mg of KOH/g)
soybean oil ^a	71.5	22.6	5.9	79
waste oil ^a	69.1	11.6	19.3	67

^aAll of the feedstocks and catalysts were placed in the reactor before the reaction. The reactor was heated to 500 °C with a heating rate of 5 °C/min.

From Table 3, it can be seen that the yield of the gas product has a great relationship with the components of the feedstock. A detailed analysis of the gas products was given in Table 4. The raw material that has a high acid value indicated a high content of free fatty acids. These components can be directly

Table 4. Main Components in Gas Products

composition	percentage (%)	
	soybean oil	waste oil
H ₂	5.7	10.6
N ₂	3.2	2.5
CO	20.9	18.7
CO ₂	32.3	35.2
CH ₄	6.4	8.6
C ₂ H ₆	5.5	5.5
C ₂ H ₄	2.3	1.9
C ₂ H ₂	4.3	3.9
>C ₃ ^a	19.4	13.1

^aThe percentage of compounds (>C₃) were calculated by mass difference.

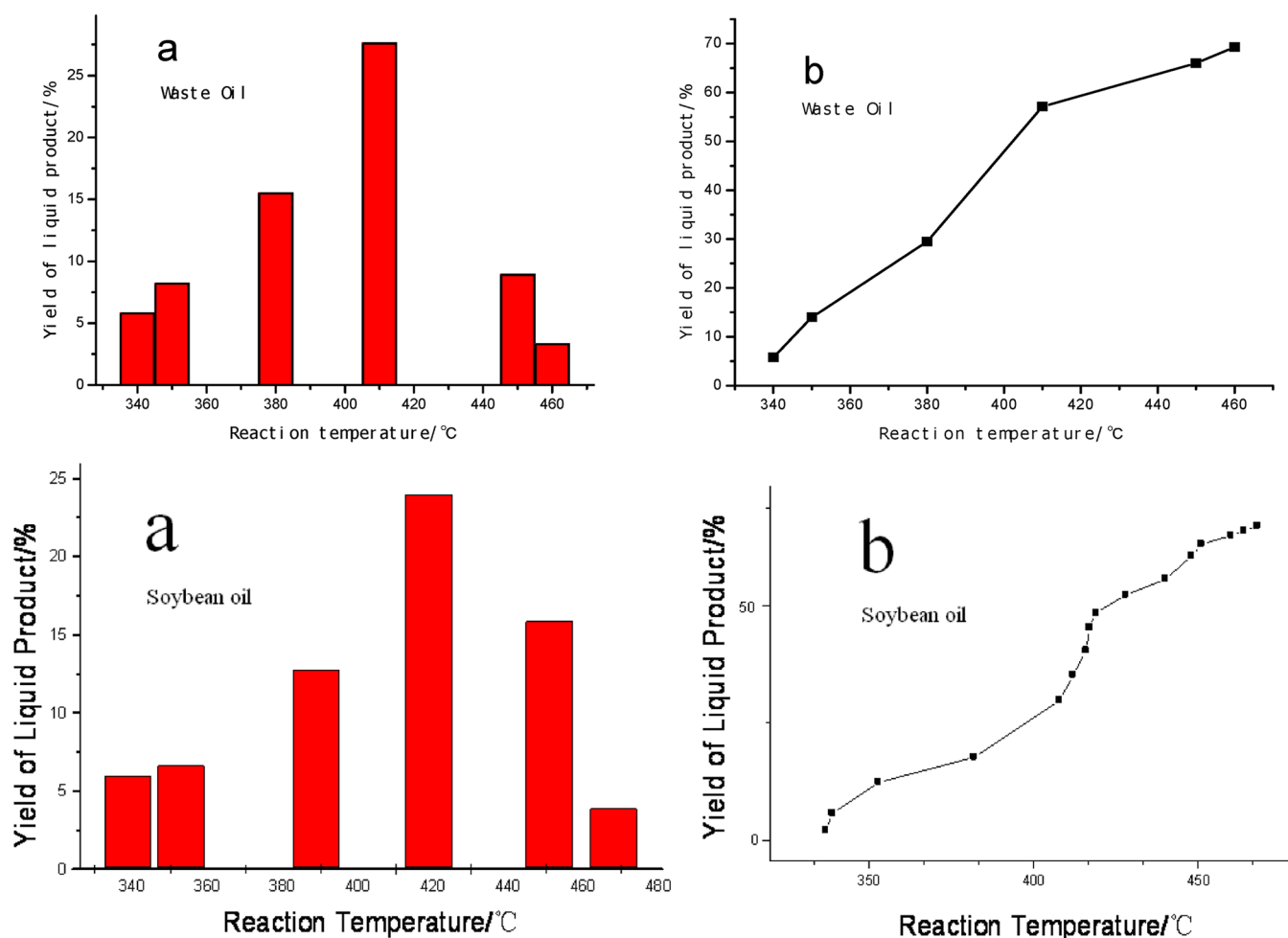


Figure 3. Distribution of the product yield versus reaction temperature: (a) yield of product in different reaction temperatures and (b) cumulative yield of product versus reaction temperature.

converted into olefins and paraffins through decarboxyl reactions. That means that the possibility of secondary decomposition reactions can be decreased dramatically. It is well-known that thermal and catalytic cracking of triglycerides, such as soybean oils, result in the formation of fatty acids and acrolein.³ After that, the formatted fatty acids were further decomposed into olefins and paraffins. During these reactions, second cracking reactions enhance cleavage at the C–C bonds (splitting decomposition reactions). That is why a high yield of gas product was observed using soybean oil as a raw material.

This conclusion can be further demonstrated by the analysis of the components in gas products. As shown in Table 4, the total content of the hydrocarbons (especially C₃–C₄ hydrocarbons) in the gas product from soybean oil is higher than the gas product from waste oil. This result indicated that secondary decomposition reactions lead to cleavage at the C–C bonds during the thermal and catalytic cracking reactions, which give a high yield of hydrocarbons. On the other hand, it is worthwhile mentioning that the content of CO₂ in the gas product is much higher than the data reported in the literature (below 10%).¹² This result showed that the decarboxylation reactions of fatty acids were significantly improved using a basic catalyst. In other words, the basic catalyst tends to generate a liquid product with a high content of alkenes or alkanes rather than fatty acids.

The coke yield of waste oil is much higher than that of soybean oil. This result may due to the high content of organic

impurities in waste oil. As indicated by elemental analysis, the content of nitrogen and phosphorus in waste oil is higher than that in refined soybean oil. The waste oil is purchased from vegetable-oil-refining plants. They were produced by acidification of soapstock. This kind of feedstock contains a lot of organic matter, such as colloids and proteins, which is an important reason leading to the high yield of coke.

The yield of bio-oil under different reaction temperatures was tested in a scale-up reactor. The reaction results are given in Figure 3. It was found that the maximum yield of product is approximately 25% at 410–420 °C using both of the raw materials (Figure 3a). With the increase of the reaction temperature, the yield of product reached 70% under 450 °C (71.5% in total at 470 °C). Figure 3b showed the cumulative yield of the product versus the reaction temperature during the reaction. It can be seen clearly that the yield of product from soybean oil increased dramatically at 420 °C. This result is in agreement with the thermogravimetry results reported the literature.¹⁰ After the temperature reached 450 °C, a further increase of the reaction temperature has no help on the increment of the product yield. Therefore, the minimum reaction temperature for the experiments in the scale-up reactor should be determined at 420 °C.

3.2. Esterification of Bio-oil in a Scaled-up Continuous Reactor. The acid value of the original bio-oil did not meet the standards of the ASTM specification for diesel fuels (Table 3).

Table 5. Effect of Different Catalysts on the Upgrading Reaction^a

properties	catalyst			
	NaHSO ₄	H ₂ SO ₄	<i>p</i> -CH ₃ C ₆ H ₄ SO ₃ H	S ₂ O ₈ ²⁻ /M–ZrO ₂ ^b
acid value (mg of KOH/g)	6	5	14	21

^aReaction conditions: reaction temperature, 90 °C; reaction time, 2 h. All of the reactions were carried out in batch operation using 2 kg of bio-oil and 50 g of catalyst. The methanol was then fed through a preheater at a rate of 0.3 kg/h. ^bThis solid acid was prepared according to the literature.¹⁵

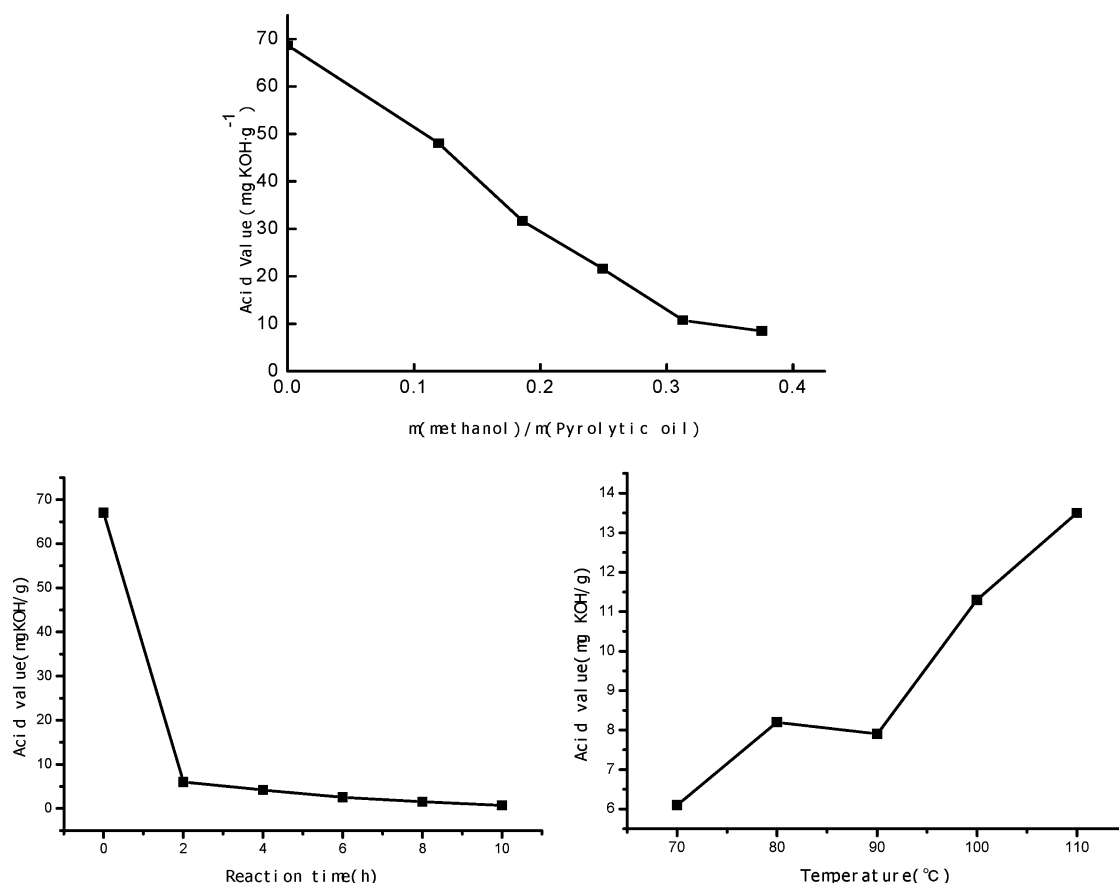


Figure 4. Effect of reaction parameters on the changes of the acid value during the esterification reaction.

This indicated that the pyrolytic products contain a small amount of fatty acids, which are not decomposed completely during thermal and catalytic cracking reactions. These undesired compounds have a high freezing point, which may greatly affect the cold-flow properties of the final products. To decrease the acid number of the pyrolytic product, a scaled-up continuous reactor was developed. The activities of different catalysts were investigated. The detailed results are shown in Table 5.

From Table 5, the acid value of the original bio-oil was reduced dramatically from 67 to 6 mg of KOH/g using NaHSO₄ as the catalyst. NaHSO₄ was chosen for use as an esterification catalyst, partly because of its low cost but also because it can be easily recovered after the reaction.

The operation parameters for the upgrading reaction were studied. The feed rate of bio-oil was fixed at 1 kg/h. At the same time, the flow rate of esterified product was also maintained at 1 kg/h. Under this reaction condition, the influence of the methanol amount on the acid number of the pyrolytic product was shown in Figure 4. With the increasing amount of methanol, the acid number of bio-oil decreased significantly. The acid number of the bio-oil can be decreased

to 8 mg of KOH/g at the feed rate of 0.32 kg/h. The relationship between the temperature and acid value of the product was also tested. Although the increment of the reaction temperature could accelerate the speed of esterification, the residence time of the methanol in the reactor decreased at the same time. The short residence time of the reactant (methanol) during the reaction severely inhibited efforts to produce the esterified product because of the low molecular interaction with the fatty acids. That is the reason why the acid value of the product increased after the temperature became higher than 100 °C.

3.3. Separation of the Pyrolytic Product To Obtain Gasoline and Diesel Fractions. The esterified products were introduced to a distillation process to obtain gasoline and diesel fractions. For this, 500 g of esterified product was distilled, and the condensate, up to 190 °C as the temperature of distillation, was quantified in 105.3 g (21.1% of the feedstock) of the gasoline fraction. After that, the product was further distilled by reduced distillation. A total of 326.8 g (65.4%) of the diesel fraction was obtained under the temperature of 300 °C at 5 kPa. The residue in the bottom is 43.4 g (8.7%), and the weight loss during the distillation process is 24.5 g (4.9%).

Table 6. Fuel Properties of the Fractionated Pyrolytic Products

	bio-oil	gasoline fraction	diesel fraction	diesel No. 2-D S15 ^a	jet fuel (A) ^b
freezing point (°C)	6	−42	−16		−51
cold plugging point (°C)	7	−40	−15		
flash point (°C)	63	34	115	52	51.1
density at 20 °C (g mL ^{−1})	0.881	0.866	0.898		0.820
viscosity at 20 °C (mm ² s ^{−1})	3.85	2.34	6.27	1.9–4.1	5.2 ^c
heat value (kJ kg ^{−1})	42.5	41.8	42.9		
acid value (mg of KOH g ^{−1})	69.3	2.3	2.5		<0.01
solubility in diesel		any proportion	any proportion		

^aASTM D975-11, Standard Specification for Diesel Fuel Oils. ^bASTM D1655 (Jet A). ^cMeasured at −20 °C.

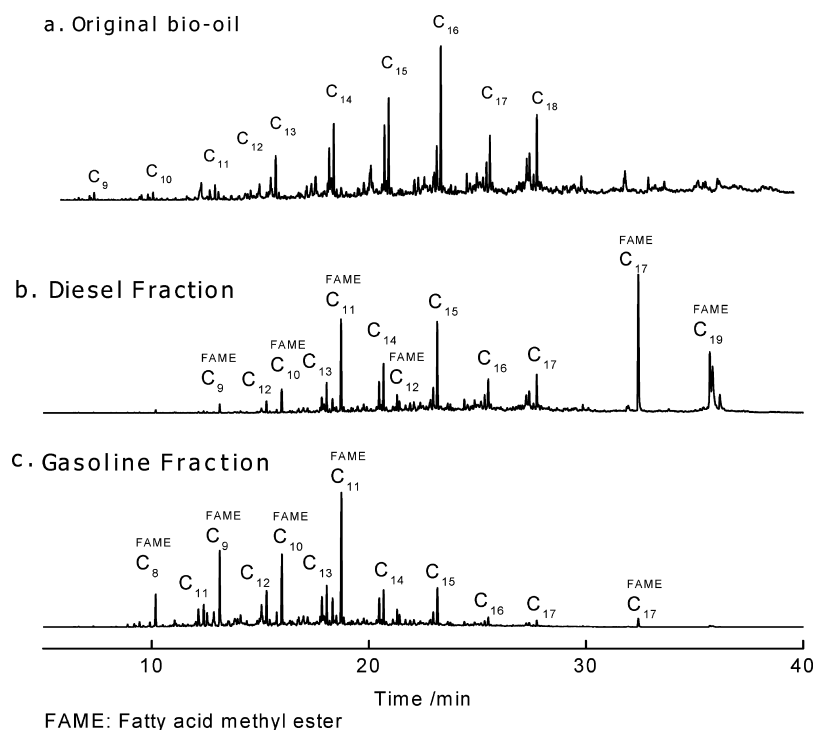


Figure 5. GC–MS analysis of the fractionated biofuels: (a) original bio-oil, (b) diesel fraction, and (c) gasoline fraction.

The main fuel properties of the esterified products are shown in Table 6. For comparison purposes, Table 6 also displays the required values for the petroleum-based fuel in ASTM standards. It seems that both the gasoline and diesel fractions show excellent cold-flow properties. Most of the fuel properties are comparable to the petroleum fuels. Besides, we tried to use the product to blend with diesel and discovered that both the gasoline and diesel fractions showed good solubility in diesel fuel. They can be blended with diesel in any proportion, which has a great potential prospect to be used as fuel additives.

The biofuels originating from all experiments were clear and yellow liquid. The components of the diesel and gasoline fractions were characterized by GC–MS (Figure 5). The results showed that all of the organic compounds closely resembled those in the MS database. The molecular distribution of the gasoline and diesel fractions lay in the range of C₈–C₁₇ and C₉–C₁₉, respectively. That means that the esterified products have a similar boiling range with petroleum-based fuel. More importantly, the carboxylic acids in the pyrolytic products were efficiently converted into their corresponding esters. This indicates that the acidity of the pyrolytic products was improved by the esterification reaction. Among the classes of compounds formed, long-chain hydrocarbons, such as alkanes

and alkenes, and oxygenated organic compounds, such as ketones, were identified. Only a small fraction of branched hydrocarbons was characterized, which indicated that the diesel fraction had good ignition quality (cetane number).¹⁵

4. CONCLUSION

We have presented an efficient catalytic route for the production of high-grade biofuels using triglyceride materials. The thermal and catalytic cracking reactions in a scale-up reactor have shown that the optimum temperature for thermal and catalytic cracking reactions is 420 °C. The undesired products (carboxylic acids) in pyrolytic products could be converted into corresponding esters by a continuous esterification process. Furthermore, fractionation of esterified products showed that fractionated products could be used as high-grade liquid fuels comparable to the petroleum fuels. The process is very stable at scale-up levels and produces diesel-range products with excellent cold-flow properties that are suitable for direct blending with conventional petroleum fuels.

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Notes

The authors declare no competing financial interest.

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