Research Article

Thi Hong Tran*, Quyen Huynh, and Minh Tan Phan

Synthesis of biological base oils by a green process

https://doi.org/10.1515/gps-2022-0008
received August 21, 2021; accepted December 13, 2021

Abstract: In this study, the chemical conversion of catfish fat (CFF) into bio-based oils using the cavitation technique has been carried out. The influence of parameters on the reaction yield, including inlet pressure, amount of reactant, temperature, and time were investigated. The results obtained have demonstrated the outstanding efficiency of applying the cavitation technique to the chemical synthesis process. The optimum conditions of ring-opening reaction of epoxy catfish oil (ECFO) were as follows: 60 psi, the molar ratio of *iso*-propanol/epoxy ring of 1.75/1, 75°C, time of 7 min, and the yield reached 91.3%. The results of FT-IR, ^{1}H-NMR, and ^{13}C-NMR analysis showed that the chemical conversion of double bonds (C═C) of CFF were converted to functional groups of hydroxyl and ether in polyol catfish oil (CFO) products through the intermediate stage of the formation of the epoxy ring. The results showed that the polyol CFO has better operating conditions at low temperature, higher viscosity, viscosity index, and oxidation stability than other oils, and the biodegradability of bio-polyol CFO was much higher than that of SN500 mineral base oil. Polyol CFO has not only been used as a substitute for mineral base oils but also as an eco-friendly green product.

Keywords: catfish fat, cavitation, biological base oils, biodegradability

*** Corresponding author: Thi Hong Tran,** Department of Petroleum Processing Engineering, Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet street, District 10, Ho Chi Minh City, 70000, Vietnam; Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, 70000, Vietnam; Industrial University of Ho Chi Minh City (IUH), Ho Chi Minh City, 70000, Vietnam, e-mail: 1585017@hcmut.edu.vn
Quyen Huynh: University Council, Ho Chi Minh City University of Natural Resources and Environment, Ho Chi Minh City, 70000, Vietnam
Minh Tan Phan: Department of Petroleum Processing Engineering, Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, 70000, Vietnam

1 Introduction

Mineral base stock oils met fully the quality standards of the substrate of a lubricant. As globally, we are facing crude depletion as well as the negative environmental impacts of used lubricants, we are forced to look at alternative resources to petroleum products in general and mineral base oils in particular. Vegetable oils or animal fats have been the most attractive substitutes and environmental lubricants [1,2]. With the main structure of triglycerides, after refining, vegetable oils could be used directly as biological base oils or bio-lubricants. However, the high pour point and the low oxidation stability of vegetable oils limited their alternative ability [2]. In previous studies, refined vegetable oils were only alternatively used to mineral base oils in low amounts in engine lubricant formulation (1–10 wt%) [3,4]. These properties of vegetable oils need to be improved so that they could meet the technical requirements of mineral base oils; the chemical conversion method was considered to solve this problem. The products of the esterification reactions of palm kernel oil, sesame oil with alcohols, have increased the viscosity index and reduced the pour point significantly. So, they have been used as substitutes for mineral base oils in lubricant formulation. However, their oxidation stability has not yet been improved, so they were found in the formulations of low-grade lubricants such as hydraulic oils ISO-VG46, T-46, and ISO VG22 [5,6]. The chemical conversion consisting of successive reactions of epoxidation of unsaturated bonds and opening of the epoxy ring with nucleophilic agents has been effective in converting vegetable oils to biological base oils. In a study by Ait Aissa et al. [7], the thermal stability and basic properties of the obtained products from reactions of epoxidation of vegetable oils and carbonation of oxirane were enhanced clearly. Turco et al. [8] used the ring-opening reaction of soybean epoxy oil with alcohols to synthesize the bio-based oils. Similarly, Thuy et al. [9] have synthesized bio-lubricant such as soybean polyol oil through successive reactions of epoxidation and the ring-opening reaction of the epoxy oil with water. In the work of Sharma et al. [10] and Somidi et al. [11], canola oil was chemically converted

by epoxidation reaction and the ring-opening reaction of epoxy oil. The basic properties of polyester oils products such as kinematic viscosity, viscosity index, oxidation stability, and pour point were improved significantly. So, they could be alternatively used as mineral base oils. It can be inferred that with a predetermined structure, most of the properties of polyol oils or polyester oils based on vegetable oils have been significantly improved. So, they could not only be used as alternatives to mineral base stock oils but also were environmentally friendly products. However, the use of vegetable oils as materials in the synthesis of bio-based oils could cause a shortage in the supply of cooking oil in food production and processing, serving human nutritional needs. Vietnam is an exporter of catfish fillet with large volumes and catfish fat (CFF) is a waste or by-product of catfish processing in large amounts. Annually, Vietnam collected more than 200,000 tons of CFF. In the past, most CFF was not normally consumed, discarded, or supplied as animal feed. This could both waste CFF and pollute the environment, especially the catfish culture environment. Previous studies have verified that the physical-chemical properties as well as the chemical structure of CFF and vegetable oils were similar [12,13]. So, in Vietnam, CFF is used as feedstocks in the production of bio-based oils with readily available, inexpensive, and nontoxic sources.

In bio-based oil synthesis reactions, vegetable oil or epoxidized oils based on vegetable oils and the reactant chemicals are heterogeneous, so the determining factor of the reaction rate is the mixing between the two reaction phases. If their mixing is high, it means that the surface area of the phase contact is large and hence the reaction will be more favorable. However, in previous studies, the reactions were carried out in low-performance mixing equipment such as magnetic stirrer or conventional mechanical stirrer, so the diffusion capacity of the reactants into the oil phase may have been difficult, which has been detrimental to the reactions.

Cavitation is a term for the rapid formation, growth, and rupture of bubbles (or holes). Hydrodynamic cavitation describes the formation of bubbles due to pressure changes in a moving fluid, resulting from a change in the fluid flow rate through a narrow opening designed on the principle of venture valve operation. The transformation of a chemical reaction in a cavitation system can be described by the change of bubbles. During the lifetime, the bubble increases in size due to more gas permeation, the gradual increase in surface area, and the decrease in external pressure. The size of the bubble can be from 3 to 400 times. When the bubble moves to a large pressure difference area, the bubble will burst and create an area of high pressure (can reach 1,000–2,000 bar) and high temperature (from 4,000 to 6,000 K), and the amount of heat is very rapidly dispersed with an estimated heat transfer rate in the range of 1 billion $K \cdot s^{-1}$. Therefore, at any given time, the temperature in the entire reacting liquid mass is the same. Besides, when the bubbles explode, it will destroy the equilibrium region of the liquid reactant phases, creating a chaotic stirring in the reaction zone, thereby enhancing the contact ability for the two liquid phases, and creating the most favorable conditions for the reaction to take place [14–18].

Other studies have demonstrated the outstanding performance of applying advanced mixing techniques to heterogeneous reaction processes. In the study of Fatt et al., biodiesel reaction from waste cooking oil and methanol, performed in the cavitation reactor, higher conversion is achieved with lower chemical consumption, temperature, and reaction time than compared to the reaction performed in a mechanical stirrer reactor [16]. The biodiesel reaction from *Cannabis sativa* oil and methanol was carried out in a hydrodynamic cavitation reactor with high conversion (97.5%) in only 20 min under other optimal parameters. Meanwhile, at the same reaction parameters, the conversion was only 26% when the reaction was carried out in a mechanical stirrer reactor [17].

It was observed that the use of a high-performance cavitation mixer as a reactor in the synthesis of bio-based oil from CFF as a starting material has increased the reaction efficiency significantly, reducing the reaction rate, reagent consumption, energy consumption, and reaction time greatly. Therefore, the process of synthesizing biological base oil from CFF as a starting material under the support of cavitation technology is a green process and sustainable development.

To develop processing toward green chemistry, the chemical conversion of CFF into bio-polyol oils, used as biological base oils using the cavitation technique was the aim of this study. The struct, as well as the characteristic properties of materials and products such as lubricity, oxidation stability, and biodegradability were determined. The bio-polyol catfish oil (OLCFO) has a high potential in use as an alternative resource to mineral base oils and in the field of reducing environmental pollution.

2 Materials and methods

2.1 Materials

CFF was bought from Phuoc Thanh Agricultural Company Limited, An Giang province, Vietnam. Hydrogen peroxide

(30 wt%), acetic acid (99 vol%), sulfuric acid (99.9 vol%), and *iso*-propanol (assay ≥76.9 vol%) originated in Vietnam. The chemicals and solvents in the analysis were of analytical pure standard and were procured from Merck.

2.2 Experimental process

2.2.1 Preparation of catfish oil (CFO) feedstock

About 10 kg of raw CFF was placed in a stainless steel tank with a capacity of 15 L, a cone bottom with a blow-down valve, and an internal heating system. A mechanical agitator was used to gently stir, and heated to a temperature of about 30–35°C for 1 h to reduce the viscosity of CFF. Then, all CFF was put in the filter tank of the vacuum plate filter system with a filter cloth of diameter 30 µm. Filtration is allowed to take place for about 3–4 h. After the pre-filtration process, the obtained CFO was stored in a dark container to be protected from direct sunlight and used as a feedstock for bio-polyol oil processing.

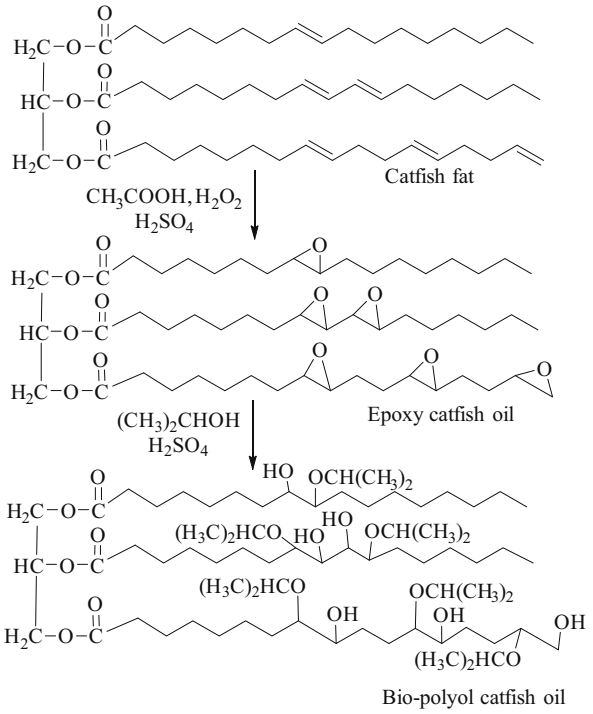

Figure 1: The synthesis reaction scheme of OLCFO from CFF.

2.2.2 The OLCFO procedure performed in the cavitation reactor

2.2.2.1 Synthesis reaction

The synthesis of OLCFO consists of consecutive reactions: the CFO epoxidation reaction of a mixture of hydroperoxide and acetic acid; and the ring-opening reaction of epoxy catfish oil (ECFO) with *iso*-propanol and the sulfuric acid catalyst. The epoxidation reaction was carried out at fixed conditions, 50 psi, 40°C, molar ratios of acetic acid/double bond (C═C) and hydroperoxide/double bond (C═C) of 1.25 and 2.75 in 4 min. In the epoxy ring-opening reaction, the investigated parameters included the inlet pressure of 40–75 psi, the molar ratio of *iso*-propanol/epoxy at 0.75–2.5, and temperature and time in the range of 55–90°C and in 4–10 min, respectively. The synthesis reaction scheme of OLCFO from CFFis shown in Figure 1.

2.2.2.2 The experimental process

The cavitation device is an orifice plate type, 1 hole with a diameter of 1 mm, and 10 L capacity, as used in our previous studies [12,13] was used as the reactor in this study. The structural diagram of the cavitation device system and the experimental procedure are shown in Figure 2.

About 5 kg of CFO feedstock was put into Tank-2. Then, calculated amounts of hydroperoxide, acetic acid, and the sulfuric acid catalyst were added to Tank-2. The valve V_2 and recirculation valve V_4 opened in about 30 s to mix the reaction mixture. The valve V_4 closed and valve V_3 opened simultaneously to pump the reaction mixture into the cavitation zone via Pump-1. The displayed values of temperature and pressure on the themometer-T_4 and the gause-P_3 were monitored. When the reaction was complete, valve V_1 opened and the raw mixture product was collected, which was washed several times with distilled water to remove the catalyst, residues, and by-products. Finally, the ECFO product was dried in a microwave oven to completely remove

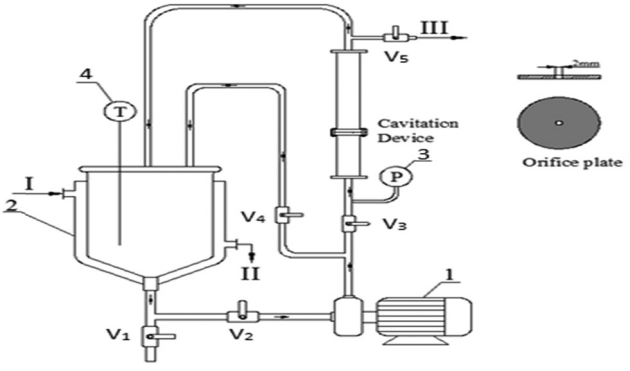

Figure 2: Schematic of the cavitation equipment.

the water from the ECFO. The epoxy content (wt%) of ECFO was determined according to the ASTM D1652 to evaluate the efficiency of the epoxidation reaction.

The experimental procedure of the ring-opening reaction of ECFO with *iso*-propanol and the sulfuric acid catalysts is similar. About 5 kg of ECFO was put into Tank-2. Next, calculated amounts of *iso*-propanol and the sulfuric acid catalyst were added to Tank-2, respectively. The reaction mixture was also stirred cyclically for 30 s. At each surveyed value of the affecting parameters in the reaction process and at interval times of 4, 6, 7, 8, and 10 min, 100 mL of sample products was taken out through valve V_1. The samples were washed several times with distilled water to remove the catalyst, residues, and by-products. Finally, the OLCFO sample was dried in a microwave oven to completely remove the water. The hydroxyl number of OLCFO was determined according to the ASTM D4274-99 to evaluate the efficiency of the reaction.

2.3 Detection method

The functional groups of samples were determined by Fourier transform infrared resonance (FT-IR) and nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR) spectroscopy. The FT-IR analysis was performed on the FT/IR Agilent, serial number C019561788. The wavenumber was in the range of 400–4,000 cm^{-1} and the ^{1}H-NMR and ^{13}C-NMR analyses were carried out on the NMR Bruker 500 MHz using $CDCl_3$ as a solvent. The oxidation stability of samples was analyzed by the TGA method and Rancimat test. The biodegradability of the samples was predicted from the values of biological oxidation demand (BOD_5), chemical oxygen demand (COD), and BOD_5/COD ratio.

2.3.1 Calculation of the yield of the reaction

The yield of the ring-opening reaction y (%) was calculated by Eq. 1:

$$y = \frac{OH_{exp}}{OH_{theo}} \times 100\% \quad (1)$$

where OH_{exp} and OH_{theo} are the hydroxyl number from experiment and theory (mg KOH per g), respectively, and were calculated according to ASTM D4274-99 by Eqs. 2 and 3:

$$OH_{exp} = \frac{V_0 - V_1}{w} \times 0.1 \times 56.1 \quad (2)$$

$$OH_{theo} = \frac{10E}{43} \times 56.1, \quad (3)$$

where V_0 and V_1 (mL) are the volumes of titration of the blank and samples, respectively; w (g) is the weight of the samples; and E (wt%) is the epoxy content of ECFO and were calculated according to ASTM D1652.

3 Results and discussion

3.1 Epoxidation reaction

The iodine value (IV) of CFO was determined by ASTM D1959 and IV reached 69 (g Iod/100 g). The epoxy content (E) of ECFO was determined according to ASTM D1652 and was found to be 10.32 (wt%); so, the yield of epoxidation reaction of CFO was determined in the cavitation reactor and achieved 92.2% [18]. When compared with the results of other studies on epoxidation reactions of vegetable oils, performed in mechanical or magnetic stirrer reactor [10,19,20], it was found that the epoxidation reaction efficiency reached a higher level with lower chemical consumption and reaction temperature, and the reaction time was many times shorter. Namely, Tran et al. carried out the epoxidation reaction of CFF with a mixture of hydroperoxide, acetic acid, and sulfuric acid catalyst using a magnetic stirrer. The reaction yield reached 83.49% at 55°C with a long reaction time of up to 5 h [19]. In the study of Hong et al., the optimum conditions of the epoxidation reaction of linolenic acid in jatropha oil were determined as follows: 45°C, molar ratio of HCOOOH/C═C was 2 and molar ratio of H_2O_2/C═C was 12, and the time reaction extended up to 2 h [21]. Similarly, Wang et al. conducted an experimental study on the epoxidation of soybean oil with a mixture of hydroperoxide and formic acid, and the choline chloride/carboxylic acid catalyst in the reaction device with a glass flask-heated magnetic stirrer. The maximum epoxide yield of 83.19% was obtained at 50°C and 8 h [22].

3.2 Effect of parameters on the yield of ring-opening reaction of ECFO

3.2.1 Effect of the inlet pressure

To determine the effect of the inlet pressure on the yield of the ring-opening reaction of ECFO with *iso*-propanol, the experiments were carried out the following conditions:

70°C, the molar ratio of *iso*-propanol/epoxy of 1.5, time in the range of 4–10 min, and the inlet pressure between 40 and 75 psi; the results are shown in Figure 3.

The data in Figure 3 show that the inlet pressure is a parameter that strongly influences the reactivity. When the pressure increased from 40 to 50 psi, along with the increasing reaction time, the reaction yield increased gradually. When the pressure increased to 60, 65, and 75 psi, initially (4–7 min), the reaction yield increased but when the time was longer, the yield did not increase but decreased slightly. In the surveyed cases, the highest yield was achieved at 60 psi and 7 min. This could be explained by the fact that the reaction performed in the cavitation reactor when the inlet pressure increased, the number of circulation cycles through the hole increased, which could increase the retention time of flow in the cavitation zone and increase the cavitation efficiency. This means the formation and the explosion of air bubbles increased. It could create a chaotic stir of reactants, so the contact of them increased the strength and reactions were more favorable. However, when the pressure increased over a limit value, which is called the supercavitation or chocked pressure ($P_{chocked}$), the flow rate of reactants or the stir/the contact of reactants could almost be constant and so the reactivity could not increase further. In this work, a $P_{chocked}$ of 60 psi cavitation system was selected. The slight decrease in the reaction efficiency when the pressure was increased to 75 psi could be because the strong agitation conditions of the cavitation system could lead to the formation of an emulsion of the product and the sulfuric acid catalyst, which could make the purification of products difficult.

In other studies, the effect of pressure on the efficiency of heterogeneous reactions, performed in a cavitation reactor, was also investigated, explained, and similar results were reported. In the study of Khan et al. [17], under other optimal conditions, the effect of the inlet pressure on the conversion (%) of the biodiesel reaction from *Cannabis sativa* oil and methanol, performed in a cavitation reactor, was investigated in the pressure range of 1–4 bar and the conversion increased when the inlet pressure increased from 1 to 3 bar but the conversion decreased slightly as the inlet pressure reached 4 bar. Bargole et al. used the response surface methodology to optimize the synthesis process of biodiesel from waste cooking oil and methanol, performed in the hydrodynamic cavitation reactor. The observed results proved that pressure could be one of the most stronger parameters of the biodiesel reactivity; the reaction yield increased sharply when the pressure increased in the range of 3–7 bar, the yield decreased when the pressure was 10 bar and it remained constant when the pressure was further increased to 15 bar [23].

3.2.2 Effect of the loading reactant

As shown in Figure 4, the increase in the molar ratio of *iso*-propanol/epoxy from 0.75 to 1.25 led to the increase in the reaction yield. When the reaction was performed at a higher molar ratio of reactants (1.75, 2, and 2.5), the yield increased in the time range of 4–7 min and it was decreased as the reaction time extended to 8 and 10 min. So, in the investigated cases, the molar ratio of *iso*-propanol/epoxy of 1.75 was confirmed as the optimal consumption reactant of the ECFO ring-opening reaction. Theoretically, the characteristic of the ring-opening reaction is irreversible and the reaction can occur at a valid molar ratio of reactants of 1. According to Thi et al. [18] and other authors [24], the ECFO has a high molecular weight and high viscosity. This could cause difficulties in the diffusion and contact of *iso*-propanol into the ECFO. So in other studies, the reaction yield was higher as the reaction was performed with a reactant ratio greater than 1.

In this study, as the molar ratio of reactants increased in the range of 0.75–1.75, the mass transfer of reactants

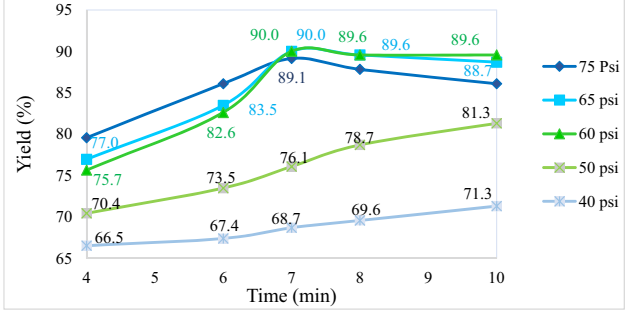

Figure 3: Effect of inlet pressure on the yield of ring-opening reaction of ECFO with *iso*-propanol, at 70°C, and a molar ratio of *iso*-propanol/epoxy of 1.5.

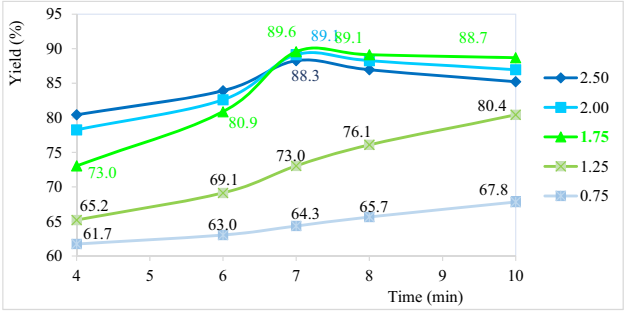

Figure 4: Effect of chemical consumption on the yield of ring-opening reaction of ECFO with *iso*-propanol, at 60 psi and 70°C.

increased and so the speed of reaction could be more favorable and the yield of reaction increased. However, when the reaction used a higher amount of the reactant, such as at *iso*-propanol/epoxy molar ratios of 2/1 and 2.5/1, an excess of *iso*-propanol may cause side effects. Besides, the excess *iso*-propanol mixed into the product leads to difficulty in purifying the product. So, the reaction efficiency was not only increased but also reduced. These have also been elucidated by the authors in other studies. At other optimal reaction conditions, Turco et al. used a molar ratio of mono-alcohol/epoxy of 10/1 to obtain the highest yield of the ring-opening reaction of epoxy soybean oil [8]. Thung et al. [9] investigated the effect of parameters on the yield of the ring-opening reaction of soybean oil with H_2O and an H_2SO_4 catalyst. The molar ratio of H_2O/epoxy oil was measured in the range 10/1 to 20/1 and the highest hydroxyl number of products were obtained at a molar ratio of reactants of 15/1, under other optimal reaction conditions.

The scientific publications showed that the amount of reactant is one of the factors that greatly affect the performance reactivity, performed in the cavitation system reactor. In the study of Fatt et al., at other optimal reaction conditions, the highest conversion of the heterogeneous biodiesel synthesis reaction performed in the cavitation apparatus was obtained at the molar ratio of methanol/oil of 6/1 in the surveyed data from 4/1 to 7/1. Mistry et al. used Box-Behnken statistical software to optimize the biodiesel process from castor oil and methanol, performed in a hydrodynamic cavitation reactor. The molar ratio of methanol/oil was one of the main factors investigated in the range from 6/1 to 10/6. The highest biodiesel yield was achieved at a molar ratio of reactants of 6/1 in other optimal reaction conditions [25].

3.2.3 Effect of temperature

The data in Figure 5 show that the temperature affected the yield of the ring-opening reaction of ECFO significantly. When the temperature increased from 55°C to 65°C, the yield of the reaction increased gradually during the whole survey period (4–10 min). When the temperature increased (75°C, 80°C, and 90°C), initially (4–7 min), the yield increased but then it decreased when the reaction time was extended to 8 and 10 min. In the surveyed cases, the optimum temperature was determined at 75°C and the yield reached 91.3% at 7 min.

This could be explained as follows: when the temperature increased, the viscosity of reactants decreased, which led to the dispersion of them easier; the contact of them increased and the reaction speed increased. So, the

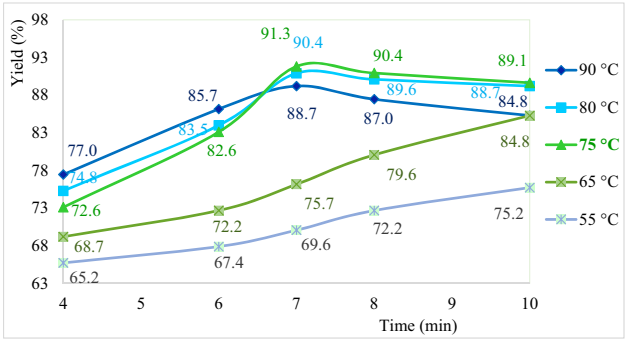

Figure 5: Effect of temperature on the yield of the ring-opening reaction of ECFO with *iso*-propanol, at 60 psi and a molar ratio of iso-propanol/epoxy of 1.5.

yield of the reaction increased significantly. At high temperatures (90°C) and the intense agitation of the cavitation zone, a little ECFO feedstock decomposed by the catalysis of sulfuric acid, and could lead to a slight decrease in the reaction yield.

The effect of temperature on the cavitation system activity or heterogeneous reaction efficiency has been similarly explained and reported by other studies. The results of the study of Mohod et al. for the biodiesel reaction from cooking oil and methanol showed that under other optimal conditions, the yield increased when the temperature increased from 40°C to 50°C and the yield decreased as the temperature reached 60°C [26]. In the study of Thi et al. [18], the optimal temperature of the CFF epoxidation reaction with hydroperoxide and acetic acid was set at 45°C in the investigated temperature range of 25–65°C.

In this work, the optimum conditions of the ring-opening reaction of ECFO with *iso*-propanol, performed in the cavitation reactor were established. The reaction yield reached 91.3% in the molar ratio of *iso*-propanol/epoxy of 1.75, 75°C, and 7 min. The obtained results demonstrated that the hydrodynamic cavitation technique could enhance the efficiency of the reaction significantly. A higher reaction yield was achieved with lower chemical consumption and reaction temperature, and a shorter reaction time. This could be further elucidated by comparing with the results of other studies on the ring-opening reaction of epoxy vegetable oils with nucleophilic agents, carried out in the conventional mixing equipment. In the study of Turco et al. on the ring-opening reaction of epoxy soybean oil with various short-chain mono alcohols, although the magnetic stirrer reactor was set at the highest stirring speed to increase the contact of reactants, the highest reaction efficiency was achieved with a high chemical consumption (alcohol/epoxy) molar ratio of 10/1

for the reaction time up to 90 min [8]. Thuy et al. synthesized polyol soybean oil from a reaction of epoxy soybean oil and water with H_2SO_4 as a catalyst, performed in a high-speed mechanical stirrer reactor. The hydroxyl number of the product reached the highest level (358.51 mg KOH per g) with a high molar ratio of water/epoxy of 15/1 and a long reaction time of 5 h [9].

3.3 Characterization analysis

The main functional groups of the CFO starting feedstock, ECFO, and the OLCFO final product were characterized by FT-IR and NMR spectral analysis methods. The results of this structural analysis are presented in the following sections.

3.3.1 FT-IR analysis

The functional groups of samples of CFO starting feedstock, ECFO, and OLCFO products were determined via the FT-IR spectra, and the analytical results are shown in Figure 6.

FT-IR spectra in Figure 6 display peaks for the main functional groups of samples. The chemical signals appearing at 1376.93, 1464.67, 2852.20, and 2919.70 cm^{-1} could be attributed to the presence of CH_3, CH_2, and CH groups. The C–O and C═O of the ester group (O–C═O) could be attributed to the presence of chemical shifts at 1112.73, 1160.94 cm^{-1}, and 723.18, 1741.41 cm^{-1}. In the FT-IR spectrum of CFO, strong chemical signals displayed at 1654.86 and 3008.85 cm^{-1}, which could be attributed to the unsaturated bond HC═CH of the CFO feedstock. The FT-IR spectrum of ECFO did not show the characteristic peaks for the double bond HC═CH, but instead, a new peak appeared at 825.50 cm^{-1}, which could be attributed to the epoxy ring in the structure of ECFO. Similarly, the FT-IR spectrum of OLCFO did not exhibit the typical peak for the epoxy group and showed a new peak at 3464.03 cm^{-1} and was attributed to the presence of the hydroxyl group (OH) in the structure of the OLCFO product. The identification of chemical signals in the FT-IR spectra and their assignment to functional groups of CFO, ECFO, and OLCFO were similar to the results of FT-IR analysis by Turco et al. [8] and Thuy et al. [9].

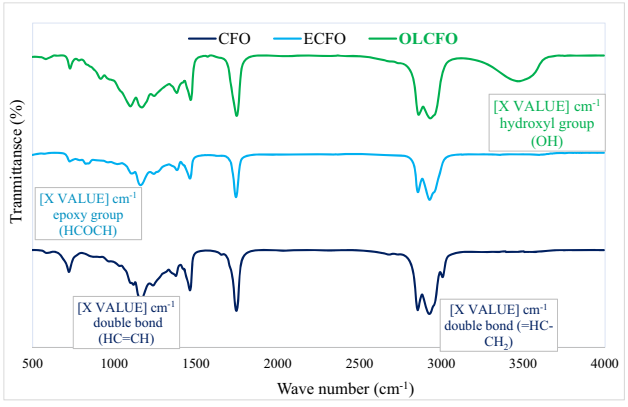

Figure 6: FT-IR spectra of CFO, ECFO, and the OLCFO product.

3.3.2 NMR analysis

The NMR analysis was used to confirm the functional groups of feedstocks and products. Figures 7 and 8 show the ^{1}H-NMR and ^{13}C-NMR spectra of CFO starting feedstock, ECFO, and the OLCFO final product.

The ^{1}H-NMR spectra in Figure 7 show the typical proton peaks for functional groups of samples. The protons of C**H**$_3$ and C**H**$_2$ of R wires were determined by the displayed peaks at 0.87–0.89 and 1.26–1.34 ppm, respectively. The protons of β-C**H**$_2$ and α-C**H**$_2$COO were verified via the displayed peaks at 1.610–2.069 and 2.291–2.327 ppm, respectively. The displayed peaks at 4.126–4.161 and 4.279–4.311 ppm confirmed the appearance of protons C**H** and C**H**$_2$ of glycerol, respectively. The ^{1}H-NMR spectrum of CFO showed the strong appearance of the peak at 5.26–5.34 ppm, which indicated the presence of the protons of the double bond **H**C═C**H** in the structure of CFO starting feedstock. The ^{1}H-NMR spectrum did not ECFO display the proton-specific peaks of the double bond. The appearance of new peaks at 1.62–1.72, 1.47–1.61, and 2.89–3.11 ppm confirmed the appearance of protons of β-C**H**$_2$ and α-C**H**$_2$ linked to the epoxy group and epoxy group (**H**COC**H**) in the ECFO structure. Similarly, in the ^{1}H-NMR spectrum of OLCFO, the proton-specific peaks related to the epoxy group were not found and the presence of new peaks at 3.41–3.47 ppm could demonstrate the appearance of protons of a hydroxyl group (O**H**) in the structure of the OLCFO product.

The carbon peaks for the functional groups of samples are presented in the ^{13}C-NMR spectrum (Figure 8). The carbon peaks of **C**H$_3$ and **C**H$_2$ of R wires were determined by the presence of chemical signals at 14.03–14.07 and 22.66–31.90 ppm, respectively. The appearance of chemical shifts at 62.09–68.91 and 172.78–173.19 ppm were attributed to the typical carbon peaks of **C**H and **C**H$_2$ of glycerol and the ester group (**C**OO). The ^{13}C-NMR spectrum of CFO showed clearly the chemical signals at 127.90–129.98 ppm, which were owing to the carbon peaks of olefinic (H**C**═**C**H) in the CFO starting feedstock.

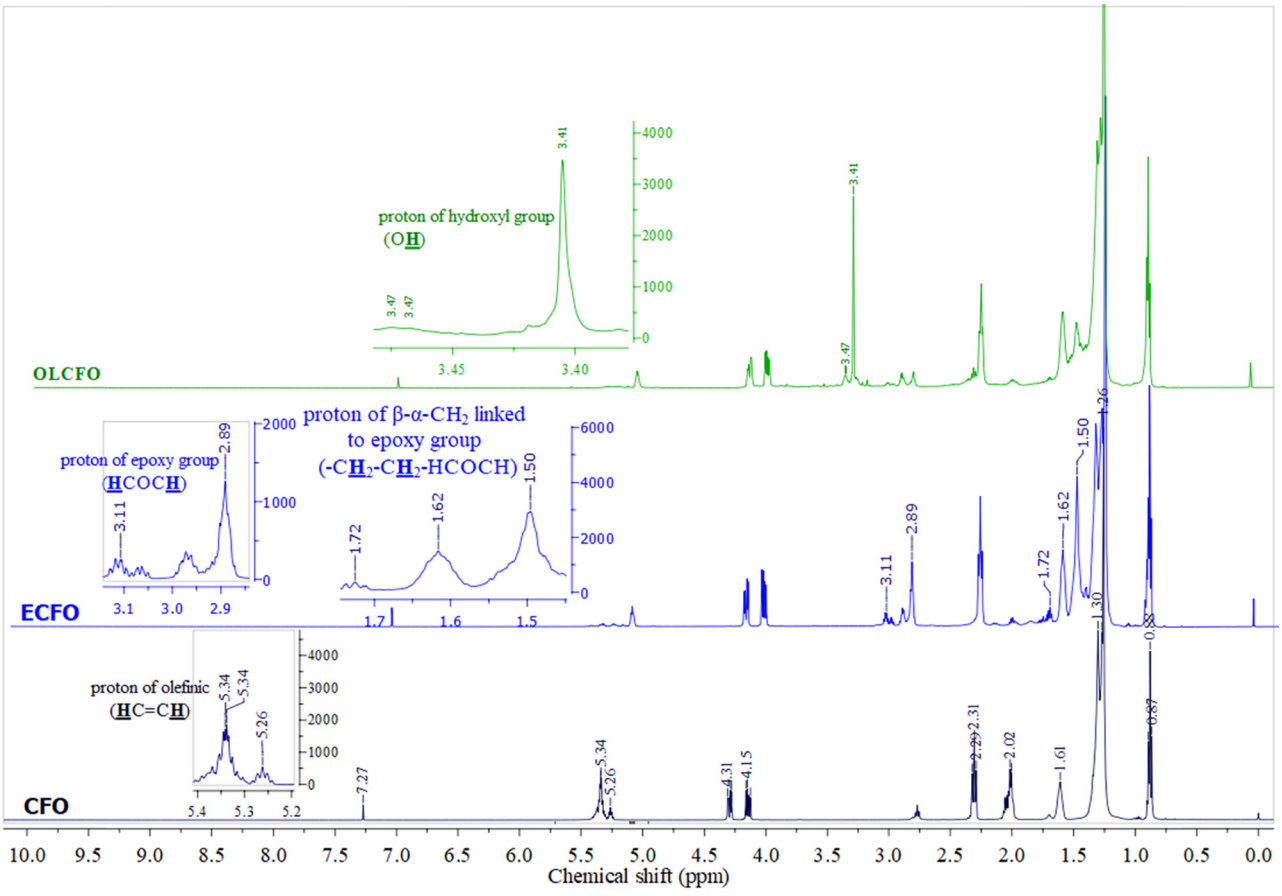

Figure 7: ^{1}H-NMR spectra of CFO, ECFO, and the OLCFO product.

The ^{13}C-NMR spectrum of ECFO did not display the typical carbon peaks for the olefinic (H**C**═**C**H) but instead showed the corresponding clear specific carbon peaks of an epoxy group (H**C**O**C**H) at 54.12–57.14 ppm. Similarly, the carbon-specific signals of the epoxy group were not found in the ^{13}C-NMR spectrum of OLCFO. The occurrence of the signals at 70.31–79.99 ppm was confirmed for the carbon-specific peaks of the methine group linked to a hydroxyl group (–H**C**–OH) in the structure of the OLCFO product.

In this study, the obtained results from the FT-IR, ^{1}H-NMR, and ^{13}C-NMR analysis match together well. These analytical results have well demonstrated that the chemical conversion of the CFO starting feedstock into the OLCFO final product through the intermediate stage of ECFO compound formation has occurred. The results of FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectrum analysis for soybean oil material, epoxy soybean oil, and polyol soybean oil products in other studies were similar to this study [8,9].

3.4 Performance properties

The performance properties of the CFO feedstock and OLCFO product could be verified via lubricating properties (thermal-viscosity properties), oxidation stability, and biodegradability. In this study, the properties of samples were determined according to suitable analytical standards for biological base oils. The results are shown in Table 1 and Figures 9 and 10.

3.4.1 Lubricating properties

The lubricating properties of the CFO feedstock, products of OLCFO were determined, and the results are shown in Table 1.

Because vegetable oils and CFO are high molecular weight compounds having the main structure of triglycerides, bio-based oils based on vegetable oils or CFO

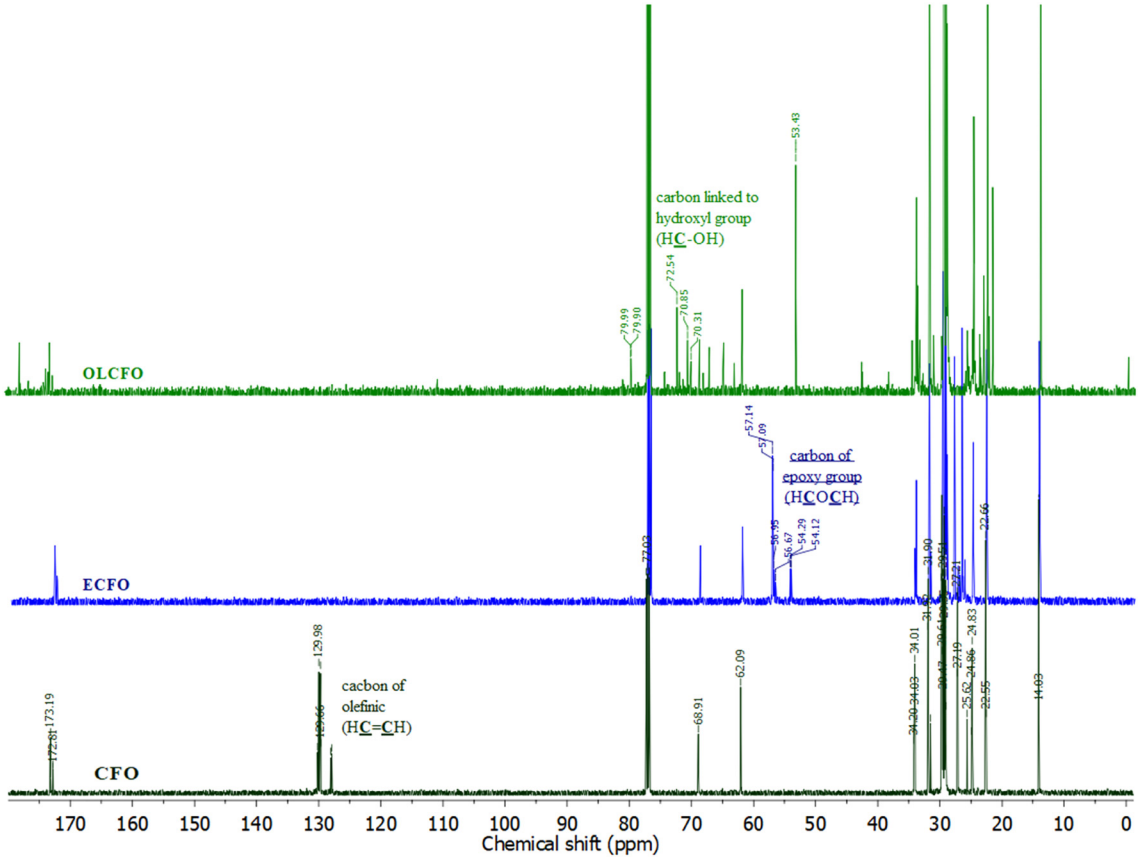

Figure 8: ^{13}C-NMR spectra of CFO, ECFO, and the OLCFO product.

have advantages such as high viscosity and high viscosity index. Based on the results of Sharma et al. [10], the presence of alternative functional groups such as ester and hydroxyl in the double bond (C═C), and the branched structure of the triglyceride chain with these functional groups could have prevented the crystallization of the OLCFO product; so, the pour point temperature of the product was significantly reduced compared to the CFO feedstock. The characteristic structure of the OLCFO can also lead to its pour point being higher than that of the SN500 mineral base oil. However, the average winter temperature in Vietnam and neighboring countries is always higher than 10°C. Besides, to establish the formulation of bio-lubricants from OLCFO, it should be noted that additives must be added to decrease the pour point. So, the possibility of using OLCFO as bio-based oils is entirely possible.

3.4.2 Oxidative stability

The oxidation stability of the CFO feedstock and OLCFO product was determined by TGA and Rancimat methods, and the results are presented in Figures 9 and 10.

Table 1: The performance properties of catfish oil feedstock (CFO), polyol catfish oil product (OLCFO) and SN500 mineral base oil (SN500)

Samples	Density	Flash point (°C)	Pour point (°C)	Kinematic viscosity (cst)		Viscosity index
				40°C	100°C	
CFO	0.916	292	22	95.26	11.30	105.2
OLCFO	0.978	304	−3	155.52	19.2	140.83
SN500 [12]	0.889	239	−6	96.03	11.59	109.07
Method	ASTM D1298	ASTM D92	ASTM D97	ASTM D445		ASTM D2270

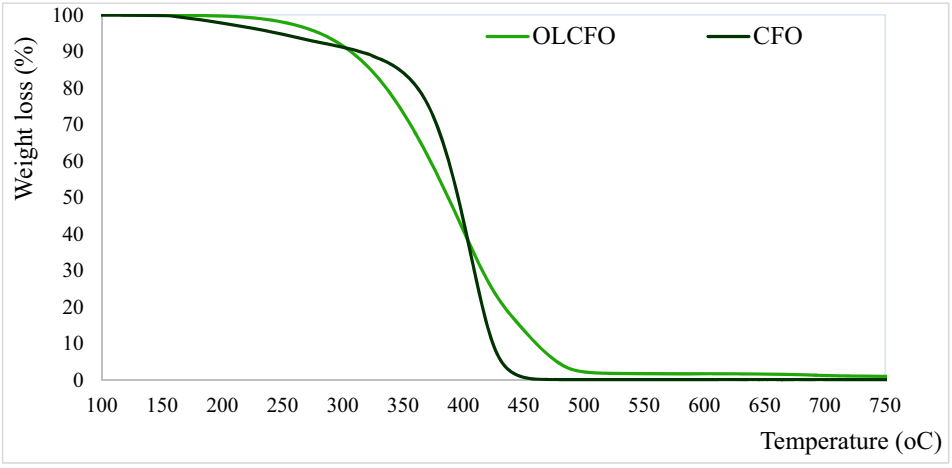

Figure 9: TGA curves of CFO and the OLCFO product.

CFO has many advantages such as high viscosity and high viscosity index, but its oxidation stability is very poor and so its substitute for mineral base oils is very low. In this study, the oxidation stability of CFO feedstock was improved by conversion to saturate its unsaturated components to form OLCFO. As shown in Figure 7 the thermal stability of the OLCFO final product was improved significantly compared to that of the CFO starting feedstock. The stability temperature and 95 (wt%) decomposition temperature of OLCFO were up to 230°C and 478°C while those of CFO were lower (174°C and 432°C).

The Rancimat curves of samples presented in Figure 8 have a similar trend. The induction time of the CFO feedstock was only 0.20 h. Meanwhile, the induction time of the OLCFO product reached a much higher value (6.73 h). This could be because the structure of the saturated OLCFO compound with the main chain of triglycerides with hydroxyl branches has created high oxidation stability. This was also verified by the results of FT-IR, ^{1}H-NMR, ^{13}C-NMR analysis as well as the difference in the iodine values of CFO and OLCFO. Similar results were also reported by Ait Aissa et al. [7], Sharma et al. [10], and Saboya et al. [27].

3.4.3 Biodegradability

According to the scientific literature, COD and BOD tests could be used to evaluate the biodegradability of materials. In this study, the BOD_5 and COD values of the OLCFO product were determined according to TCVN 6001-1:2008, SMEWW 5220D:2017 standards, and the results are shown in Figure 11.

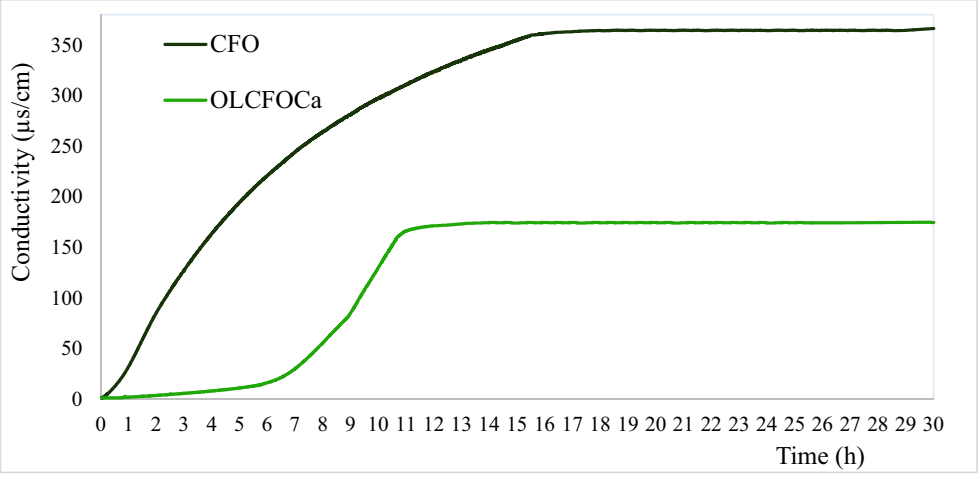

Figure 10: Rancimat curves of CFO and the OLCFO product.

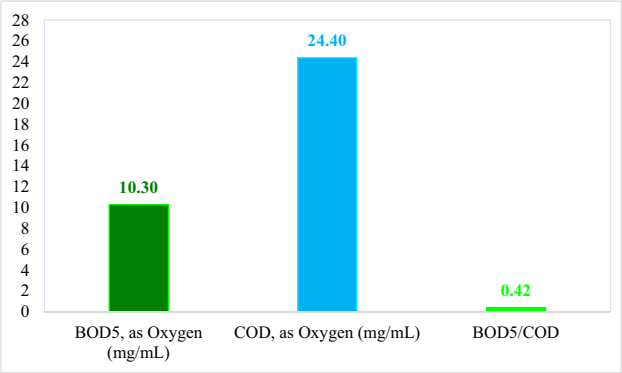

Figure 11: Values of BOD_5, COD, and the BOD_5/COD ratio of the OLCFO product.

According to some studies, when materials have a BOD/COD ratio lower than 0.2, they could be durable under natural environmental conditions. When the BOD/COD ratio of materials was in the range 0.2–0.3, they could hardly be biodegradable; and when the ratio of BOD/COD was greater than 0.3, these materials could be classified as highly biodegradable substance group [28–31]. On this basis, the displayed values of BOD_5, COD, and BOD_5/COD ratio of the OLCFO product in Figure 9 demonstrate excellent biodegradability. According to the study of Thi et al. [12], the biodegradability of SN500 mineral base oil (SN500) was much lower than that of catfish bio-polyol, and SN500 could be classified as a nonbiodegradable material. This has also been explained and evaluated by Choi et al. [28]. They also stated that the hydrocarbon component of SN500 could be nonchemically decomposed and were nonbiodegradable compounds. So, a large number of oxygen molecules were required to perform the chemical and biological degradation of SN500. Hydrocarbons with the structure of long alkyl R chains could cause negative effects on the inoculated microorganisms, which could lead to the low values of BOD/COD ratio for SN500. Based on the COD, BOD_{28}, and BOD_{28}/COD ratio values of samples, Almutair observed that biodegradation of mineral oil-contaminated wastewater was difficult and its biodegradability was lower than that of saponin solution [30]. In a study by Zhang et al. [31], the BOD/COD ratio was used to estimate the biodegradability and a load of removal pollutants in wastewater. They also demonstrated that the highest efficiency of the wastewater process was achieved at a BOD/COD ratio of nearly 0.5. The biodegradability of four types of ionic liquids was evaluated by Oliveira et al. Their results showed that the biodegradability of all ionic liquids was very low because the BOD, COD (as oxygen, $mg{\cdot}mL^{-1}$), and BOD/COD ratios were in the range of 27.11–33.30, 1,506–2,876, and 0.01–0.02. The most nonbiodegradable sample was found that contained an R linear alkyl chain in its structure [29].

OLCFO can be used as an alternative to mineral base oil. This could not only contribute to reducing the scare of dependence on crude oil resources but also reduce the negative impact on the environment.

4 Conclusion

In this work, OLCFO has been successfully synthesized from CFF raw material using the cavitation technique. The results obtained showed that the use of a cavitation device as the reactor increased the reaction yield. At 50 psi, the yield of the epoxidation reaction reached a high value (92.2%) with low reagent consumption (molar ratio of $H_2O_2/CH_3COOH/C{=}C$ = 2.75/1.25/1), low reaction temperature (40°C), and a short time (only 4 min). Similarly, at 60 psi, the reaction yield of the catfish epoxy oil ring-opening reaction was 93% at 75°C, a molar ratio of *iso*-propanol/epoxy of 1.75/1 in just 7 min. The properties of OLCFO products such as lubricity and oxidation resistance were enhanced significantly compared to the CFO feedstock and it could be suitable to be used as an alternative to SN500 mineral base oil. The analytical data on biodegradability showed that OLCFO could be a highly biodegradable substance. In this study, the use of raw materials as waste, by-product, and product as a mineral-based oil substitute, environmental friendliness, together with the application of advantaged stirring technique based on cavitation techniques have brought many green characteristics to the process. So, it can be envisaged that the synthesis of OLCFO from CFF, performed in the cavitation reactor will develop sustainably.

Acknowledgement: We acknowledgement the support of time and facility from Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for this study.

Funding information: This research was funded by Ho Chi Minh City University of Technology (HCMUT), VNU-HCM under grant number BK-SDH-2020-1585017.

Author contributions: Hong Tran Thi: writing – original draft, editing, completing the manuscript; Quyen Huynh: review – methodology, analysis method; Tan Phan Minh: review and editing – methodology and content of the manuscript.

Conflict of interest: Authors state no conflict of interest.

References

[1] Bart JCJ, Gucciardi E, Cavallaro S. Biolubricants. Cambridge: Woodhead Publishing Limited; 2013.

[2] Jolanta I, Justyna C, Rafał G, Michał S, Julia W, Iwona S, et al. Designing lubricating properties of vegetable base oils. Molecules. 2018;23:1–11. doi: 10.3390/molecules23082025.

[3] Azwar M, Faisal M, Rashid N, Rahimi M. Physical property modification of vegetable oil as bio-lubricant using ZDDP. ARPN J Eng Appl Sci. 2015;10:6525–8.

[4] Hameed TM, Khudhair MM, Abdulridha LA. Study the effect of friendly environmental materials addition on viscosity index and pour point of engine diesel lubricating oil. J Al-Nahrain Univ Sci. 2018;21:105–11. doi: 10.22401/jnus.21.3.12.

[5] Alang MB, Ndikontar MK, Sani YM, Ndifon PT. Synthesis and characterisation of a biolubricant from cameroon palm Kernel seed oil using a locally produced base catalyst from plantain peelings. Green Sustain Chem. 2018;8:275–87. doi: 10.4236/gsc.2018.83018.

[6] Heikal EK, Elmelawy MS, Khalil SA, Elbasuny NM. Manufacturing of environment friendly biolubricants from vegetable oils. Egypt J Pet. 2017;26:53–9. doi: 10.1016/j.ejpe.2016.03.003.

[7] Ait Aissa K, Zheng JL, Estel L, Leveneur S. Thermal stability of epoxidized and carbonated vegetable oils. Org Process Res Dev. 2016;20:948–53. doi: 10.1021/acs.oprd.6b00040.

[8] Turco R, Tesser R, Vitiello R, Russo V, Andini S, Di Serio M. Synthesis of biolubricant basestocks from epoxidized soybean oil. Catalysts. 2017;7:1–11. doi: 10.3390/catal7100309.

[9] Thuy NT, Duc VM, Liem NT. Synthesis of bio-polyols by epoxide ring opening reaction with H_2O as a reagent. Vietnam J Chem. 2017;55:411–6. doi: 10.15625/2525-2321.2017-00482.

[10] Sharma RV, Somidi AKR, Dalai AK. Preparation and properties evaluation of biolubricants derived from canola oil and canola biodiesel. J Agric Food Chem. 2015;63:3235–42. doi: 10.1021/jf505825k.

[11] Somidi AKR, Das U, Dalai AK. One-pot synthesis of canola oil based biolubricants catalyzed by MoO_3/Al_2O_3 and process optimization study. Chem Eng J. 2016;293:259–72. doi: 10.1016/j.cej.2016.02.076.

[12] Thi HT, Minh TN, Quy-Diem D, Kim TN, Kim TDT, Minh TP. Green chemistry for the preparation of bio-based oil from catfish fat using a cavitation system. Rasayan J Chem. 2019;12:2058–64. doi: 10.31788/RJC.2019.1245289.

[13] Thi HT, Minh TN, Thanh NC, Nguyen N, Thanh T, Van HP. Synthesis bio-based oil from catfish fat, blending bio-lubricant. ARPN J Eng Appl Sci. 2021;16:837–44.

[14] Musmarra D, Prisciandaro M, Capocelli M, Karatza D, Iovino P, Canzano S, et al. Degradation of ibuprofen by hydrodynamic cavitation: reaction pathways and effect of operational parameters. Ultrason Sonochem. 2016;29:76–83. doi: 10.1016/j.ultsonch.2015.09.002.

[15] Ebrahimi B, He G, Tang Y, Franchek M, Liu D, Pickett J, et al. Characterization of high-pressure cavitating flow through a thick orifice plate in a pipe of constant cross section. Int J Therm Sci. 2017;114:229–40. doi: 10.1016/j.ijthermalsci.2017.01.001.

[16] Fatt L, Yusup S, Rashid A, Aziz A, Bokhari A. Intensification of biodiesel synthesis from waste cooking oil (Palm Olein) in a Hydrodynamic cavitation reactor, the effect of operating parameters on methyl ester conversion 2015;95:235–40. doi: 10.1016/j.cep.2015.06.018.

[17] Khan IA, Prasad N, Pal A, Yadav AK. Efficient production of biodiesel from Cannabis sativa oil using intensified transesterification (hydrodynamic cavitation) method. Energy Sources A Recover Util Env Eff. 2020;42:2461–70. doi: 10.1080/15567036.2019.1607946.

[18] Thi HT, Minh TN, Do QD, Thanh NC, Minh TP. Applying cavitation technique to optimize the synthesis of catfish epoxide oil, a biological compound with high chemical activity. Rasayan J Chem. 2021;14:194–203. doi: 10.31788/RJC.2021.1415926.

[19] Tran HT, Truong PV, Phan TM. Preparation bio-lubricant from Catfishfat. ARPN J Eng Appl Sci. 2018;13:9707–14.

[20] Wang Z, Kuninobu Y, Kanai M. Palladium-catalyzed oxirane-opening reaction with arenes via C–H bond activation. J Am Chem Soc. 2015;137:6140–3. doi: 10.1021/jacs.5b02435.

[21] Hong LK, Yusop RM, Salih N, Salimon J. Optimization of the in situ epoxidation of linoleic acid of Jatropha curcas oil with performic acid. Malaysian J Anal Sci. 2015;19:144–54.

[22] Wang J, Liu Y, Zhou Z, Fu Y, Chang J. Epoxidation of soybean oil catalyzed by deep eutectic solvents based on the choline chloride-carboxylic acid bifunctional catalytic system. Ind Eng Chem Res. 2017;56:8224–34. doi: 10.1021/acs.iecr.7b01677.

[23] Bargole S, George S, Kumar Saharan V. Improved rate of transesterification reaction in biodiesel synthesis using hydrodynamic cavitating devices of high throat perimeter to flow area ratios. Chem Eng Process Process Intensif. 2019;139:1–13. doi: 10.1016/j.cep.2019.03.012.

[24] Silviana S, Anggoro DD, Kumoro AC. Kinetics study of waste cooking oil epoxidation with peroxyacetic acid using acid catalysts. Rasayan J Chem. 2019;12:1369–74. doi: 10.31788/rjc.2019.1235190.

[25] Mistry U, Thakkar K, Kodgire P, Kachhawaha SS. Biodiesel production from castor seeds (Ricinus communis) oil using Hydrodynamic cavitation. In Twelve International Conference on Thermal and Engineering. Gandhinagar: ICTEA; 2019. p. 1–3.

[26] Mohod AV, Gogate PR, Viel G, Firmino P, Giudici R. Intensification of biodiesel production using hydrodynamic cavitation based on high speed homogenizer. Chem Eng J. 2017;316:751–7. doi: 10.1016/j.cej.2017.02.011.

[27] Saboya RMA, Cecilia JA, García-Sancho C, Sales AV, de Luna FMT, Rodríguez-Castellón E, et al. Synthesis of biolubricants by the esterification of free fatty acids from castor oil with branched alcohols using cationic exchange resins as catalysts. Ind Crop Prod. 2017;104:52–61. doi: 10.1016/j.indcrop.2017.04.018.

[28] Choi YY, Baek SR, Kim JI, Choi JW, Hur J, Lee TU, et al. Characteristics and biodegradability of wastewater organic matter in municipal wastewater treatment plants collecting domestic wastewater and industrial discharge. Water (Switz). 2017;9(6):409. doi: 10.3390/w9060409.

[29] Oliveira MVS, Vidal BT, Melo CM, de Miranda RD, Soares CM, Coutinho JAP, et al. (Eco)toxicity and biodegradability of protic ionic liquids. Chemosphere. 2016;147:460–6. doi: 10.1016/j.chemosphere.2015.11.016.

[30] Almutairi M. Method development for evaluating the effectiveness of hydrocarbons on BOD, UBOD and COD removal in oily wastewater. Water Sci Technol. 2020;81:2650–63. doi: 10.2166/wst.2020.324.

[31] Zhang B, Ning D, Yang Y, Van Nostrand JD, Zhou J, Wen X. Biodegradability of wastewater determines microbial assembly mechanisms in full-scale wastewater treatment plants. Water Res. 2020;169:115276. doi: 10.1016/j.watres.2019.115276.