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UTILIZATION OF CATFISH FAT BY-PRODUCTS FOR THE BIOLOGICAL BASE OILS SYNTHESIS

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ABSTRACT

In this work, catfish fat by-product was utilized as feedstock in the synthesis of biological base oils. The study performs the effect of parameters on the reaction yield. 91.2% in (H_2O_2/CH_3COOH/C=C) molar ratio of 4.5/1.5/1.0, the temperature of 50 ^{o}C, and 3 hours reaction time. The yield of the ring-opening reaction of epoxy with acetic anhydride reached at 90.2% in (acetic anhydride/epoxy) molar ratio of 1.5/1.0, the temperature of 95 ^{o}C, and 4.5 hours reaction time. The main functional groups of catfish oil starting material, epoxy catfish oil, and polyester catfish oil final product were identified by FT-IR and ^{1}H-NMR spectral analysis methods. The observed results show that the catfish oil epoxidation reaction with a mixture of H_2O_2 and CH_3COOH and the ring-opening reaction of epoxy with $(CH_3CO)_2O$, H_2SO_4 catalyst has occurred strongly and obtained product of catfish polyester oil could use as an alternative to mineral base oils and an environmentally friendly product.

Keywords: catfish fat, biological base oils, environmental.

INTRODUCTION

The manufacturing of lubricants increases annually on a global scale. In recent years, the need for lubricants has grown in Vietnam and other Southeast Asian nations. Because they almost perfectly satisfy the quality standards of commercial lubricants, mineral base oils are utilized as substrates in the blending of lubricants. Concerns regarding dependence on fossil fuels and environmental contamination brought on by the usage of mineral lubricants were raised, however, by the dearth of crude oil sources and the slow biodegradation of mineral base oils. These problems have prompted researchers to look at mineral lubricant substitutes. Vegetable oils could be thought of as a viable substitute feedstock for the manufacturing of bio-based oils or bio-lubricants due to characteristics like high viscosity, renewable resources, and simple biodegradability production [1].

Vegetable oils were either utilized directly as bio-based oils or blended with additives and used as bio-lubricants. In the study by Azhari *et al.*, bio-lubricants were blended with canola oil, corn oil, and zinc dialkyl dithiophosphate anti-friction and anti-wear additives [2]. By adding 6 (weight percent) castor oil to the formulation of engine lubricants, Hameed and his colleagues conducted a bio-lubricant formula [3].

A simple and easy technique was employing vegetable oils directly as bio-based or bio-lubricants. However, when blending bio-lubricants, only a limited proportion of vegetable oils are substituted for the mineral base oils. Therefore, the method's effectiveness was similarly low, particularly regarding its effect on the environment. This could be a result of the high molecular weight triglyceride chemical structure of vegetable oils, which contain several impurities, unsaturated compounds, and free fatty acids, making it difficult for some of their properties, such as pour point temperature, viscosity index, and oxidative stability, to meet the technical specifications of mineral base oils. Therefore, a solution is required to enhance the qualities of vegetable oils so they can be utilized instead of mineral oils.

According to several research, the chemical conversion of vegetable oils into mineral oil substitutes was successful. Which, the epoxy-opening epoxide ring method and the two-stage transesterification approach have been utilized more frequently [4]. Jatropha oil was transformed into bio-based oil in a study by E.K. Heikal *et al.* The authors used two esterification reactions with a potassium hydroxide catalyst. These reactions involved the reaction of the oil with methanol to produce methyl esters and the reaction of methyl esters with trimethylolpropane to produce polyester oil. The viscosity index and pour point temperature of polyester oil products were improved, and they could now satisfy ISO VG46 grade of industrial oil technical requirements[5]. Similarly, M.B. Alang *et al.*, O. Ocholi *et al.*, created bio-based oil from original feedstocks including sesame seed oil with mono alcohol and trimethylolpropane and Cameroon palm kernel oil. The authors used two esterification processes and a base catalyst. These research results demonstrated the usage of ester oil products as bio-lubricants. However, their oxidative stability was not increased since the trans-esterification process involved reactions in the carboxyl group of fatty acids in the triglycerides, delaying the conversion of nearly double bonds (C=C) in unsaturated molecules. In consideration of this, only low-grade

lubricants like T-46 and ISO-VG22 hydraulic oil may be made using vegetable ester oils [6,7].

The chemical method used to synthesize bio-lubricants from vegetable oils could be a conversion process consisting of 2 consecutive reactions, which are the epoxidation of unsaturated components of vegetable oils and the ring-opening reaction of epoxy with a nucleophilic agent to form the esterified vegetable oils. Abdullah *et al,* and Salimon et al, synthesized bio-based oil via an epoxidation reaction of oleic acid, linoleic acid (main unsaturated ingredients in vegetable oils), and an opening reaction of the epoxy ring with oleic acid. The pour point temperature, lubricity, and oxidative stability of esterified oil products had improved [8,9]. Similarly, Sharma *et al*., modified the properties of canola oil by reactions of epoxidation and ring opening of canola epoxy with acetic anhydride. The canola polyester oil product had a low pour point temperature, high oxidation stability, and excellent lubricity so it could be used as a bio-lubricant [10].

It can be said that obtained polyester oil product from the conversion of vegetable oil through 2 consecutive reactions of epoxidation and epoxy ring opening has not only improved the oxidative stability and the lubricating properties, reduced pour point temperature, but also it could be as biodegradable. So the suitable effective method in the synthesis of bio-based oils from vegetable oils can be the epoxy-opening epoxide ring with acetic anhydride. However, there was a concern that these studies for bio-base oil synthesis via the epoxy-opening epoxide ring method used edible oils as feedstock. This could cause an edible oil shortage in food consumption. This problem may be solved when the bio-base oil synthesis uses by-products of other manufacturing processes as feedstock, provided that its characteristics can be as similar to edible oils.

Vietnam is one of the largest exporters of catfish meat in the Southeast Asia region. In recent years, the export catfish meat processing industry has been developing strongly and catfish fat can as a waste/by-product in large quantities[11]. According to the results in other previous studies showed that catfish fat has characteristic properties similar to edible oils [12, 13]. So, it can be said that catfish fat can be one of the most potential alternative sources for feedstock in the synthesis of bio-based oils. This would not only produce an environmentally friendly product but also reduce dependence on petroleum materials and reduce production costs.

This study focuses on the synthesis of polyester oil from catfish fat through the chemical process involving 2 consecutive reactions, which are epoxidation and opening of the epoxy ring. The influence of parameters on the reaction yield was investigated and discussed and the spectral analysis methods including FT-IR and NMR have been used to identify the main functional groups of samples. Polyester catfish oil can be forecasted to have a high ability to replace mineral base oils and is an environmentally friendly product. It can be said that the polyester catfish oil synthesis would contribute to reducing

the dependence on crude oil sources and minimize the negative impacts on the environment.

EXPERIMENTAL PART

Material and Methods

Material

Raw catfish fat (semi-solid) was bought from AGIFISH, An Giang province, Viet Nam. Catfish oil (liquid) (Iodine value of 69 gIod/100g) obtained from the catfish fat refining processes. Sodium hydroperoxide (AR, 30 wt.%), glacial acetic acid (AR, 99 %), sulfuric acid (AR, 99 %), and anhydrous sodium sulfate (AR, 99%) were purchased from the Viet Nam Chemsol company. Anhydride acetic ($\geq$ 99.5 (v.%)) and pure chemicals, indicators used in the titration analysis purchased from Sigma-Aldrich.

Method

Synthesis of polyester catfish oil

Catfish oil feedstock reparation

Catfish fat has been pre-treated through a filtration process using a plate-frame filter device with a filter cloth with a pore diameter of 30 µm to remove mechanical impurities. Next, the catfish fat was degummed to remove the hydrophilic impurities, plastic, etc. Finally, the liquid of catfish fat called catfish oil was stored in a dark container, to avoid direct sunlight and used as materials for the synthesis of catfish polyester oil [12].

Epoxidation reaction of catfish oil

Epoxidation reaction of catfish oil (CFO) with sodium hydro peroxide, acetic acid (H_2O_2, CH_3COOH), and H_2SO_4 catalyst was carried out in a glass flask with a magnetic stirrer. Parameters were investigated as molar ratio of (hydro peroxide/acetic acid/unsaturated compounds of catfish oil) ($H_2O_2/CH_3COOH/C=C$) (1.5/1.0/1.0 – 7.0/2.0/1.0) temperature (30 °C - 65 °C) and time (1 h - 5 h). The weight percent epoxide catfish oil (EP) was determined according to the ASTM D1652 [10,14].

Ring-opening reaction of epoxy catfish oil

The epoxidized catfish oil epoxy ring opening reaction with (CH_3CO)$_2O$ agent, H_2SO_4 catalyst was conducted under the support of a magnetic stirrer. Parameters of reaction were studied as (acetic anhydride/epoxy) molar ratio in the range of (1/1 - 2/1), the temperature in (75 °C - 110 °C), and time in (2.5 h – 6.5 h). The ester value of polyester catfish oil product (ES) was tested according to the ASTM D5558-95 [10,14].

Analytical method

The characterization of samples was analyzed by FT-IR, ^{1}H-NMR, ^{13}C-NMR analysis. The FT-IR analysis was performed in the FT/IR Agilent, model - 4700 type A,

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serial number C019561788. The ^{1}H-NMR, and ^{13}C-NMR analyses were carried out in the NMR Bruker 500 MHz, CDCl$_3$ solvent.

Calculation

The yield (Y) of epoxidation of catfish oil was calculated by Equation (1)

$$Y = \frac{O_{exp}}{O_{theo}} \times 100\% \tag{1}$$

Where:

O_{exp}, O_{theo}: experimental and theoretical mass percent of oxirane oxygen

O_{exp} was calculated by Equation (2)

$$O_{theo} = \frac{IV_0/2A_I}{100 + (IV_0/2A_I) \times A_O} \times A_O \tag{2}$$

IV_0 (gIod/100g): iodine value (IV) of catfish oil
A_I = 126,9 (đvC), A_O = 16 (đvC): Molecular Mass of Iodine, Oxygen

O_{exp} is calculated according to the ASTM D1652 standard
The efficiency of the epoxy ring opening reaction with (CH$_3$CO)$_2$O was calculated by Equation (3) by Equation (1)

$$Y = \frac{EV_{exp}}{EV_{theo}} \times 100\% \tag{3}$$

Where:

EV_{exp}, EV_{theo}: experimental and theoretical ester values of polyester catfish oil (mgKOH/g)

According to ASTM D1652, ASTM D5558-95, EV_{theo} and EV_{exp} were calculated by Equation (4), and Equation (5) as follows:

$$EV_{theo} = \frac{10E}{43} \times 28.05 \tag{4}$$

$$EV_{exp} = \frac{V_0 - V_1}{w} \times C \times 28.05 \tag{5}$$

Where:
E (wt.%):   epoxy mass percent of catfish epoxy oil
V_0 (mL):   Titration of blank
V_1 (mL):   Titration of sample (mL)
C (N):   Equivalent concentration of HCl acid
W (g):   Sample weight

RESULTS AND DISCUSSIONS

Catfish Oil Epoxidation Reaction

Effect of reactant consumption
From the iodine value (IV) of catfish oil feedstock, the number of moles of the C=C double bond of the catfish oil was calculated and converted to a value of 1.0. Experiments investigating the influence of the mole ratio

H$_2$O$_2$/CH$_3$COOH/C=C (Hy/Ac) on the yield of epoxidation reaction were performed at 45 °C in the time of 1 hour to 5 hours and the results are presented in Figure-1 following:
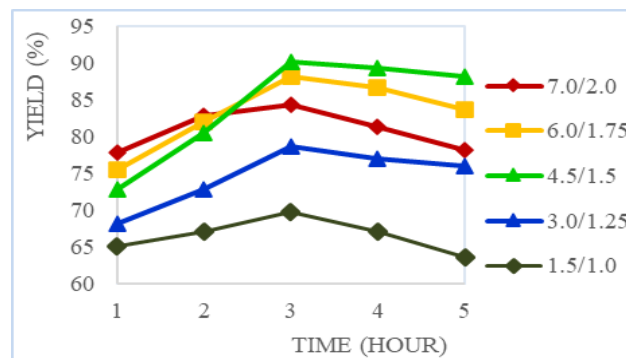
Figure-1. The affection of molar ratio (H$_2$O$_2$/CH$_3$COOH on the efficiency of epoxidation reaction.

Data in Figure-1 shows that the reaction yield increased in the increasing molar ratio of (H$_2$O$_2$/CH$_3$COOH) (Hy/Ac) in the range of (1.5/1.0 - 3.0/1.25). The molar ratio of (Hy/Ac) increased to 4.5/1.5, the yield increased gradually in a period of 1 to 3 hours and then it decreased slightly. Similarly, when the molar ratio (Hy/Ac) was increased to 6/1.75 and 7/2.0, the yield gradually increased in the time of (1 - 3 hours) and then it also tended to decrease slightly and the maximum yield in these 2 cases was lower than the maximum yield in the case of the reaction carried out with a molar ratio of (Hy/Ac) of (4.5/1.5). In investigated cases, the value of the molar ratio of (H$_2$O$_2$/CH$_3$COOH) was (4.5/1.5) giving the maximum yield of epoxidation reaction for a reaction time of 3 hours.

This can be explained by the fact that the reaction to create acetic peracid is reversible and occurred with a theoretical molar ratio of (Hy/Ac) of (1.0/1.0) but H$_2$O$_2$ could be decomposed in sulfuric acid, so the actual reaction could be occurred in loading reactants [15, 16]. When the number of used reactants of H$_2$O$_2$ and CH$_3$COOH increased, the formation of acetic peracid could be increased, leading to an increase the reactivity. So the efficiency of the epoxidation reaction increased. But the molar ratio of (Hy/Ac) reached 6.0/1.75 and 7.0/2.0, the amount of acetic peracid could be excessed and a small amount of epoxy catfish oil product participated in the ring-opening reaction with these excessed reactants. L.K.Hong *et al*, have also explained similarly in the study of the epoxidation reaction of the unsaturated component in jatropha oil. The results showed that the yield increased when the molar ratio of H$_2$O$_2$/unsaturation components and HCOOH/ unsaturation components increased in the range of (3.0/1.0 - 9.0/1.0) and (0.5/1.0 - 2.0/1.0) but the yield decreased with the ratio of reactants exceeded the above thresholds[17]. J.Wang *et al* presented a similar result for the epoxidation of soybean oil with a performic acid agent.

The authors confirmed that, because soybean oil was highly viscous, the reaction was more favorable when the reaction used the amount of reactant corresponding to the H_2O_2/HCOOH molar ratio >1[18].

Effect of Reaction Temperature

The investigating experiments on the effect of temperature on the rate of epoxidation reaction were carried out at the molar ratio of H_2O_2/CH_3COOH of 4.5/1.5 for 1-5 hours and results are shown in Figure-2 following:
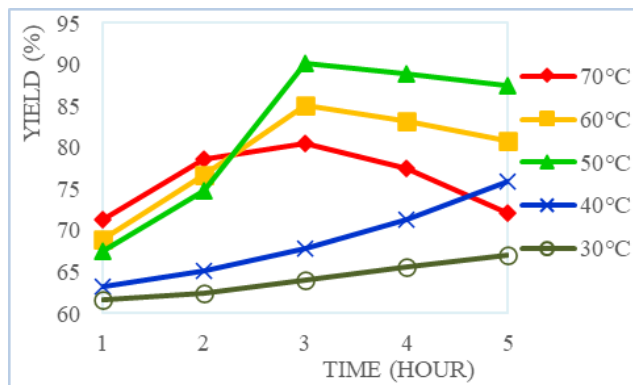
**Figure-2.** The effect of temperature on the yield of catfish oil epoxydation reaction.

Data in Figure-2 shows that temperature has affected strongly the reaction yield. When the temperature increased from 30 °C to 50 °C, the reaction yield increased gradually during the survey period (1 - 5 hours). But when the temperature increased to higher levels, 60 °C, and 70 °C, the yield decreased even though the reaction time was extended to 5 hours.

This may be explained that the increase in temperature reduced the viscosity of the catfish oil and this resulted in easier diffusion of the reactants into the catfish oil, increasing the phase contact surface between the reactants, improving heat transfer and mass transfer in the reaction mixture, thus increasing the reaction rate. The reaction yield was drastically reduced when performing the reaction at high temperature and extending the reaction time to 4 hours and 5 hours This could be because the reaction proceeded under high temperature, the long reaction time, and the H_2SO_4 acid catalysis, an amount of H_2O_2 could be decomposed. This leads to the CH_3COOOH forming reaction occurring incompletely, an excess of CH_3COOH that has not participated in the reaction and this excess CH_3COOH may have caused a side reaction to cleavage the epoxy ring of the product, reducing response performance. [16].

This could be consistent with the research results of L. K. Hong and colleagues on the jatropha epoxidation reaction with performic acid. The authors demonstrated that the reaction efficiency increased with increasing temperature between 35 °C and 45 °C, and the temperature increase higher than 45 °C led to epoxy ring cleavage of the product, reducing the yield reaction [17]. In the study of J. Wang and colleagues on the epoxidation reaction of

soybean oil with performic acid as an agent, authors also explained that the reaction yield was low when performing the reaction at low temperature because of the high viscosity of soybean oil, which could lead to a slower mass transfer rate, but when the reaction was performed at too high temperature, the reaction yield did not increase but tend to decrease due to the decomposition of the hydroperoxide agent and the epoxy ring cleavage side reaction of epoxy oil products[18]. Similarly, the results of the study by S. Silviana and colleagues on the kinetics of the waste cooking oil epoxidation reaction with agent as mixture of H2O2 and CH3COOH, H2SO4 acid catalysts showed that, at fixed reaction conditions, the reaction yield increased rapidly with the increase of temperature from 40 °C to 50 °C but when the reaction temperature exceeded the threshold of 50 °C, epoxy ring-opening side reaction occurred and this reduced the yield of epoxidation reaction [19].

Thus, it can be concluded that, in the surveyed cases, the epoxidation yield of catfish oil reached the highest value at 91.2% with the reaction temperature of 50oC, the molar ratio of H2O2/CH3COOH of 4.5 /1.5 for 3 hours. Increasing the temperature to 70 °C and prolonging the reaction time to 5 hours, the epoxidation reaction may not take place completely because an amount of H_2O_2 may be decomposed causing a shortage of the reactant. Furthermore, the epoxy ring cleavage side effect of the product may have occurred causing a significant reduction in the reaction yield to only 72.1%. The obtained results from the catfish oil epoxidation reaction are also elucidated via the results of FT-IR and ^{1}H-NMR, ^{13}C-NMR analysis, presented in Figure-3, Figure-4 and Figure-5 with coding samples including catfish oil material (CFO), catfish epoxy oil obtained from reaction carried out at high temperature (70 °C), longed time to 5 hours ((EP(overheat)) and catfish epoxy oil obtained from the reaction carried out at the optimal reaction conditions (EP(optimal)).
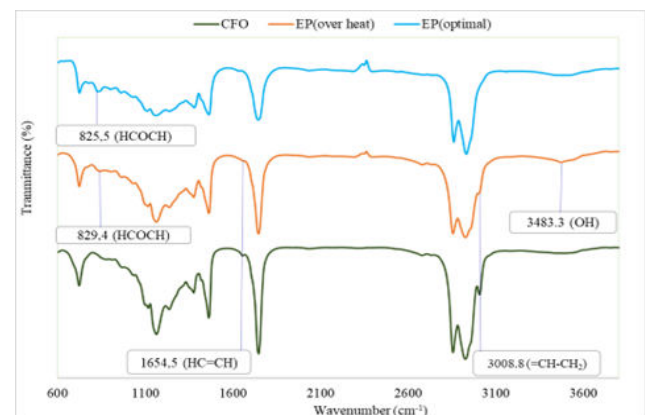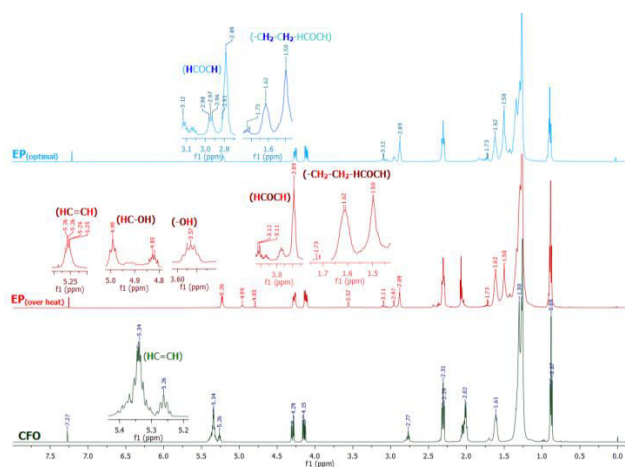

Figure-3. FT-IR spectrum of CFO, EP(over heat), and EP(optimal).

The FT-IR spectra of CFO described the characteristic peaks for the main functional groups of catfish oil. Compared with the FT-IT spectrum of the CFO, the FT-IR spectrum of the EP(over heat) appeared a

characteristic new peak of the epoxy ring at 829.4 cm^{-1}. However, there was a weak appearance of peaks at 1654.5 cm^{-1}3008.8 cm^{-1} and 3483.3 cm^{-1} that characterize the double bonds of carbon with carbon and hydroxyl group (OH). This has shown that at high-temperature conditions (70 ^{o}C) and long reaction time (5 hours), the catfish oil epoxidation reaction occurred incompletely, there was still an undisclosed amount of carbon-carbon double bonds and epoxy ring-opening side reaction with CH_3COOH, H_2O occurred, reducing the reaction yield. Similarly, the FT-IR spectrum of EP$_{(optimal)}$ appeared as a characteristic peak of the epoxy group (825.5 cm^{-1}) but characteristic peaks for the =C–H group (1654.5 cm^{-1} and 3008.8 cm^{-1}) were not found. This could indicate that most of the C=C double bonds of catfish oil have been epoxidized. The results of FT-IR spectrum analysis were also reported similarly in other studies on the epoxidation reaction of vegetable oils [17,18].

The ^{1}H-NMR spectra of the samples are presented in Figure-4 following as:

Figure-4. ^{1}H-NMR spectrum of CFO, EP$_{(overheat)}$ and EP$_{(optimal)}$.

In Figure-4, characteristic peaks for the main functional groups of catfish oil appeared in the ^{1}H-NMR spectrum of CFO. In particular, the protons of CH_3, and CH_2 of the R chains were confirmed by the appearance of peaks at (0.87 ppm - 0.89 ppm) and (1.26 ppm - 1.30 ppm). The protons of β-CH_2, α-CH_2 of the R chain bound to the ester group (-COO) were verified by the presence of peaks at (1,610 ppm - 2.02 ppm), (2.29 ppm - 2.32 ppm). The appearance of signal peaks at (4.13 ppm - 4.16 ppm), (4.28 ppm - 4.31 ppm) could be specific to the protons of CH, CH_2 of the glycerol wires. The presence of chemical signals at 7.27 ppm determined the protonation of the solvent $CHCl_3$. The ^{1}H-NMR spectrum of CFO clearly describes the occurring signals (5.26 ppm - 5.34 ppm), which confirmed the characteristic protons of the olefin unsaturated component (HC = CH).

The characteristic protons of the main functional groups of catfish oil appeared in the ^{1}H-NMR spectrum of EP$_{(optimal)}$. No appearance of the characteristic proton peak for the double bond was found (HC = CH) and instead a strong appearance of new peaks at (2.89 ppm - 3.11 ppm), (1.48 ppm - 1.5 ppm), (1.62 ppm - 1.72 ppm), which were characterized for the protons of epoxy ring (HCOCH) and β-CH_2, α-CH_2 bound to the epoxy ring in the structure of epoxy catfish oil. Similarly, the specific protons for the main functional groups of catfish oil appeared in the ^{1}H-NMR spectrum of EP$_{(over\ heat)}$. However, the weak appearance of the proton-specific peak for the double bond (HC = CH) and the proton-specific peak of the hydroxyl group (OH) also appeared at 3.57 ppm and 4.99 pmm. This showed that the catfish oil epoxidation reaction did not take place completely, there was still an amount of carbon-carbon double bond and the epoxy ring-opening side reaction with H_2O occurred, reducing the reaction efficiency.

The results of the ^{1}H-NMR spectrum analysis of the samples were consistent with the results of the FT-IR spectrum analysis of the samples presented in the previous section. The results of the ^{1}H-NMR spectrum analysis of the samples in this study could be also explained similarly to results in other studies on the epoxidation of vegetable oils [17,18].

Ring-Opening Reaction of Epoxy Catfish Oil

The catfish oil epoxidation reaction was carried out in optimal conditions and epoxy catfish oils (EP) as a feedstock for epoxy ring-opening reaction with acetic anhydride agent. EP determined the weight percent epoxide (E) according to the ASTM D1652 and E reached at 8.92 (wt.%).

Experiments to investigate the effect of the molar ratio of acetic anhydride/epoxy (An/Ep) on the yield of epoxy ring-opening reaction were performed at the temperature of 85°C in the time from 2.5 hours to 6.5 hours and the results are displayed in Figure-5.
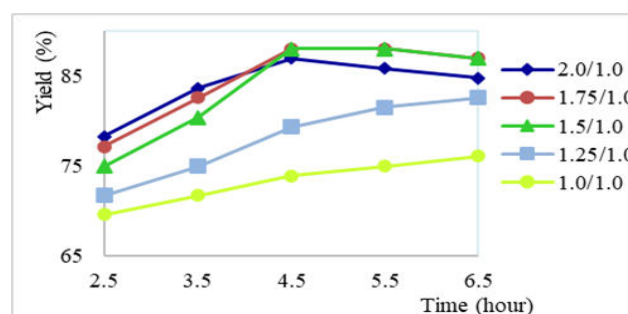
Figure-5. Effect of molar ratio of acetic anhydride/epoxy ring on the yield of ring-opening reaction.

The data in Figure-5 shows that when the molar ratio of acetic anhydride/epoxy (An/Ep) increased from 1.0/1.0 to 1.25/1.0 with the increase in the time in the range of 2.5 hours - 6.5 hours, epoxy oil ring-opening reaction yield increased accordingly. As the molar ratio of (An/Ep) increased to values of 1.5/1.0, 1.75/1.0, and 2.0/1.0, the reaction yield gradually increased in the time of 2.5 h to 4.5 h, and then the yield decreased slightly when the reaction time was extended to 5.5 hours and 6.5 hours. In the investigated cases, the reaction yield reached

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the highest value of 88% when the reaction used the molar ratio (An/Ep) of 1.5/1.0, 85oC for 4.5 hours.

According to reaction theory, the valid ratio of (An/Ep) in epoxy oil ring-opening reaction with acetic anhydride nucleophile is 1/1. The results of some other studies have determined that vegetable epoxy oils are compounds with a large molecular weight and high viscosity [17,18,19], so during the ring-opening reaction of vegetable epoxy oil with large-volume nucleophiles. For small molecules weight such as carboxylic acids and short-chain derivatives, diffusion of agents into the epoxy oil phase could be difficult. Therefore, to obtain a high yield of plant epoxy oil ring-opening reaction, the reaction used the molar ratio of ring-opening agent/epoxy > 1.0/1.0.

In this study, catfish epoxy oil had high molecular weight and high viscosity. So, the reaction used a molar ratio of (An/Ep) at 1.0/1.0, and the yield of the reaction was low. The reaction yield increased when using the molar ratio of the reactant increased to 1.25/1.0 and 1.5/1.0. The slight decrease in the reaction yield when increasing the molar ratio of (An/Ep) to 1.75/1.0 and 2.0/1.0 could be because in these cases an excess of acetic anhydride and the excess reactant could be mixed into the product. This could lead to difficulty in the purification step of products, so the yield decreased slightly [10]. In the study of T.T.H. Le for the oxirane ring-opening reaction, the PTSA acid catalyst, the surveying results of the influence of parameters showed similar trends. At other reaction conditions fixed, the yield increased gradually when the mass ratio of acetic anhydride/epoxy oil increased from 1.0/1.0 to 1.5/1.0 and the yield decreased slightly with the continued increase in this ratio to a value of 1.75/1.0[20]. The effect of loading reactants on the conversion of the ring-opening reaction of epoxide was also presented similarly by A.K.R. Somidi et al When the molar ratio of acetic anhydride/epoxy increased from 1.0/1.0 to 2.0/1.0, the reaction yield increased rapidly. The yield was almost constant and tended to decrease slightly when the molar ratio of acetic anhydride/epoxy increased to 3.0/1.0 [21].

Effect of Temperature Reaction

The effect of temperature on the yield of the epoxy ring-opening reaction was carried out at a molar ratio of (An/Ep) of (1.5/1.0), in the time of (2.5 h ÷ 6.5 h) and the results are shown in Figure-6 below:
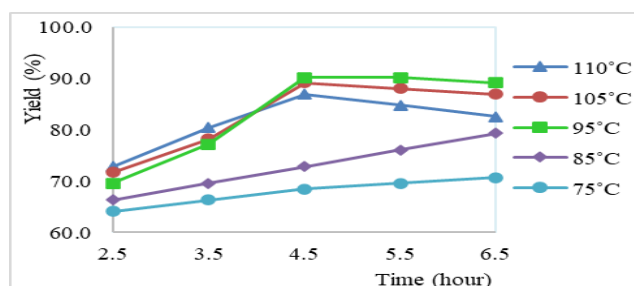

Figure-6. Effect of temperature on the yield of the ring-opening reaction.

The observed data in Figure-6 demonstrated that temperature could be one of the main influencing parameters of this reaction. In the case of 4.5 hours, when the temperature increased to 75 $^{\circ}$C, 85 $^{\circ}$C, the reaction yield increased from 68.5 % to 72.8 % and the highest yield of 90.2 % was obtained at 95 $^{\circ}$C. However, the temperature increased to 105 $^{\circ}$C, and 110 $^{\circ}$C, and the yield of the reaction decreased clearly (89.1 %, 87.0 %). This may be explained that in high temperatures, the viscosity of reactants was low, the mixing of reactants was better and the rate of heat transfer and mass transfer in the reaction mixture could be increased. This results in increased reactivity. The decrease in reaction yield when performing the reaction at higher temperatures, 105 $^{\circ}$C, and 110 $^{\circ}$C may be because the high temperature (110 $^{\circ}$C) has reduced the viscosity of the catfish epoxy oil a lot, so when the reaction time was prolonged to 6.5 hours, the emulsion will become emulsified. These could make it difficult to separate and purity the product or at 110 $^{\circ}$C and the presence of sulfuric acid catalysts, the amount of epoxidized catfish oil feedstock could be decomposed before participating in the ring-opening reaction with acetic anhydride agent, so the reaction yield decreased[10]. In the study of A.K.R. Somidi *et al*, the effect of temperature on the conversion of the epoxide ring opening reaction with acetic anhydride tended to be similar to the results in this study [21].

The optimal conditions of the ring-opening reaction of epoxy catfish oil were determined. These were the molar ratio of acetic anhydride/epoxy of 1.5/1, reaction temperature of 95 $^{\circ}$C, reaction time of 4.5 hours, and the highest yield of reaction reached at 90.2 %. These results are also confirmed by FT-IR, ^{1}H-NMR analysis results of epoxy catfish oil feedstock (EP) and product of polyester catfish oil (ES). The results are detailed in Figure-7, Figure-8 respectively.
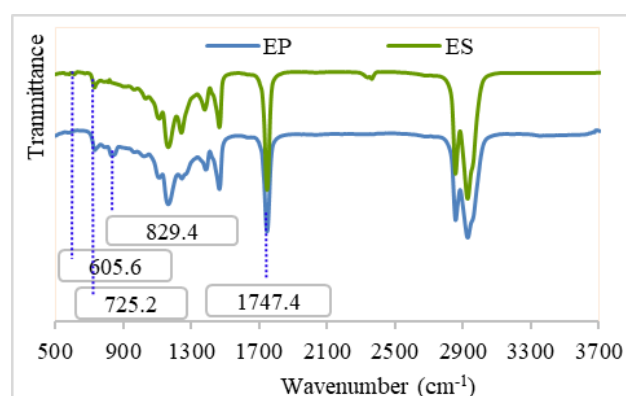

Figure-7. FT-IR spectrum of EP and ES.

As seen in Figure-7, the FT-IR spectra of epoxy catfish oil (EP) show characteristic peaks for its major functional groups. The appearing peaks at 1376.9 cm^{-1}, 1464.7 cm^{-1}and 2852.2 cm^{-1}, 2919.7 cm^{-1}could verify the presence of CH_3, CH_2 and CH groups. The CO and C=O groups of the ester functional group (COO-) were determined through the occurring peaks at 1112.7 cm^{-1},

1160.9 $cm^{-1,}$ and 725.2 cm^{-1}, 1747.4 cm^{-1}. The FT-IR spectrum of EP appeared clearly peak at 829.4 cm^{-1}, which could be typical for epoxy ring (HCOCH).

Similarly, the FT-IR spectra of the polyester catfish oil (ES) appeared most of the characteristic peaks for the main functional groups in the structure of EP and did not find the appearance of the specific peak for the epoxy ring instead the strong appearance of the new peak at 605.6 cm^{-1}, which could characterize for the ester functional group (COO-) and the strengthening of the peaks at 725.2 $cm^{-1}$and 1747.4 cm^{-1} could prove the occurrence of the methylester group (CH_3COO-) in the structure of ES. This showed that the epoxy ring-opening reaction with acetic anhydride agent occurred thoroughly and the results of FT-IR spectral analysis were consistent with the obtained results in the survey on the influence of parameters on the reactivity of epoxy ring opening reaction with acetic anhydride agent.

The results of FT-IR spectrum analysis in this study were similarly explained in other studies on the ring-opening reaction of epoxy vegetable oils with acetic anhydride agents [10,20,21].

Results of ^{1}H-NMR Analysis

The ^{1}H-NMR spectrum of epoxy catfish oil (EP) and polyester catfish oil (ES) is shown in Figure-8.
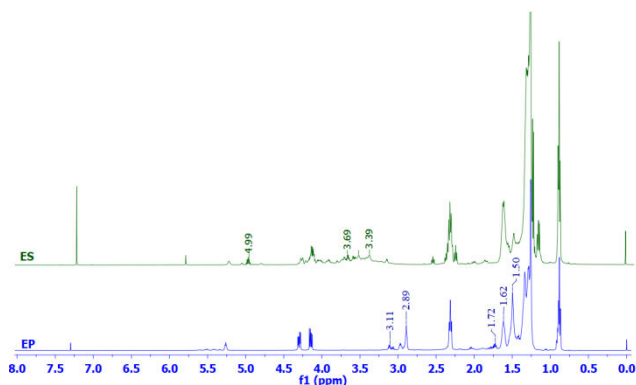

Figure-8. ^{1}H-NMR spectrum of EP and ES.

In Figure-8, characteristic peaks for contained protons in the main functional groups of epoxy catfish oil appeared in the ^{1}H-NMR spectrum of EP. In particular, the CH_3 and CH_2 protons of the R chains were confirmed by the appearance of peaks at (0.87 ppm - 0.89 ppm) and (1.26 ppm - 1.30 ppm). The protons of β-CH_2, α-CH_2 of the R chains bound to the ester group (COO-) were verified by the presence of peaks at (1.610 ppm - 2.02 ppm), (2.29 ppm - 2.32 ppm). The appearance of signal peaks at (4.13 ppm - 4.16 ppm), (4.28 ppm - 4.31 ppm) could be specific to the protons of CH, CH_2 of the glycerol wires. The presence of chemical signals at 7.27 ppm determined the protonation of the solvent $CHCl_3$. The ^{1}H-NMR spectrum of EP clearly shows signals at (2.89 ppm - 3.11 ppm), (1.5 ppm - 1.72 ppm), which could be characteristic for protons of epoxy ring (HCOCH) and β-CH_2, α-CH_2 bound to epoxy ring in the structure of EP.

Most of the characteristic protons of the major functional groups of epoxy catfish oil appeared in the ^{1}H-NMR spectrum of polyester catfish oil (ES) and no characteristic proton peaks for epoxy rings instead there was a strong appearance of new peaks at (3.39-3.69 ppm) and 4.99 ppm, which could characterize for protons of the methylester group (CH_3COO-) and protons bound to the methyl ester group (HC-$COOCH_3$).

The results of the ^{1}H-NMR spectrum analysis of samples were consistent with the results of the FT-IR spectrum analysis of samples presented in the previous section. The obtained results also confirmed that the ring-opening reaction of epoxy catfish oil with acetic anhydride, and sulfuric catalyst acid occurred completely at the established reaction conditions.

CONCLUSIONS

This study has successfully synthesized the polyester catfish oil from catfish fat by-products. The appropriate conditions of reactions were established. The results of FT-IR, ^{1}H-NMR spectrum analysis showed that polyester catfish oil is a high molecular weight compound and has the main chemical structure of triglyceride chains, branching with methylester groups. Therefore, it can be concluded that polyester catfish oil can not only be used to replace mineral base oils but also is a highly biodegradable compound.

REFERENCES

[1] J. Ilowska, J. Chrobak, R. Grabowski, M. Szmatola, J. Woch, I. Szwach, J. Drabik, M. Trzos, R. Kozdrach and M. Wrona. 2018. Molecules. 23, 8, 1.

[2] M. A. b. Azhari, M. F. b. Tamar, N. R. b. M. Nuri and M. R. b. Yusoff. 2015. ARPN Journal of Engineering and Applied Sciences 10, 15, 6525.

[3] T. M. Hameed, M. M. Khudhair and L. A. Abdulridha. 2018. Journal of Al-Nahrain University. 21, 3, 105.

[4] G. Karmakar, P. Ghosh and B. Sharma. 2017. Lubricants. 5, 4, 44.

[5] E. K. Heikal, M. S. Elmelawy, S. A. Khalil and N. M. Elbasuny. 2017. Egyptian Journal of Petroleum. 26, 1, 53.

[6] M. B. Alang, M. K. Ndikontar, Y. M. Sani and P. T. Ndifon. 2018. Green and Sustainable Chemistry. 8, 3, 275.

[7] O. Ocholi, M. Menkiti, M. Auta and I. Ezemagu. 2018. Egyptian Journal of Petroleum. 27, 3, 265.

www.arpnjournals.com

[8] B. M. Abdullah, S. I. Zubairi, H. Z. Huri, N. Hairunisa, E. Yousif and R. C. Basu. 2016. PloS one. 11, 3, 1.

[9] J. Salimon, B. M. Abdullah and N. Salih. 2016. Arabian Journal of Chemistry. 9, 2, S1053.

[10] R. V. Sharma, A. K. Somidi and A. K. Dalai. 2015. Journal of agricultural and food chemistry. 63, 12, 3235.

[11] Viet N. Pham, Van H. Nguyen, Thi Lan A. Tran and Si T. Trang. 2019. Waste and Biomass Valorization. 11, 4195.

[12] T. H. Tran, M. T. Nguyen, Q.-D. Do, K. T. Nguyen, T. K. T. Dao and M. T. Phan. 2019. Rasayan Journal of Chemistry. 12, 4, 2058.

[13] T. H. Tran, M. T. Nguyen, Q.-D. Do, T. N. Cao and M. T. Phan. 2021. Rasayan Journal of Chemistry. 14, 1, 194.

[14] V. B. Borugadda and V. V. Goud. 2015. Energy Science & Engineering. 3, 4, 371.

[15] M. R. Janković, S. a. V. Sinadinović-Fišer and O. M. Govedarica. 2014. Industrial and Engineering Chemistry Research. 53, 22, 9357.

[16] O. I. Slavgorodskaya, V. G. Bondaletov, A. A. Lyapkov, J. P. Ustimenko and D. Vervacke. 2014. Procedia Chemistry. 10, 555.

[17] L. K. Hong, R. Yusop, N. Salih and J. Salimon. 2015. The Malaysian Journal of Analytical Sciences. 19, 1, 144.

[18] J. Wang, Y. Liu, Z. Zhou, Y. Fu and J. Chang. 2015. Industrial and Engineering Chemistry Research. 56, 29, 8224.

[19] S. Silviana, D. D. Anggoro and A. C. Kumoro. 2019. Rasayan Journal of Chemistry. 12, 3, 1369.

[20] T. T. H. Le and H. H. Nguyen. 2015. Vietnam Journal of Chemistry. 53, 210.

[21] A. K. R. Somidi, U. Das and A. K. Dalai. 2016. Chemical Engineering Journal. 293, 259.