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Catfish Fat Modification for Biobased Oils and Biolubricants

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This study used catfish fat by-products to synthesize bio-based oils and develop a bio-lubricant formula. FT-IR and ^{1}H-NMR spectroscopic analysis identified the main functional groups of materials and products. The TGA method and Rancimat tests were used to determine the samples' thermal and oxidation stability. The biodegradability of the samples was evaluated through tests to assess chemical oxidation demand (COD) and biological oxidation demand (BOD). Thermal stability and oxidation stability of polyol and polyester catfish oil products are higher than those of catfish fat material a lot, reaching values of 239 °C, 251 °C and 8.4 h, 12.6 h, equivalent to with SN150, and SN500 mineral base oils. Based on the SAE20W50 engine lubricant formulation, bio-lubricant formulations have been established with the replacement of mineral base oils by polyol oil and polyester catfish oil at values of 30 wt% and 40 wt%, but they not only have equivalent features compared to SAE20W50 lubricants but also have higher biodegradability, the BOD_5/COD ratio value of the bio-lubricant blends reached at 0.49, 0.38 higher than that of mineral lubricant, as 0.23. Catfish fat by-product, which is readily available, and abundant, was used in the manufacturing of environmentally friendly products, that will develop sustainably.

1. Introduction

Because vegetable oils are renewable and may be used to replace mineral lubricants and they can be ecologically friendly compounds, so bio-based oils and bio-lubricants based on vegetable oils were considered a perfect option (Iłowska et al., 2018). Refining vegetable oils to create bio-based oils doesn't have to be complicated to do. Because refined vegetable oils have a low antioxidant capacity and poor operation at low temperatures, their ability to substitute mineral-based oils or mineral lubricants is restricted. The properties of vegetable oils may be better if their structure and chemical composition are altered. Due to their high unsaturated fatty acid content, vegetable oils are a good candidate for the epoxidation process that forms the oxirane ring compound. Additionally, due to their high chemical activity, they can readily react with a variety of nucleophiles to form more complex structural products, like polyester or polyols, which can enhance their capacity to function at low temperatures as well as their oxidation stability. To produce polyol compounds, which enhanced oxidation stability and cold-weather operation, Turco and associates investigated the chemical transformation of soybean oil by responses of epoxidation and epoxy oil's ring-opening (Turco et al., 2017). According to research findings from Mohd's group, the polyester palm oil product of reactions with palm oil epoxidation and opening oxirane ring with oleic acid has greatly improved its oxidation stability and capacity to function at low temperatures (Mohd et al., 2017). In additional research, canola oil was epoxidized and the epoxy ring was opened with acetic anhydride to produce polyester canola oil products. These products outperform canola oil material in terms of oxidation stability and cold temperature performance in addition to having superior lubricating qualities (Sharma et al., 2015).

Vegetable oils such as palm oil, sunflower oil, peanut oil, and soybean oil can bring many great benefits to human health. So, the usage of vegetable oils as raw materials for bio-based oil manufacturing can cause vegetable oil shortages in the food processing sector. Vietnam is one of the largest countries in the world in the field of processing and exporting catfish fillet meat. In processing, fillet meat products account for about (50–70

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wt.%) of catfish, the remainder is by-products and catfish fat makes up the largest portion. Information from the Ministry of Agriculture and Rural Development of Vietnam shows that in 2016 and 2020, the catfish harvest reached more than 1.25 - 1.9.10^6 t and it can be forecast that the catfish farming and processing industry for export will grow strongly shortly (Vietnam, 2014). Therefore, Vietnam can provide a stable and plenty of catfish fat up to 400.10^3 t/y.

In previously published work, the liquid portion of catfish oil received from the catfish fat via filtration and then chemically transformed into a bio-lubricant (Tran et al., 2019). In another study, catfish oil obtained from catfish fat filtration was converted into polyester oil, which was used to replace SN500 mineral base oil in preparing bio-lubricants (Tran et al., 2021). Although these studies did not use the maximum amount of catfish fat by-products or the lubricant formulation was not developed flexibly, the results showed that catfish fat's physicochemical characteristics and chemical makeup are similar in comparison to vegetable oil. Therefore, catfish fat may be utilized as a feedstock to make bio-based oils.

This paper reported on the chemical transformation of catfish fat, which modifies the molecular structure of the fat through the processes of epoxidation and oxirane ring-opening reactions, enhancing the basic properties of the products and used as biological base oils. Formulas for blending bio-lubricants from bio-based oil based on catfish fat were developed to evaluate the ability to replace mineral-based oils with bio-based oils.

2. Materials and Methods

2.1 Materials

The AGIFISH Company in Angiang province, Vietnam, provided the catfish fat (CFF). The chemicals used in the research such as glacial acetic acid 99.99 vol%, hydroperoxide (30 wt.%), *iso*-propanol (86 vol%), and sulfuric acid (99.9 vol%), originated from Vietnam. Acetic anhydride, 99.99 vol% (laboratory pure chemical). Mineral base oil SN150, SN500, and some additives originated from ExxonMobil Company, Singapore. To ensure the stability of CFF materials during storage, CFF was filtered to remove mechanical impurities, and hydration with water to separate hydrophilic impurities after that, CFF was stored in dark containers, away from direct sunlight (Varga et al., 2018).

2.2 Chemical conversion of catfish fat

Catfish fat was epoxidized with a mixture of (H_2O_2 and CH_3COOH) to obtain epoxy catfish oil. Next, the opening epoxy ring with iso-propanol and acetic anhydride to obtain polyol, and polyester catfish oil (OLCFO, ESCFO). Reactions were carried out at fixed conditions and using a sulfuric acid catalyst (Phan and Lam, 2023).

2.3 Blending bio-lubricant

Building a formula for blending SAE20W50 lubricant from SN150, and SN500 mineral base oil and additives. Based on the SAE 20W-50 lubricant formula, bio-lubricant blends were created by replacing mineral base oils with OLCFO, and ESCFO. Analyze the typical properties of blends and choose the optimal bio-lubricant blending formula.

2.4 Method of Detection

Nuclear magnetic resonance spectroscopy (^{1}H-NMR) and infrared spectroscopy (FT-IR) were used to identify the main functional groups of samples. The antioxidant ability was analyzed by thermogravimetric analysis (TGA) and RANCIMAT methods. The biodegradable properties of samples were evaluated through the value of biological oxidation demand and chemical oxidation demand. The properties were determined according to TCVN and ASTM standards.

2.5 Calculation formula

The catfish epoxidation reaction yield, Y (%) was computed as shown in Eq(1) (Tran et al., 2022):

$$Y = \frac{T}{A} \times 100\ \% \qquad (1)$$

Where T and A are the theoretical and actual weight percent of oxirane (wt.%). T was calculated as shown in Eq(2):

$$T = \frac{IV/2MW_I}{100 + (IV/2MW_I) \times MW_O} \times MW_O \qquad (2)$$

Where IV – catfish fats iodine value (gIod/100 g). MW_I and MW_O are molecular weights of iodine and oxygen (ĐVC).

A was calculated according to the ASTM D1652 standard.
The opening epoxy ring reaction with iso-propanol yield, Y (%) was computed as shown in Eq(3):

$$Y = \frac{TH}{AH} \times 100\ \% \tag{3}$$

Where TH, AH – the theoretical and actual hydroxyl number (mg KOH. g^{-1}). TH was calculated as shown in Eq(4):

$$TH = \frac{10 \times E}{43} \times 56.1 \tag{4}$$

AH was calculated according to ASTM D4274-99 standard
The opening epoxy ring reaction with ethanoic anhydride yield, Y (%) was computed as shown in Eq(5) (Tran et al., 2022):

$$Y = \frac{TE}{AE} \times 100\ \% \tag{5}$$

Where TE and AE are the theoretical and actual ester numbers (mg KOH. g^{-1}). TE was calculated as shown in Eq(6):

$$TE = \frac{10\ x\ O}{43} \times 28.05 \tag{6}$$

Where O is the weight percent of oxirane (wt.%). AE was computed according to ASTM D5558-95 standard

3. Results and Discussion

3.1. Characterization of materials and products

FT-IR spectra displayed the main functional groups of materials and products as shown in Figure 1. The distinctive peaks in the catfish fat (CFF) material's FT-IR spectrum represented the basic functional groups in the CFF structure. Peaks appeared at 725.2 cm^{-1}, and 1,743.6 cm^{-1} verifying the presence of the functional groups of esters (O-C=O); the double bonds of carbon to carbon (HC=CH, =CH-CH$_2$) were confirmed by the appearing peaks at 1,654.9 cm^{-1} and 3,008.9 cm^{-1}. In the FT-IR spectrum of epoxy catfish oil (EPCFO), the absence of peaks at 1,654.9 cm^{-1}, and 3,008.9 cm^{-1} and the appearance of a new peak at 840.9 cm^{-1} proves that the unsaturated bonds of carbon to carbon in CFF have been converted into the epoxy ring groups (HCOCH). Polyol catfish oil's (OLCFO) FT-IR spectra did not appear during the vibration at 840.93 cm^{-1} and the new peak appeared at 3,448.6 cm^{-1} showing that the epoxy ring groups have been converted into the hydroxyl (OH) groups. So, the presence of OH groups in the OLCFO structure is verified. FT-IR analysis results of another study also demonstrated the presence of oxirane rings in epoxidized soybean oil products through the appearance of a pick at 849 cm^{-1} or the appearance of ring-opening side reactions. epoxy created an OH bond through the pick appearing at 3,426 cm^{-1} (Phan et al., 2023). The typical peak for the epoxy ring did not appear in the spectrum of the polyester catfish oil (ESCFO). The simultaneous appearance of a new peak at 609.5 cm^{-1} with the strengthening of peaks at 725.2 cm^{-1} and 1,743.6 cm^{-1} in the FT-IR spectra of ESCFO demonstrates the presence of ester structures in the product. These are also consistent with the FT-IR analysis results in the previous study. The peaks at 831 cm^{-1} identified the epoxy rings in the structures of epoxy canola oil. The methyl ester in canola polyester oil was confirmed through peaks at 725 cm^{-1}, 604 cm^{-1}, and the strengthening of the peak at 1,750 cm^{-1} (Sharma et al., 2015).

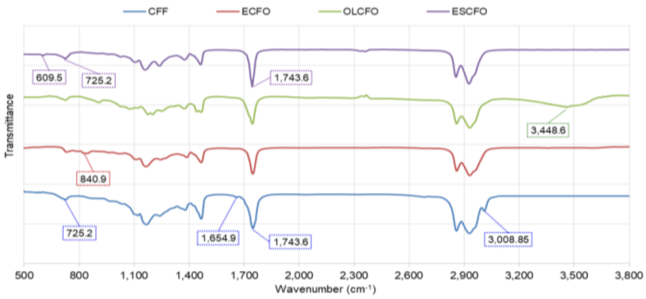

Figure 1: FT-IR spectra of catfish fat, epoxy catfish oil, and polyol, polyester catfish oil.

As illustrated in Figure 2, the typical peaks for the samples' protons in the ^{1}H-NMR spectra were found. The ^{1}H-NMR spectrum of catfish fat (CFF) appeared signals at (5.26 - 5.34 ppm), confirming the protons of the unsaturated component (HC = CH) in CFF. The ^{1}H-NMR spectra of epoxy catfish oil (EPCFO) did not show the typical signals for the proton of the unsaturated component; instead, new peaks at (2.89 - 3.12 ppm) and (1.5 - 1.73 ppm) described the epoxy ring's protons (HCOCH), as well as β-CH_2, α-CH_2 connected to the *oxirane* ring in the EPCFO molecule. The group's hydroxyl proton (-OH) in the structure of polyol catfish oil (OLCFO) was defined by the new peaks at (3.39 - 3.53 ppm) in the ^{1}H-NMR spectra of OLCFO, which replaced the typical peaks of the oxirane group's protons that appeared in the ^{1}H-NMR spectra of EPCFO. These are consistent with the previous research. In the ^{1}H-NMR spectrum of epoxidized soybean oil, the appearance of chemical oscillations at 2.7-3.1 ppm represented the protonation of the oxirane ring, and when performing the epoxy ring-opening reaction with alcohol, the ^{1}H-NMR spectrum of the products did not find this chemical shift (Turco et al., 2017). The typical signals for the proton of the epoxy ring were absent from the ^{1}H-NMR spectrum of polyester catfish oil (ESCFO). Furthermore, the additional emergence of peaks at 3.39–3.69 ppm and 4.99 ppm in ^{1}H-NMR spectra of ESCFO demonstrate the methyl ester (CH_3COO-) group's protons being present in the ESCFO structure. Similar discussions were also found in another study. Protons of unsaturated bond HC=CH and epoxy rings in the structure of canola oil and epoxy canola oil were identified by peaks at (5.2 – 5.4 ppm), and (2.7 – 3.1 ppm). After performing the oxirane opening reaction by acetic anhydride, the methyl ester (CH_3COO-) group's protons in canola polyester oil were confirmed through peaks at 3.7 ppm (Sharma et al., 2015).

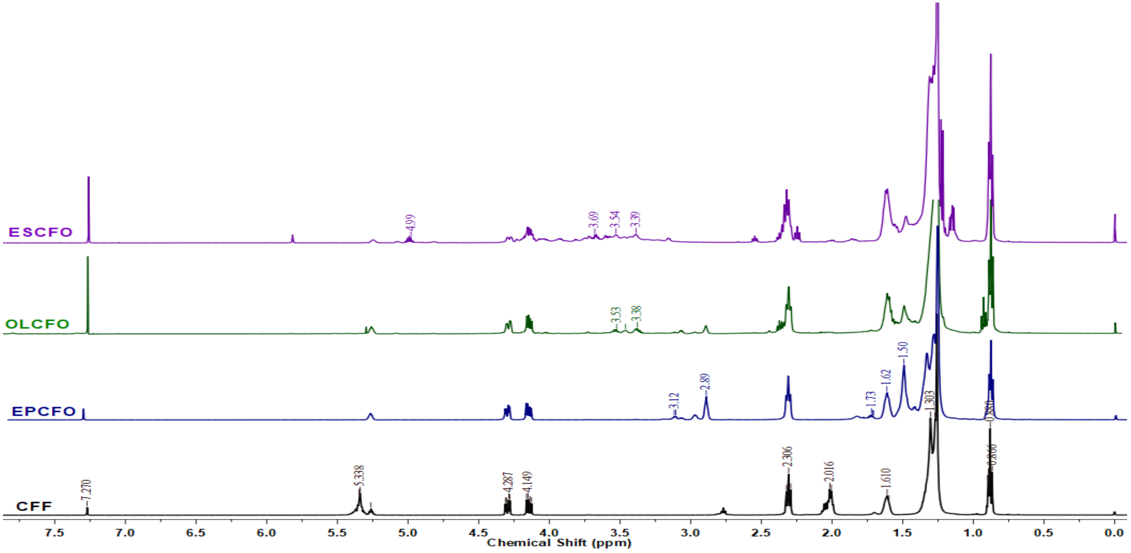

Figure 2: ^{1}H-NMR spectra of catfish fat, epoxy catfish oil, and polyol, polyester catfish oil.

The formation of EPCFO, OLCFO, and ESCFO products through reactions of catfish fat epoxidation and oxirane opening using agents such as ethanoic anhydride and iso-propanol are confirmed by the reliable findings of ^{1}H-NMR and FT-IR analysis.

3.1 Blending bio-lubricant

The SAE20W50 lubricant blend was built as 85.93 wt.% mineral base oils (SN150, SN500) and 14.07 wt.% additives. Based on the SAE20W50 formula, bio-lubricant blends with replacement of mixture of (SN150, SN500) by polyol, polyester catfish oil (OLCFO, ESCFO) at weight percentage of 20, 30, 40 and 50 coded as 20OLBioLub, 30OLBioLub, 40OLBioLub, 50OLBioLub and 20ESBioLub, 30OLBioLub, 40ESBioLub, 50ESBioLub.

3.2.1. Characteristic properties of materials and products

Typical properties of catfish fat (CFF), polyol, polyester catfish oil (OLCFO, ESCFO), mineral base oils SN150, SN500, SAE20W50 lubricant, and bio-lubricant blends are determined. The results are presented in Table 1. The typical properties of polyol and polyester catfish oil products (OLCFO, ESCFO) have improved a lot compared to starting material catfish fat (CFF). These products and all bio-lubricant blends had a higher density, flash point, kinematic viscosity (KV), and viscosity index (VI) than SN150, SN500 base oils, and SAE 20W50 lubricants. This can be because catfish fat is a high molecular compound whose main chemical structure is triglyceride chains, so it requires a lot of energy to burn and has high viscosity. The superiority in KV, and VI of OLCFO, and ESCFO may be because, after the conversion process, catfish fat structure was improved with the formation of new bonds of hydroxyl (OH), methyl ester (CH_3COO) functional groups with the carbon chain R of triglyceride ester, increasing the saturation of OLCFO, ESCFO and with this new structure of them also created hydrogen bonds intramolecular between OH/ $OOCCH_3$ groups. This has increased significantly the KV and VI for OLCFO and ESCFO products (Mohd and Salimon, 2017). The R alkyl carbon chains of the triglyceride chains in the OLCFO, ESCFO structure were branched with (-OH)/(CH_3COO-) groups creating a surrounding steric barrier for individual molecules, preventing self-stacking and hindering the crystallization of molecules. This has created low pour points for OLCFO and ESCFO, -5 °C, 2 °C compared to 20 °C of CFF. Furthermore, with the new structure of triglyceride with increased saturation and branching with hydroxyl, isopropyl, and methyl ester groups, bringing high oxidation stability to OLCFO and ESCFO products, 8.4 h, 12.6 h, and 234 °C, 249 °C compared to CFF materials only at 0.2 h and 174 °C.

Table 1: The characteristic properties of samples

Samples	Density (g/cm^3)	Flashpoint (°C)	Kinematic viscosity (CST)		Viscosity index	Pour point (°C)	Thermal stability (°C)	Oxidative stability (h)
			40 °C	100 °C				
SN150	0.88	201	39	6	95.91	-6	265.5	≥ 30
SN500	0.889	230	96.03	11.59	109.07	-6	258.5	≥ 29.3
CFF	0.916	251	95.26	11.30	105.2	20	174	≥ 0.2
OLCFO	0.978	255	148.05	18.04	135.6	2	239	≥ 8.4
ESCFO	0.996	262	156.04	19.58	144.18	-5	251	≥ 12.6
SAE20W50	0.900	230	166.24	19.67	136.25	-20	302	≥ 31.7
20OLBioLub	0.921	234	170.83	20.32	138.64	-18	284	28.5
30OLBioLub	0.924	240	174.14	20.92	141.63	-16	270	26.2
40OLBioLub	0.925	246	178.03	21.52	144.01	-13	253	22.6
50OLBioLub	0.926	250	182.01	22.32	147.92	-10	231	18.2
20ESBioLub	0.922	240	171.04	20.41	139.33	-20	291	29.5
30ESBioLub	0.925	245	176.12	21.44	144.78	-18	282	28.4
40ESBioLub	0.927	251	180.32	22.62	151.74	-16	268	27
50ESBioLub	0.930	255	184.02	23.82	158.77	-12	250	25.4
Analytical method	ASTM D1298	ASTM D92	ASTM D445		ASTM D2270	ASTM D97	TGA	RANCIMAT

In the previous study, the authors explained that the product of the reaction of epoxidation of soybean oil and epoxy ring opening with 2-butanol alcohol has the most branched structure so it had the highest viscosity, about 600 mm^2.s^{-1} (Turco et al., 2017). In other research, the bio-lubricants synthesized from canola oil via epoxidation and the reaction of epoxy with ethanoic anhydride to open its rings that have low pour points and high kinematic viscosity compared to the starting material canola oil (Sharma et al., 2015) SN150 and SN500 are produced from crude oil, so their chemical composition is paraffinic, naphthene, aromatics, and hybrid forms, so SN150 and SN500 have a lower pour point and higher oxidative stability than OLCFO and ESCFO, but this difference is not large. Furthermore, in the bio-lubricant formula from OLCFO and ESCFO, an additive of pour point depressant and anti-oxidation was added, which completely overcomes this problem and the data in Table 1 have proven this, out of 8 bio-lubricant blends, up to 5 blends have operated in cold conditions and oxidation stability equivalent to SAE20W50 lubricant, as 20OLBioLub, 30OLBioLub and 20ESBioLub, 30ESBioLub, 40ESBioLub. To replace mineral base oils in the greatest amount, bio-lubricant blending formulas have been established with the replacement of mineral base oils by polyol, and polyester catfish oil as 30 wt.% and 40 wt.%.

3.2.2 Biodegradability

The chemical oxidation demand (COD) and biological oxidation demand (BOD_5) are determined to evaluate the biodegradability of samples, and their results are displayed in Figure 3.

As the data presented in Figure 3 shows, SN150, SN500 mineral base oil, and SAE20W50 mineral lubricant have BOD_5/COD ratio values in the range of (0.15 - 0.23), lower than that of all polyol oil, polyester catfish oil (OLCFO, ESCFO), and bio-lubricant (30OLBioLub, 40ESBioLub). This can indicate that OLCFO, ESCFO and 30OLBioLub, 40ESBioLub bio-lubricants have much higher biodegradability than SN150, SN500 mineral base oil, and SAE20W50 mineral lubricants. This can be because hydrocarbon components of SN150, and SN500 are compounds that are not capable of degrading both chemically and biologically. To chemically decompose SN500 can require a large amount of oxygen and hydrocarbons in SN150, SN500 components with long R alkyl chains may cause negative effects on inoculated microorganisms during BOD determination. This results in a low BOD_5/COD ratio value of SN150, and SN500. In a previous study, evaluating the biodegradability of wastewater including dissolved organic contaminants, authors provided a similar explanation (Choi et al., 2017). The other research indicated that the BOD/COD ratios of ionic liquids were low, only 0.01 to 0.02, so their biodegradability was extremely poor and the most non-biodegradable sample was found to have a linear alkyl chain R in its chemical structure (Oliveira and Al., 2016). Therefore, it can be said that mineral-based oils and lubricants are considered hazardous waste. In addition, predictions about the depletion of fossil resources globally as well as their low renewable capacity led to the research and production of bio-based oils, and bio-lubricants are becoming increasingly necessary.

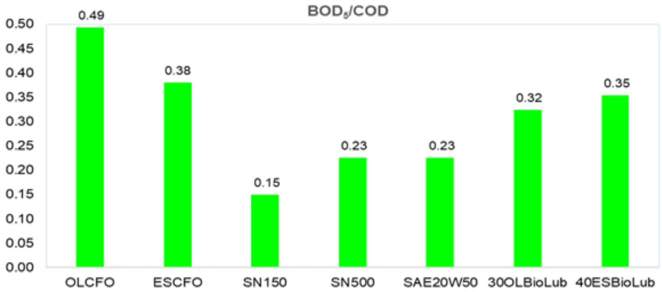

Figure 3: The BOD_5/COD ratio value for bio-base oils, mineral base oils, lubricants, and bio-lubricants

4. Conclusion

The study used catfish fat by-products as a starting material to produce bio-based oils and prepared bio-lubricants. Polyol polyester oil products and bio-lubricants blended from them have not only increased oxidation stability, possibly equivalent to SN150, SN500 mineral base oils, and SAE 20W50 mineral lubricants, but also highly biodegradable. Their values for thermal stability and oxidative stability are 239 °C, 251 °C, and 8.4 h, 12.6 h, and the BOD_5/COD value ranged from (0.32 - 0.49). The results show that polyol, polyester catfish oils, and bio-lubricant blends are not only capable of being used to replace SN150, SN500 mineral base oils, and SAE20W50 lubricants but also environmentally friendly products.

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