

GREEN CHEMISTRY FOR THE PREPARATION OF BIO-BASED OIL FROM CATFISH FAT USING A CAVITATION SYSTEM

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ABSTRACT

This research shows the production of *bio-based* oil in green chemistry. Catfish fat was treated to refined catfish oil by physical processes. Degum of catfish fat was performed in cavitation equipment. The blending *bio-lubricant* from refined catfish oil was prepared base on the SAE 20W50 engine lubricant formula. Thermogravimetric analysis (TGA) was used for determining the oxidation resistance of samples. The biodegradability of samples was studied by COD test and BOD test. The properties of materials and products were determined according to the TCVN standard and ASTM standard. The study finds that the efficiency of degumming of catfish fat was increased considerably in using cavitation technique. The optimal conditions of degumming were temperature at 40 °C and time of 3minutes. After physical treatment, refined catfish oil can be used as *bio-based* oil and the blend of *bio-lubricant* added 20 (wt.%) refined catfish oil can meet the quality standards of SAE20W50 commercial lubricant nearly. Production of *bio-based* oil from catfish fat can develop sustainably because of its green nature as *biological* materials, environmentally friendly products, production processes that limit the use of chemicals and apply green technology.

Keywords: Catfish Fat, Cavitation, *Bio-based* Oil, *Bio-lubricant*

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INTRODUCTION

Nowadays, the demand for lubricants in Vietnam and Asian countries increases. Meanwhile crude oil resources for the production of lubricants and fuels can be limited. On the other hand, waste lubricant is a big problem for the environment. This prompted scientists to consider the alternative and environmentally friendly materials. Vegetable oils can be one of the sources of renewable and *biodegradable* materials. Vegetable oils can be used as *bio-lubricant*, such as palm oil, soybean oil, olive oil¹. However, the oxidative stability and the ability to work at low temperatures of *bio-lubricants* were not high. Because vegetable oils contain certain impurities (gums, waxes)². For the purpose of enhancing the features of *bio-lubricant*, some research mixed vegetable oils with additives. Soybean oil, rapeseed oil, castor oil or high oleic sunflower oil were mixed with improving viscosity additive (ethylene-vinyl acetate copolymer or ethylcellulose) and pour point depressant additive. The tribology properties of product were improved³. In other research, *bio-lubricant* was blended from canola oil, corn oil, and zinc dialkyldithiophosphate (ZDDP) additive. The result presented that, ZDDP was reduced the coefficient of friction for *bio-lubricant*⁴. The vegetable oil processing can be degummed, dewax and dry. Degum of vegetable oils was carried out in water with the extreme agitating system to increase the contact between oil and water because they are two dissolved phases². In order to improve the performance of processing with insoluble phases, scientists have searched for advanced mixing techniques, such as mixing techniques of the

ultrasound power, mixing techniques of the cavitation energy. Preeti B. Subhedar and partner were carried out the heterogeneous reaction of waste cooking oil and methyl acetate in ultrasound device as reactor. Comparing with process carried out in classical stirring reactor, reaction performed on ultrasound equipment was not only decreasing time reaction (25 hours down to 3hours) and loading catalyst (6 wt.% down to 3 wt.%) but also increasing yields (90.1 % rise to 96.1%)⁵. 2014, Ganesh L.Maddikeri et al applied hydrodynamic cavitation as reactor for reaction of waste cooking oil and methyl acetate. The effect of the process on cavitation was higher than that of process performed on ultrasound devices⁶. Hydrodynamic cavitation technique was applied to the synthesis *biodiesel* from palm olein and methanol by Lai fatt Chuah and partner. The conversion of reaction was increased and the time reaction was decreased clearly⁷. So it can say clearly that, in the heterogeneous reaction, it is the higher of the surfacing acreage of contacting phases, the faster of the reaction velocity and the higher of the efficiency. Some of the studies were carried out on vegetable oils materials; neither study on animal fats. Animal fats have a triglyceride structure similar to that of vegetable oils². Viet Nam is one of the world's leading exporter of fillet catfish. Usually, the fillet portion is only accounted about 1/3 of catfish weight. So fat, skin, head, bone are the by-products of catfish processing and fat accounts for the largest share⁸. The time before, the large number of catfish fats were discarded or used for animal food. In Viet Nam, only Sao Mai company produces cooking oils from catfish fat. So the catfish fat is an abundant and available resources in Viet Nam. Beside it, in the catfish fat degum, water and catfish fat was heterogeneous together². So the main technological factor of degum can be the contactation of two phases. So in this study, the agitation base on cavitation technology was applied in degum of catfish fat. It can improve the effect of catfish fat degum.

Generally, the production of *bio-based* oil from catfish fat in this study can develop sustainably because of its green properties such as, available and biological materials, the friendly environmental product, the process of applying new techniques, limiting the use of chemicals.

EXPERIMENTAL

Material

Catfish fat was bought by Phuoc Thanh Agricultural Products Import Export Company Limited. Mineral base oil SN500 and some additives were provided from Petrochemical Hoa Viet Company in Dong Nai province, Viet Nam.

General procedure

The catfish fat processing involved three steps: degum, dewax and dry². Degum was assisted by a cavitation system which is presented in Fig.-1.

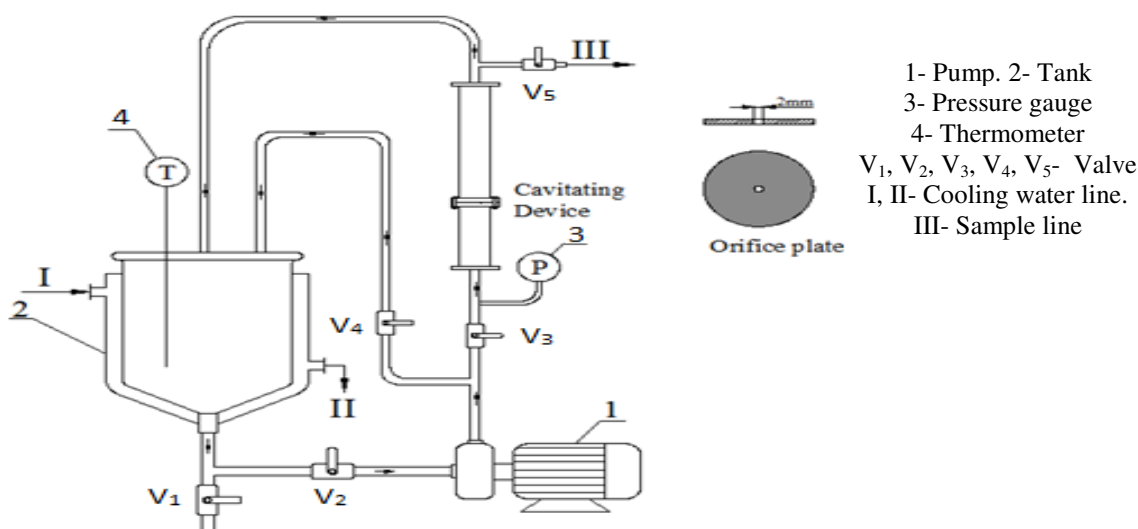


Fig.-1: The Cavitation System

Device Description and Equipment Operation

The cavitation system is equipped with one 2 mm hole on an orifice plate⁷. Materials (water and catfish fat) were fed to the tank -2. The drain valve V_1 and recycle valve are closed, valves V_2 and valve V_3 are opened so the feed can be entered the cavitation device by using the power of pump. The input pressure of feed was measured by the pressure gauge -3. The flow pressure was dropped from the input pressure to normal pressure. By decreasing the pressure, liquid is heated and evaporated to form cavitation in the system. The temperature of system was recorded by using the thermometer -4 and controlled by using a cold / hot water flow from I to II.

Procedure of Catfish Fat Processing

Catfish fat degum was conducted by mixing water with catfish fat in the cavitation system. 5kg catfish fat and water (2wt.%) of catfish fat) was put in to the tank of cavitator. The pressure was set up at 60 psi. The temperature carried out in range of (30 °C ÷ 60 °C). The time carried out in range of (1 minute ÷ 7 minute). When degum finished, mixture settled for 20 hours, valve V_1 was opened to drain the lower layer, collect the top layer as product and the product was determined acid value according to potentiometric titration method - ASTM D664. Next, it is dewax. Dewax equipment is a cone-shaped cylindrical container, made of stainless steel. A mixing system consists of a 2-stage engine and paddle right in the center of the container. The container has an outer cooling jacket shell. The dewax was conducted by the cooling method. 5kg of product of degum was put in to the dewax device. The mechanical stirrer was installed and speed of stirrer was set up at 120 rpm. Ice water and salt was added to the area of the cooling jacket of dewax device. The temperature carried out range of (8 °C ÷ 17 °C). The time carried out in range of (4 hour ÷ 10 hour). When cooling time completely, the mixture was heated to about 20 °C, bottom valve opened to the mixture flowed into the filter by filtered cloth (hole diameter of cloth, $d = 5\mu\text{m}$). The liquid oil passed to the filtration as product, it was determined the pour point according to the ASTM D97. After dewax, catfish oil was dried in vacuum drying equipment (pressure of vacuum was set at 0.1 atm) to receive refined catfish oil (RCFO). RCFO was determined the water content according to the ASTM D95.

Blending Bio-lubricant

Firstly, the engine lubricant SAE20W50 was prepared from the mineral oils (SN500) and additives⁹. From the SAE20W50 lubricant formular, the additives was fixed, the SN500 was replaced by RCFO in range of 10 (wt.%), 20 (wt.%), and 30 (wt.%) and these blends were coded *10BIO*, *20BIO* and *30BIO* respectively. Determination the properties of *bio-lubricant* blends according to the technical standards of commercial lubricants SAE20W50. Finally, the substitutability of *bio-lubricants* for mineral lubricants was assessed base on the results of analytical results.

Detection Method

The potentiometric titration method carried out in 848 Titrino Plus – Metrohm, pH electrode in Industrial University of HCMC, Viet Nam (*IUH*). TGA test was carried out in LINSEIS STA-PT 1600, under nitrogen, temperature in range of (25 °C ÷ 800 °C), heating rate at 10 °C/minute in *Biomass* laboratory of Research Institute for Sustainable Energy, University of Technology, HCMC National, Viet Nam. *Biodegradability* of samples were analyzed by *biochemical* oxygen demand (BOD) test and chemical oxygen demand (COD) test in which, sample of *bio-based* oil was diluted 10 times and samples of mineral base oil, *bio-lubricant* was diluted 100 times in distilled water. The properties of materials and products were determined according to the TCVN standard and ASTM standard in Petroleum Laboratory of Faculty of Chemical Engineering, University of Technology, Viet Nam National University HCMC, in Petroleum Laboratory of Faculty of Chemical Engineering, Industrial University of HCMC, Viet Nam.

RESULTS AND DISCUSSION

Effect of the Time and the Temperature in Degum of Catfish Fat

The results of experiments in degum are shown in Table-1. The data in Table - 1 shows that, the decreasing of acid value with increasing temperature and the time in range of (30 °C ÷ 40 °C) and (1

minute ÷ 3 minute) respectively. The process efficiency was only slightly reduced when the temperature increased from 40 °C to 60 °C and the time increased from 3 minute to 7 minute at the system pressure value of 60 psi. The optimum conditions of degum are the time of 3 minutes and temperature of 40 °C. This can explained that, in conditions of 3 minutes, 40 °C, the contactation of water with hyrophilic compounds occurs fully, so the productivity of degum increased, it reached at the highest level. But the time and the temperature increased continuously, the emulsion of gums and water can be created and the formation of emulsion can be a problem in separation product.

Table-1: Effect of the Time and the Temperature on the Yield of Degum

The time was set at 3 Minute ²	Temperature (°C)	Acid Number (mgKOH/g)	The temperature was set at 50 °C	Time (minute)	Acid Number (mgKOH/g)
	30	2.915		1	2.916
	40	2.890		3	2.890
	50	2.895		5	2.900
	60	2.905		7	2.903

After degum, acid number of catfish fat decreased from 2.920 (mgKOH/g) down to 2.890 (mgKOH/g), decreased 1.03 %. Degum vegetables oils with water in mechanical agitator, the acid number decreased about of 0.1 – 0.4 %, in 40 minute, 60 °C². So the effect of degum catfish fat in the cavitator reactor was better than that of vegetables oils degum in mechanical agitator. The temperature process decreased from 60 °C to 40 °C and more over we see that, performing degum catfish fat in the cavitator reduced the mixing time a lot, from 40 minutes down to 3 minutes (13.33 times). Using cavitator equipment gave better results because of its high mixing ability.

Effect of the Time and the Cooling Temperature on Dewax

The results of experiments in dewax are shown in Table-2. The data in Table-2 presents that, the pour point of product decreased in increasing of the cooling time in range of (4 hour ÷ 8 hour) and decreasing of cooling temperature in range of (18 °C ÷ 12 °C). After dewax, the operation of catfish fat at low temperature can be improved because the pour point of catfish fat decreased from 20 °C to 9 °C¹⁰. When comparing to some *bio-based* oil such as coconut oil, rubber seed oil, the pour point of catfish fat is between the pour point of two bio-based oil, (22 °C ÷ -9 °C)¹¹. After the dewax, catfish oil was dried in vacuum drying cabinet to receive refined catfish oil. Vacuum pressure was set up 0.1 atm and drying time was 4 hour. The water content (v.%) of RCFO was determined by ASTM D95 and the result was 0.01 (v.%).

Table-2: Effect of the Time and the Temperature on the Yield of Dewax

The cooling temperature was set at 10 °C ²	Time (hour)	Pour Point (°C)	The cooling time was set at 8 hour	Temperature (°C)	Pour Point (°C)
	4	15		9	9
	6	12		12	9
	8	9		15	12
	10	9		18	15

Blending Bio-lubricant

The SAE20W50 engine lubricant formular was designed and it can be described in Table-3. Base on the SAE20W50 lubricant formular, *bio-lubricant* blends of 10BIO, 20BIO and 30BIO were prepared. Results of determination the properties of RCFO, SN500, *bio-lubricant* blends and SAE20W50 lubricant blend are shown in Table-4 and Table-5 respectively.

Table-3: Composition of SAE20W50 Engine Lubricant Formular⁹

Mineral Based Oil (wt.%)	Additives %(wt)			
	Improving Viscosity	Improving Alkalinity	Pour Point Depressant	Multifunctional Additives
85.938	6.218	1.854	1.255	4.735

Table-4: The Density, Flash Point, Pour Point, Kinematic Viscosity and Viscosity Index of RCFO, SN500, *Bio-Lubricant* Blends and 20W50 Lubricant Blend

Properties	20W50	10BIO	20BIO	30BIO	SN500	RCFO	Standard Test Method
Density	0.889	0.901	0.907	0.910	0.889	0.913	ASTM D2896
Flash point (°C)	239	249	251	255	239	289	ASTM D92
Pour point (°C)	-20	-16	-12	-8	-6	8	ASTM D97
Kinematic viscosity (cSt)							
- 40 °C	211	202.08	196.05	184	96.03	94.48	ASTM D445
- 100 °C	21.5	22.20	22.42	22.71	11.59	12.03	
Viscosity index	121.84	132.92	138.68	142.69	109.07	119.00	ASTM D2270

The data in Table-4 shows that, some properties such as, density, flash point, kinematic viscosity (at 40 °C, 100 °C) and viscosity index of RCFO were meet the technical requirements of mineral base oil SN500 and these properties of *bio-lubricant* blends were also meet the technical requirements of SAE20W50 lubricant. In the research of M.C Herna'ndez-Cruz and partners, chicken fat was treated by physical refining (gumming, bleached and fractionation). The density, viscosity (mm²/s) at 40 °C, 100 °C and viscosity index of chicken fat after physical refining was 0.899, 37.25, 8.18 and 203.076¹². When compare with other *bio-based* oils from vegetables oils, such as sunflower oil, rubber seed oil and coconut oil, the kinematic viscosity (at 40 °C, 100 °C) and the viscosity index of refined catfish oil was higher¹¹. In the research of Michael Bong Alang and partners, the synthesized biolubricant from Cameroon palm kernel seed had kinematic viscosity (at 40 °C, 100 °C) and viscosity index of 509.80 cSt, 30.80 cSt and 120¹³. Although RCFO has a higher pour point temperature than that of SN500, the climate of Vietnam and Asian countries, the average temperature in winter may be over 10 °C, so RCFO can use as bio-based oil. Beside it, in the blending *bio-lubricants* from RFCO, one note thing was added amount of pour point depressant additive to improve the ability to work at low temperatures of *bio-lubricants*. So it can say that, the ability of RCFO as a *bio-based* oil can be possible.

Some properties of samples such as, total base number (TBN), metal content, carbon conradson, oxidation stability and BOD/COD are shown in Table-5.

Table-5: The TBN, Metal Content, Carbon Conradson, Thermal Oxidation and BOD/COD of RCFO, SN500, *10BIO*, *20BIO*, *30BIO* and 20W50

Properties	SAE 20W50	<i>10BIO</i>	<i>20BIO</i>	<i>30BIO</i>	SN500	RCFO	Standard Test Method
TBN (mgKOH/g)	10.2	8.9	8.1	7.6	-	-	ASTM D2896-15
Metal content (%wt)	0.547	0.434	0.250	0.235	0.451	0.172	ASTM 4628-16
Carbon conradson (%wt)	0.5200	0.4890	0.4792	0.4522	0.4990	0.2090	ASTM D189
Oxidation stability - decomposition temperature (°C)							TGA method
- Onset							
- 5 (wt.%)	261	239	235	231	258.5	200	
- 50 (wt.%)	315	290	284	280	320	294.5	
- 95(wt.%)	426	402	394	400	435	319	
- 99 (wt.%)	511	471	461	468	521	347	
	786	507	594	522	748.5	361	
BOD (mgO ₂ /mL)	161	13.7	13.2	12.8	158	11.5	TCVN 6001-1:2008
COD (mgO ₂ /mL)	712	62.2	43.9	42.7	700	37.4	SMEWW 2012(5220-D)

The change of TBN of samples decreases in order to *10BIO*, *20BIO*, *30BIO*. This can explain that the RCFO can be contacted amount of free fatty acid², it can cause the decreasing the TBN of *bio-lubricant*

blends. In this study, the total base number (TBN) of engine lubricant SAE 20W50 is higher than that of bio-lubricant blends. However, the quality standard of commercial SAE20W50 lubricant specified TBN is min 6.9 (mgKOH/g)¹⁴. So TBN of *bio-lubricant* blended from RCFO can meet the quality requirements of lubricant commercial SAE20W50.

From the metal content and the carbon Conradson content of samples show that, the cleaning burning ability of RCFO and *bio-lubricants* may be higher than that of SN500 mineral base oil and engine lubricant SAE20W50⁹. Because, both metal content and the carbon Conradson content of mineral base oil SN500 and SAE 20W50 lubricant are higher than that of RCFO and *bio-lubricants*. It can explain that mineral base oil was produced from heavy distillation of crude oil, it can contain amount of metal and residue¹⁵.

In the result of TGA test, the decomposition temperature of samples was decreased in order of 10BIO, 20BIO, 30BIO. This can be explained by there refining catfish fat process is simple, it is included filter, degum (hydration), dewax and dry. After physical treatment, some impurities (sediment, gum, wax, and water) were removed but structure of catfish fat was not converted. Therefore, the amount of unsaturated compound contained in RCFO can make the heat resistance of it was not higher than that of mineral oil SN500². However, in blending *bio-lubricant*, adding amount of additives were improved the oxidation-resistant of them significantly. The results of TGA were showed details, the stable thermal of all blends of *bio-lubricants* created at (231 °C ÷ 239 °C). In the range of (280 °C ÷ 290 °C), *bio-lubricant* blends were decomposed by 5 % (wt) and samples bio-lubricant were decomposed 95 % (wt) in range of (461 °C ÷ 471 °C). These temperatures of SAE 20W50 lubricant were 261 °C, 315 °C, and 511 °C. So the difference in temperature decomposition of samples is not too large. When compared with other biobased oils or *bio-lubricants*, thermogram of RCFO and *bio-lubricant* in this study can be similar to those of them. After physical refining, chicken fat started decomposed below 274 °C and it was decomposed up to 98 % (wt) in 489 °C¹³. In the research of Amith Aravin, stable thermal under oxygen environment of *bio-lubricant* from rubber tree seed oil was 250 °C and after 300 °C, decomposition of *bio-lubricant* occurred strongly¹².

The data of the BOD test and COD test of samples in table -5 show that the biodegradability of RCFO and *bio-lubricants* may be easier than that of mineral base oil SN500 and SAE20W50 lubricant. The demand for biochemical oxygen and chemical oxygen in water of mineral base oil SN500 and engine lubricant SAE20W50 are higher than that of RCFO and all blends of *bio-lubricant*¹¹.

From above the results and discussion find that the properties of 20BIO blend can meet nearly the technical requirements of commercial SAE20W50, so it was chosen as the optimal bio-lubricant formulation in this study.

CONCLUSION

The efficiency of the treatment Catfish fat to *bio-based* oil increased significantly in using a cavitation reactor. Efficient of degumming achieved the highest in 3 minutes, 40 °C. The pour point of product of dewaxing decreased from 20 °C down to 8 °C. The analysis results showed that refined catfish oil can be used as *bio-based* oil. Because refining catfish oil can not only meet the properties according to the mineral base oil standards but it is also easily *biodegradable*. The blend of *bio-lubricant* was added 20 (wt.%) of refined catfish oil can use as a replacement SAE20W50 engine lubricant. The potential for the development of *bio-lubricant* production from catfish fat is enormous because of its sustainability.

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