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Trimethylolpropane-based Biolubricant Synthesis from Sweet Almond (*Prunus amygdalus dulcis*) Seed Oil for Use in Automotive Applications

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Abstract: This paper presents the synthesis of a sweet almond oil-based trimethylolpropane biolubricant and the evaluation of its temperature-dependent viscosity properties. The oil was converted into biodiesel by the transesterification process after extraction, refining, and acid-alkaline transesterification. After, biolubricant was produced by further transesterifying biodiesel with trimethylolpropane at 105 °C at a ratio of 3.9:1 for a 60-minute reaction time with a potassium hydroxide catalyst concentration of 1 wt.%. According to the American Standard Test Methods (ASTM), the biolubricant's pour point and index of viscosity were determined to be -4 °C and 267.50, respectively. The measured viscosities were 42.80, 30.18, 21.39, 12.25, and 8.90 cSt. at 30, 40, 60, 80, and 100 °C, demonstrating an inverse relationship between temperature and lubricant viscosity. The difference between the FTIR spectra of the biodiesel and the biolubricant at 1755.74 versus 1743.96 cm^{-1} verifies the ester group. Sweet almond oil has a higher iodine content than unsaturated glycerides (9.52 g of iodine per 100 g of oil sample) and contains 53.478% more unsaturated fatty acids than saturated fatty acids and 71.725% unsaturated fatty acids for biolubricant. Linoleic acid made up the majority of the fatty acids in the oil and synthetic biolubricant, with percentages of 31.44 and 45.93%, respectively. The biolubricant and oil from sweet almonds contained palmitic, linoleic, and oleic acids. The biolubricant has the potential to function as light gear oil for automobiles because its characterization results correlate favorably with the ISO VG-32 criteria.

Keywords: transesterification, biolubricant, biodiesel, sweet almond, trimethylolpropane.

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1. INTRODUCTION

Energy consumption has increased as the world population has grown, as well as the level of industrialization and modernization. Society has changed significantly over the past century and has become increasingly dependent on fossil fuels, causing a gradual exhaustion of fuel supplies to the point where this nonrenewable energy source is expected to be depleted in the medium term, resulting in increased research and development efforts for alternatives to standard fossil fuels for energy. Biolubricant is the sole renewable energy option capable of replacing petroleum in the transportation sector (1). To enhance the management of natural resources and the environment in order to improve people's quality of life and the preservation and utilization of biodiversity, the automobile and machine industries have begun to focus on improving environmentally friendly and energy-efficient technology. Technology geared toward lowpollution fuel combustion and exhaust, as well as vehicle economy, is projected to decrease environmental issues. Lubrication is required in the engine parts to decrease friction between them (2).

Vegetable oil has become a substitute for future fuels and oleochemical needs as a result of growing worldwide concern over climate change. Inevitably and gradually, renewable raw materials will need to replace fossil fuels (petrol, gas, and carbon) in the production of fuel and goods for the chemical industry. Currently, green lubricants manufactured from renewable raw resources are gradually replacing petroleum-based lubricants. Vegetable oils are typically used to create biolubricants because they have great application-related qualities like very low toxicity and high biodegradability, as well as good lubricity, a high viscosity index, and good stability. Factors that have fueled global research and development of lubricants derived from renewable resources in order to promote their widespread use in a variety of applications (3,4). Vegetable oils do, however, have some technical shortcomings that need to be addressed, particularly those pertaining to stability and the constrained range of viscosity values that are now available. Their polar properties and long-chain fatty acids produce a highly durable lubricant layer that reduces wear and friction by having a strong interaction with metallic surfaces (5).

In recent years, a wide range of vegetable oils have been researched to learn more about their features and potential for use as lubricants. A valuable raw resource for the production of eco-friendly lubricants is almond oil, which is derived from sweet almond seeds because of its favorable low-temperature performance and high concentration of olefinic double bonds. Almond oil has been found to be more fluid at lower temperatures than many vegetable oils (5–7). This study's aim was to produce and assess sweet almond oil's lubricating potential and test the effects of the lubricant's viscosity at various temperatures.

2. MATERIALS AND METHODS

Sweet almond fruit seeds were bought at a market in Ilorin, while chemicals and reagents like iso-propyl alcohol (IPA), phenolphthalein, hexane, methanol, sodium hydroxide, sulfuric acid, hydrochloric acid, sodium chloride, charcoal, trimethylolpropane (TMP), potassium hydroxide, glacial acetic acid, thiosulfate, chloroform, and Wiji's reagent were obtained from Sigma-Aldrich.

2.1. Extraction and Refinement of Crude Sweet Almond Oil

The dried sweet almond seeds were sized down using a local grinder. After that, they spent 48 hours submerged in n-hexane at a 2:1 n-hexane to seed ratio. The solution was sieved and distilled to remove the hexane and collect the oil at the bottom of the flask. Each soak bottle underwent two of these steps. The crucial step in the manufacturing of biodiesel is crude oil refinement since the crude oil contains contaminants, such as phosphorus compounds, which can be eliminated by using refining methods described by Mustapha *et al.* (8).

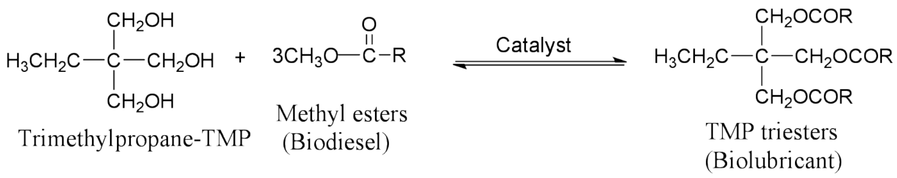
2.2. Trans-esterification

A 20% weight-to-weight methanol and 5% weight-to-weight tetraoxosulfate (iv) were heated and stirred for an hour at 60 to 65 ^{o}C and the stirrer's speed was set to 700 rpm, and refined sweet almond oil (RSAO) samples were taken using a pipette to determine the oil's% FFA.

Afterward, a refluxing condenser, a magnetic stirrer, a thermometer and a two-nec, round-bottomed flask was filled with 100 g of the refined sample, which was weighed and placed on a hot plate. A 1.0 g of potassium hydroxide (KOH) was put in 89.54 mL of methanol and then added to the flask as the catalyst. The reaction products were then allowed to settle for several hours to produce two distinct liquid phases before the flask was eventually removed from the hot-plate. The top portion of sweet almond biodiesel (SABD) was separated from the bottom portion (glycerol) by decantation, and the excess catalyst was then washed away three times with warm water heated to 80 °C until the wash water became clear. Finally, the ester section was dried at 100 °C for 30 minutes.

2.3. Synthesis of Biolubricant

In the biolubricant synthesis, the reaction vessel containing 20 mL of sweet almond methyl ester (SAME) was filled, stirred, and heated to 70 °C. KOH, the catalyst, was measured out and dissolved in 5 mL of methanol. The catalyst mixture was heated for 10 minutes before being added drop by drop to the reaction vessel. A 1.0 g of trimethylolpropane (TMP) was put into the mixture and the reaction lasts for four hours at a temperature of 100 °C (6).



$$H_3CH_2C-C(CH_2OH)_3 + 3CH_3O-C(=O)-R \xrightleftharpoons{Catalyst} H_3CH_2C-C(CH_2OCOR)_3$$

Figure 1: Synthesis of trimethylolpropane-based biolubricant.

2.4. Characterization of Biodiesel and Biolubricant

The American Oil Chemists' Society (9) standard was used to evaluate the oil's qualities, while the ASTM Standard would be used to characterize the biolubricant that was produced (10).

2.5. Determination of temperature on viscosity

The synthetic biolubricant sample's viscosity was determined at 30, 40, 60, 80, and 100 °C. First, the sample was transferred into a 100-mL beaker. The oil sample was heated to the required temperature while being stirred constantly on a heating mantle. The Brookfield® (Synchrolectric Viscometer: RVT) was turned on to measure the viscosity of the sample, and it was left running until a stable reading was recorded.

2.6. Gas Chromatography-Mass Spectrometry (GCMS) Analyses

Utilizing an Agilent 19091J-413: 3516.15684; GCMS analyses were performed to evaluate the fatty acid composition of oil. The carrier gas used was helium in a capillary column (HP-5: 5 5% Phenyl Methyl Siloxane) linked to a GCMS Agilent 5975 inert XL mass selector detector (MSD: 3000 eV) (1 mL/min). The analyte separation was achieved by configuring at 45 °C (hold time: 1.1052 min), increase to 325 °C at 1.5487 mL/min for 0 min, and then finish at 0.57353 mL/min for 2 min. for mass spectrometry (MS Source: maximum temperature of 250 °C, MS Quad: maximum temperature of 150 °C). The quantity was calculated using the total ion corresponding area (TIC) in scan mode (scan range 50-600) throughout the course of 35.5 minutes.

2.7. Fourier Transform Infrared (FTIR) Determinations

The University of Ilorin's FTIR 8400 S Shimadzu spectrometer established the functional unit and the vacuum hydraulically pressed a 0.01 g sample with 0.01 g of KBr creates translucent pellets after homogenization of pellets with pestle and mortar. A detector connected to a computer continued to collect waves while it scanned a sample in the infrared, providing descriptions of the material's spectra. Samples were typically scanned between 600 and 4000 cm^{-1} of absorption. The fundamental spectrum type of the tested sample was determined by the study's findings to be its chemical composition, molecular structure, and particular functional groups.

3. RESULTS AND DISCUSSION

3.1. Sweet Almond's Properties

The values of the refined oil's characteristics are displayed in Table 1. The FFA was 2.82% and the acid value was 5.611 (mg/KOH), respectively, while refined oil has an FFA of 0.738% and an acid value of 1.475 (mg/KOH).

Table 1: Physicochemical properties of refined sweet almond oil.

Test	Refined Oil
Color	Gold
Density (g/cm^3, 40 °C)	0.87± 0.01
Specific gravity (g/mL, 30 °C)	0.89± 0.04
Viscosity (cp, 40 °C)	4.0± 0.03
Kinematic viscosity (cSt)	4.59
Acid value (mg/KOH)	5.6 ± 0.019
Free fatty acid (FFA) (%)	2.82%
Iodine value (I_2/100g)	9.52 ± 0.01

To prevent excessive saponification of the oil, the FFA level of the oil must be decreased via esterification to 1% or less. Refined oil has a viscosity of 4.0 cSt and the success of the oil to biodiesel conversion was demonstrated by the viscosity reduction to 3.8 cSt.

3.2. Biodiesel and biolubricant properties

Viscosity is an important aspect of lubricating oil, as seen in Table 2. It measures the fluid's flow resistance at the proper temperature. At 40 and 100 °C, the biolubricant's viscosity was 42.1 and 8.9 cSt, respectively.

This result is significantly higher than the ISO-specified requirements for the light gear oil viscosity grade, 28.8 and 4.1 cSt. The biolubricant that was developed appears to have a higher viscosity index (VI), which suggests that it can be used successfully over a wide temperature range. It may be feasible to connect the temperature-dependent reduction in viscosity with the force of attraction between liquid molecules (18). A dimensionless quantity called the viscosity index is used to indicate the correlation between a product's kinematic viscosity and temperature. Viscosity index of 130 is suitable for use in a wide range of engines because viscosity decreases as the index rises and vice versa.

The discovered value complies with light gear oil ISO VG220 and ISO VG46. Additionally, as shown in Table 2, it has a greater viscosity index than biolubricants derived from other vegetable oils including sesame and jathropa. The usability of a lubricant at low temperatures is determined by its pour point. The biolubricant made from sweet almonds has a -6 °C pour point. This figure complied with the ISO VG 32 standard standards' -6 °C gear oil temperature limit. Table 2 further reveals that this study's pour point of 1.3 °C reported for neem oil-based lubricant by Mohammed *et al* (11) was comparable. This result illustrates that at lower temperatures, sweet almond biolubricant can perform without clogging the filter.

To evaluate a lubricant's flammability, one looks at its flash point to be 210 °C which is the biolubricant made from sweet almond oil's flash point. Compared to the corresponding biodiesel's 138 °C value, this flash point value is a significant improvement (19). This elevated flash point is the outcome of basic oil's chemical modification. The result meets the 204–250 °C temperature range of the ISO VG 68 and ISO VG 32 standard well. As can be seen in Table 2, the outcomes are nearly in line with the stated 262 °C for the biolubricant made from neem oil.

Sweet almond oil-based lubricants were particularly safe to use and store because they were created without methanol.

3.3. Temperature Effects on Sweet Almond Oil's Viscosity

Table 2 provides a list of the various viscosity grades that ISO demands. The main grading standards are the pour point and viscosity index. At temperatures between 30, 40, 60, 80, and 100 °C, respectively, the measured viscosities were 42.80, 30.18, 21.39, 12.25, and 8.90 cSt.

The data in Figure 1 demonstrate the negative relationship between lubricant viscosity and temperature. The calculated viscosity index was based on the obtained viscosities at 40 and 100 °C, was then used to calculate the viscosity grade.

The lubricant's molecules are attracted to one another by a cohesive force that lessens with increasing temperature, decreasing the lubricant's viscosity (18,19).

The lubricant's extremely high viscosity index may possibly be responsible for this slight drop in viscosity with rising temperature. This variance also shows that the synthetic biolubricant is acceptable for use as motor oil due to its amazing stability across such a wide temperature range (16, 17).

3.4. Fourier Transform Infrared (FTIR) Analyses

The transmittance versus wave number plot of the infrared radiation spectrum results in a horizontal variation in the bond vibration energy. Figure 3 peak plots show low transmittance and considerable absorption. The wave number on the horizontal as we move, axis gets bigger to the left. Peak less regions show that photons are not absorbing at that frequency, demonstrating that the molecule does not contain that specific bond at that frequency. Figure 3 presents the results of the FTIR analysis of the chemical composites of RCO (a), CAME (b), and CABL (c). The key IR peak regions for RCO and CAME were revealed by the FTIR spectroscopy data, indicating that chemical alterations were observing the fingerprints (500-4000 cm^{-1}). In the spectral spectrum of 1487.17 cm^{-1}, mono, di, and triglycerides of the glycerol group O-CH$_2$ were found (a). O-H stretching vibration (alcohol) was 2855.76 - 2695.76 cm^{-1}. In a comparable FTIR observation, Silva *et al*. (21) also observed that the C-H was an aliphatic stretching vibration. The IR spectrum between 1701.46 and 1750.45 cm^{-1} in RCO and CAME coincides with the presence of an ester carbonyl group. The FTIR spectra of CABL and CAME exhibit absorption bands at 1755.74 and 1743.96 cm^{-1}, respectively. These absorption bands, which were used to demonstrate the presence of oxygen in CABL and CAME, were created by the C-O and C=O stretching vibrations in ester (18). The figure shows that the hydroxide group peak in RCO, which was quite prominent (3a) and may be ignored in CAME (3b), was recorded at 3701.19 cm^{-1}. This shows that the bio-lubricant esterification reaction was very close to being finished (3c).

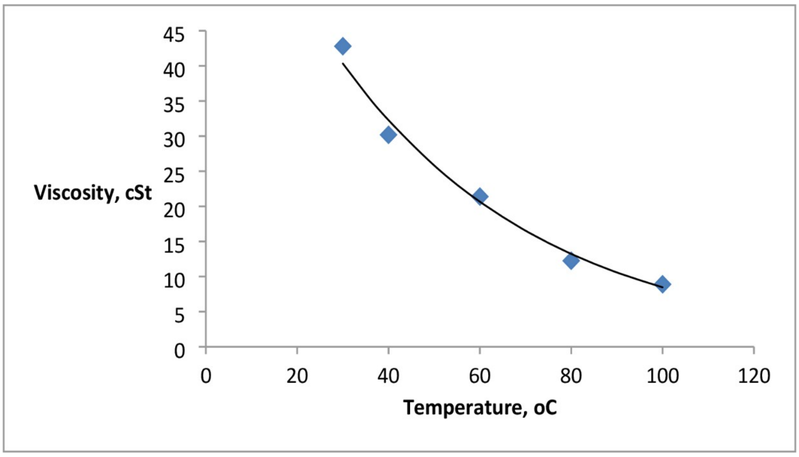
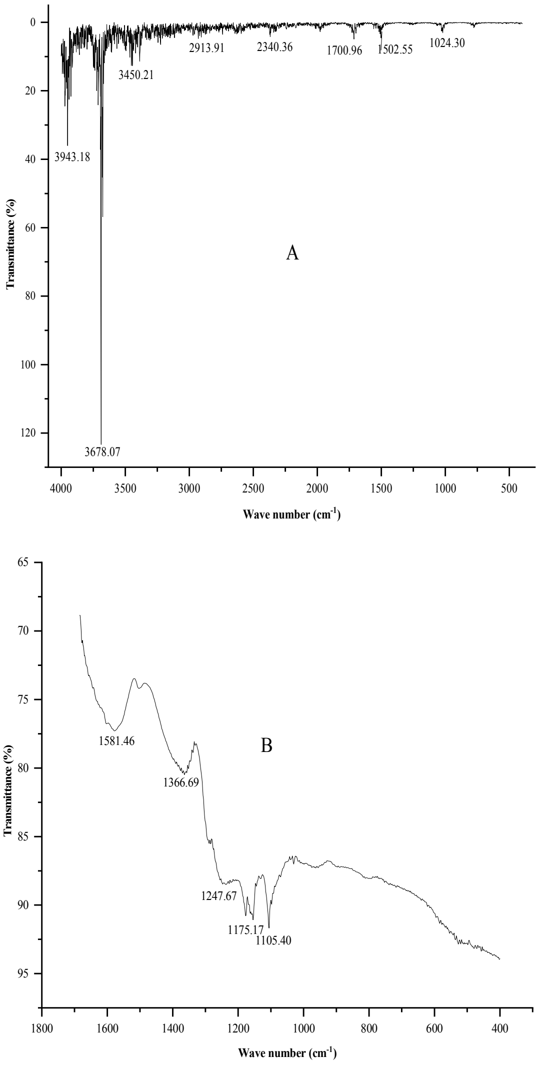


Figure 2: Effect of temperature on SABL viscosity.



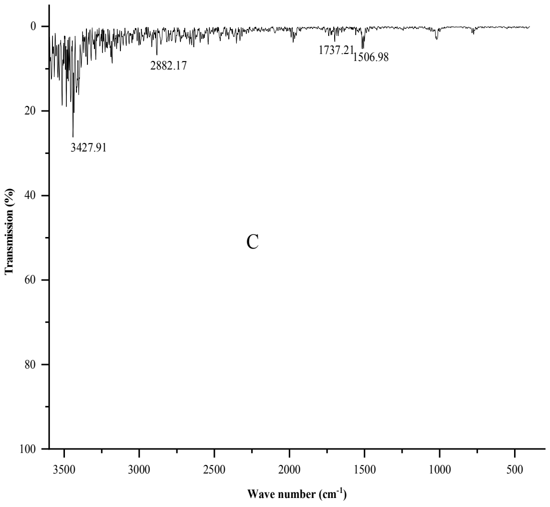


Figure 3: FTIR spectra of (A): RSAO (B): SAME (C): SABL.

Table 2: Properties of Sweet Almond biodiesel and biolubricant.

Properties	**Biodiesel**	**Sweet Almond Lube**	**[a]Jathropa Lube**	**[b]Neem Lube**	**[c] Sesame Lube**	**[d] ISO Viscosity Grade**		
						46	**32**	**68**
Flash point (°C)	138	210	-	262	-	220	204	250
Pour point(°C)	-8	-6	-7	1.3	-12	-10	-6	< - 10
Viscosity 40 °C, (cSt)	37.2	42.1	55.17	190	35.43	≥41.4	≤28.8	>61.4
Viscosity 100 °C, (cSt)	8.0	8.9	10.96	70	7.93	≥4.1	≥4.1	> 4.10
[e] ASTM D2270 Viscosity index	195.72	198.79	195.22	397	206	≥90	≥90	> 198

[a] (10); [b] (11); [c] (12); [d] (13); [e] (16)

3.5. Assessment of Free Fatty Acid

To quantify free fatty acids, GC-MS analyses were used. Castor oil was chosen for GC-MS analysis for fatty acid profile evaluation based on the high lubricating qualities discovered in synthetic biolubricant evaluation. Table 3 shows the castor oil's fatty acid makeup before it was esterified into a biolubricant using GC-MS analysis.

Table 3: Sweet almond oil and biolubricant FFA content (wt.%).

Refined sweet almond oil (RSAO)			**Sweet almond biolubricant (SABL)**		
Fatty acid	**Satn**	**Area (wt.%)**	**Fatty esters**	**Satn**	**Area (wt.%)**
Palmitic acid	$C_{16}H_{32}O_2$	15.087	Pentadecanoic acid, 14-methyl-, methyl ester	$C_{19}H_{36}O_2$	7.683
Linoleic acid	$C_{18}H_{32}O_2$	31.439	Palmitic acid methyl ester	$C_{16}H_{32}O_2$	28.275
Oleic acid	$C_{18}H_{34}O_2$	16.710	Linoleic acid ethyl ester	$C_{18}H_{32}O_2$	45.926
1,15-Pentadecanedioic acid	$C_{15}H_{28}O$	5.326	Oleic acid ester	$C_{18}H_{34}O_2$	18.116
Others		31.438			
Total FAME		68.562	Total Triester		100
Total unsaturated FFA		53.475	Total unsaturated FFA		71.725

Note: Results were extracted from the GC-MS spectra. Satn: Saturation.

According to the GC-MS results, the RSAO contains 53.48% more unsaturated fatty acids than the saturated ones (15.087%), including palmitic acid, linoleic acid, oleic acid, and 1,15-pentadecanedioic acid and biolubricant has 71.73%. As a result, the oil has a higher iodine content (9.52 of iodine per 100 g of sample), since unsaturated glycerides have a limited ability for iodine absorption. Given that most vegetable oils do not coagulate at room temperature and have a high unsaturation level, this oil is good for the synthesis of biolubricants (20, 22). Figures 4 and 5 display the fatty acid profiles of the RSAO and SABL having 71.725% percentage contents. Comparable variations between the RSAO and SABL showed hardly any compositional alterations.

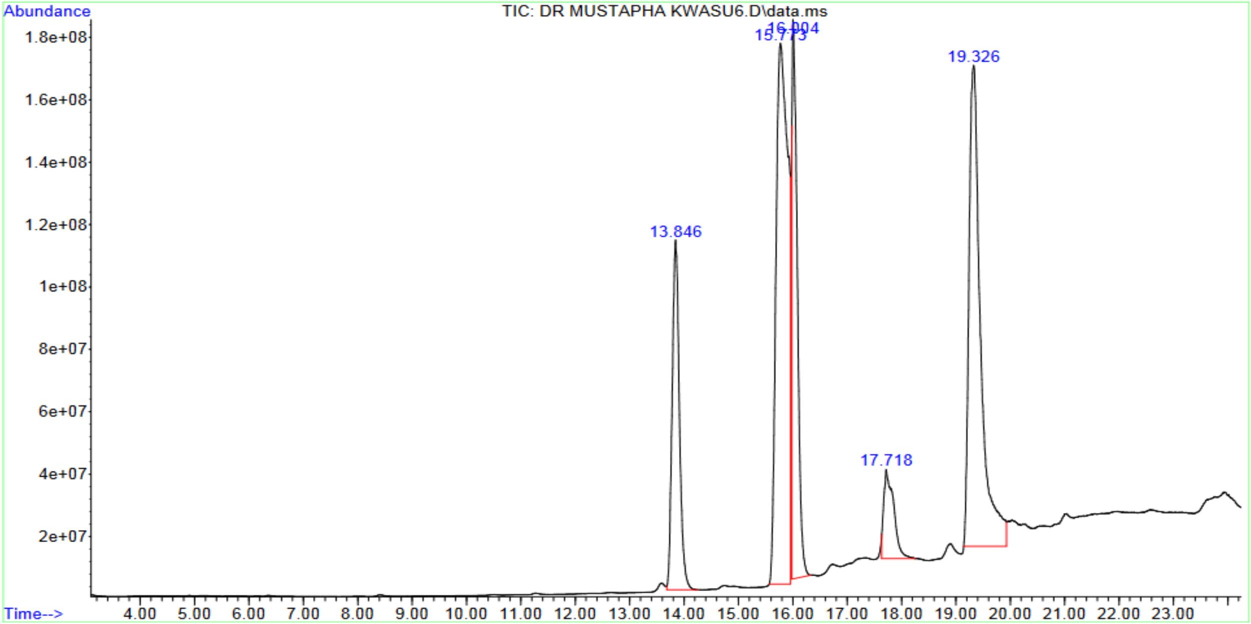


Figure 4: Fatty acids profile in refined SAO .

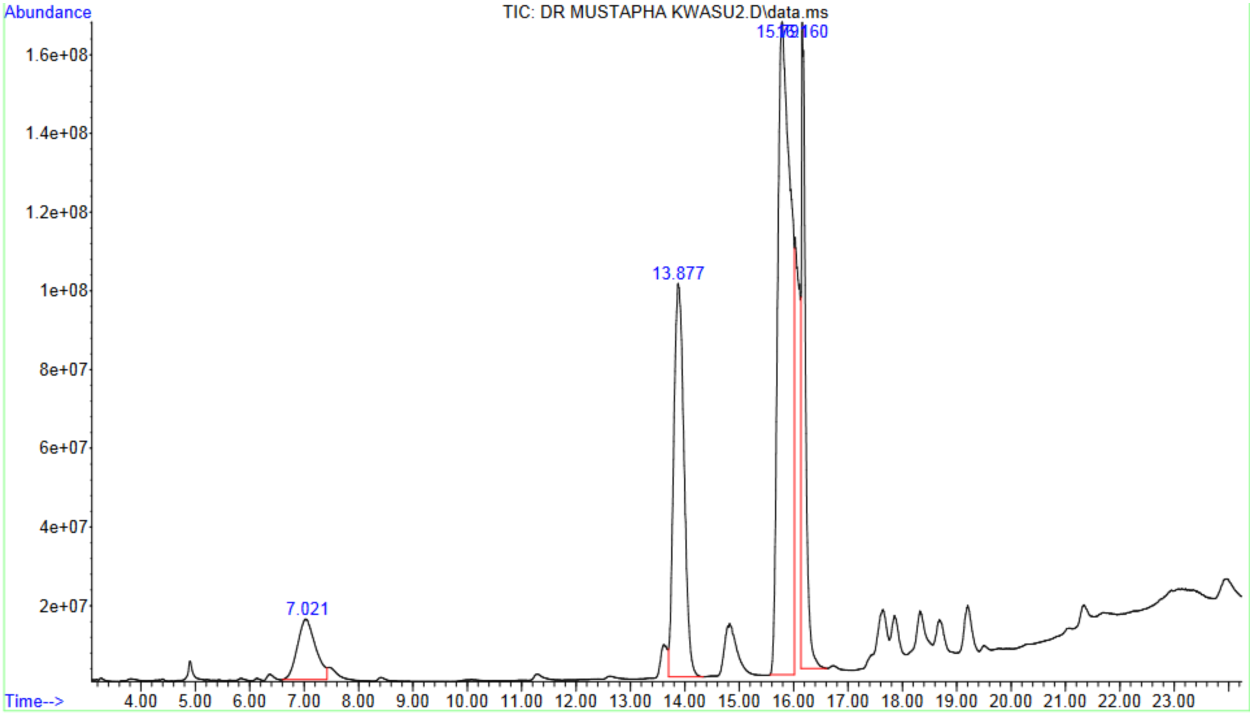


Figure 5: Fatty acids profile in SABL.

4. CONCLUSION

The trans-esterification process created the sweet almond biodiesel, which was then used to synthesize a biolubricant and evaluate its primary lubricating properties. When compared to ISO standards, these characteristics match those of viscosity grade VG-32 exactly. Therefore, synthetic biolubricants can successfully replace petroleum-based lubricants in industrial and agricultural machinery. The number of carbonyl groups in the produced bio-lubricant, which showed the evolution of the lubricant, occurred from 1743.96 cm^{-1} in SAME to 1755.74 cm^{-1} in the biolubricant when it was evaluated by FTIR. This study has shown that castor plant oils have the potential to be used to make ecologically friendly lubricants that are notably consistent with the specifications for automobile light gear oil.

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