RESEARCH ARTICLE OPEN ACCESS

Synthesis of Biolubricant from Citrus Sinensis Seed Oil (CSSO)

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Abstract

The focus of this work is to chemically synthesize and characterize *Citrus sinensis seed* oil (CSSO) to produce biolubricant using the transesterification of *Citrus sinensis seed*methyl ester with trimethylolpropane (TMP) method. Solvent extraction method was employed to extract the CSSO. The CSSO and *Citrus sinensis seed*biolubricant (CSSBL) physicochemical properties were determined by employing standard methods. The predominant functional groups of the CSSO and CSSBL were determined using Fourier transform infrared (FTIR) spectrometry. The oil yield obtained for *Citrus sinensis seed*was 53.33 wt% at 55 , 150 min, and 0.5 mm particle size using n-hexane as solvent. The viscosity at 40 , density, and cloud point of the CSSBL produced using the methods of transesterification with TMP were 28.22 mm^2s^{-1}, 894 kg/m^3, and 9.5 , respectively. The physicochemical properties of CSSBL sample indicated that it conforms with the ISO VG 32 standard. As such, the *Citrus sinensis seed*biolubricant has a huge potential as a biolubricantbasestock. The FTIR results shows the presence of C-H functional groups, which indicates that the biolubricant is biodegradable. The XRD results indicated that the CSS sample is crystalline in nature.

1. Introduction

Due to environmental degradation, as well as depletion of none renewable minerals, researches are now being directed in the area of renewable raw material sources (Sharma and Singh, 2010). Presently, the global price of crude oil which is the main world energy source, have also gone up, as a result of its none-renewable nature, as well as the ongoing Russia-Ukrainian war. In other words, there is need to explore and develop environmentally friendly oil sources to avert these short-comings. Bio-oils are viable alternative to petroleum since they are biodegradable, as well as renewable with limited or no impact on the environment (Agu et al. 2022). As such, the benefits and applications of bio-oils are numerous as they can be used for the production of bio-transformer fluid, bio-diesel, bio-hydraulic, bio-lubricant etc (Agu et al., 2019).

The industrial applicability of bio-oils for production of the aforementioned products has increased. In other words, the demand for oil bearing seeds and nuts for extracting vegetable oils for this purpose has also increased (Agu et al. 2022). Several research works have explored the use of various types of seeds, nuts and kernels as viable oil sources for both domestic and industrial applications. These seeds/nuts/kernels include but not limited to *Colocynthis vulgaris shrad*(Agu et al., 2018), *Irvingiagabonensis*(Agu et al., 2020), *Terminaliacatappa L.* kernel (Menkiti et al., 2015), *Gmelina arborea* (Agu et al. 2022), *Chrysophyllumalbidum*(Dzarma et al., 2022), Palm kernel (Egbuna et al., 2021) and *Jatrophacurcas*(Menkiti et al., 2017). Although a significant number of these seeds/nuts are food competing, it became necessary to explore none food competing one like the *Citrus sinensis* seeds, for possible use in bio-lubricant production.

Citrus sinensis otherwise known as sweet orange is most popular members of citrus and it belongs to the Rutaceae family and Aurantioideae subfamily (Ezekoye et al., 2019; Aydeniz-Guneser, 2020). In 2016, an estimated 145.5 million tonnes of citrus were produced across the globe. Sweet orange (*Citrus sinensis*) is ranked top among the citrus fruits, having about 50 % of total global citrus production worldwide (Aydeniz-Guneser, 2020). Its seeds are often considered waste as they are thrown away after taking the juices, hence, a viable raw material for extraction bio-oil, since it is none food competing. Number researches have shown that oil yields of *Citrus sinensis* to vary, depending of a number of factors. For instance, its oil yields have been reported to be 34.00 % (Ezekoye et al., 2019) and 51.8 % (Saidani et al., 2004). In other words, researchers have directed its applicability in the production of good number of products, such as biodiesel (Ezekoye et al., 2019), pesticides (Anaya-Gil et al., 2021) and current study explore its feasibility for biolubricant production.

Over the years, several methods have been reported for the production of biolubricant from vegetable oils. Some of the popular methods includes but not limited to bi-stage transesterification using methanol, with subsequent trimethylolpropane (TMP) introduction and epoxidation-esterification. The use of TMP has been extensively reported in the literature with the likes of Egbuna et al. (2021), Menkiti et al. (2017), Heikal et al. (2017), Sarno et al. (2020), and Encinar et al. (2020), having applied the method using Palm kernel oil (PKO), *Jatrophacurcas*, Palm oil, waste cooking oil and castor bean biodiesel, respectively for biolubricants production. On the other hand, epoxidation-esterification method has also been used by researches like Salimon et al. (2011), Egbuna et al. (2021), Kulkarni et al. (2013) and Efeovbokhan et al. (2020) for biolubricants production from oleic acid, palm kernel oil, mustard oil and castor oil, respectively.

This present study therefore seeks to evaluate the feasibility of biolubricant production, its physicochemical and other vital characterizations from *Citrus sinensis* seeds oil. The research is necessitated by the limited, as well as none existence of robust and extensive research in this regards, hence, the need to close the research gap. Furthermore, the scanning electron microscopic (SEM) analyses, as well as the X-ray diffraction (XRD) analyses of the milled *Citrus sinensis* seeds were also evaluated.

2. Materials and methods

2.1. Materials

Citrus sinensis seeds (CSS) were gathered from its orchard in Michael Okpara University of Agriculture, Umudike, Abia State, in South-East Nigeria and identified by laboratory technologists of Crop Science Department of the University. Nevertheless, Conraws Ltd. Enugu, supplied all analytical grade chemicals used for the research.

2.2. Methods

2.2.1. Sample preparation

The outermost coatings of *Citrus sinensis* seeds (CSS) were carefully removed, while the kernels were separated, cleaned and demoisturized by sun drying. Thereafter, it was subsequently oven dried at 60 °C for 12 hours. Lastly, size reduction of dried CSS was carried out using electric grinder, and then separated with sieve plate size of 0.5 mm to ensure very fine particle size diameter.

2.2.2. Extraction Process to obtain *Citrus sinensis* seeds (CSS)

Extraction of oil from the CSS sample was carried out following the Association of Official Analytical Chemists (AOAC) 963.15 methods (AOAC, 1990), using soxhlet extractor. In this procedure, an average particle size of 0.5 mm and 15 g of the ground seeds were packed in a thimble of the soxhlet extractor. Thereafter, the extractor was filled with 150 ml of n-hexane. The extraction of oil was carried out at temperature of 55 °C and for time duration of 150 mins. The obtained oil yield at the end of the extraction time was calculated and recorded. The temperature of extraction was calculated using an electronic thermometer (Hanna HI-9063), while the time was estimated by a stop watch. Equation 1 was

used to calculate the oil yield, following AOAC method no. 920.85. At the end of the extraction process, rotary evaporator (model N- 1000S-W, EYELA, Tokyo, Japan) was used to remove the solvent at 60 °C. 1:5 (15 g: 150 ml) was the solute to solvent ratio used for the extraction process. The extraction processes carried out under the set conditions were performed three times and the average values reported, while the total extraction yield was obtained using AOAC 920.85 standard method (1990).
The oil yield of CSS oil was calculated using equation 1.

$$\%\,YieldofCSSOil = \frac{weight\ of\ oil\ extracted\ (g)}{weight\ of\ sample\ (g)} \times 100 \qquad (1)$$

2.2.3. Physicochemical properties of CSSO and CSSO bio-lubricant samples

Oil yield (AOAC 920.85) was determined according to AOAC approved techniques (AOAC, 1990). Then again, viscosity index (ASTM D2270), viscosity (ASTM D445) and specific gravity (ASTM D1217 – 15), were determined using ASTM standard methods. Also, the pour and flash points were determined using ASTM D97 and ASTM D93 standard methods, respectively. Each physicochemical property was measured three times, and the average values of the properties were determined and noted.

2.2.4. Transesterification experiment/Synthesis of *Citrus sinensis* methyl ester

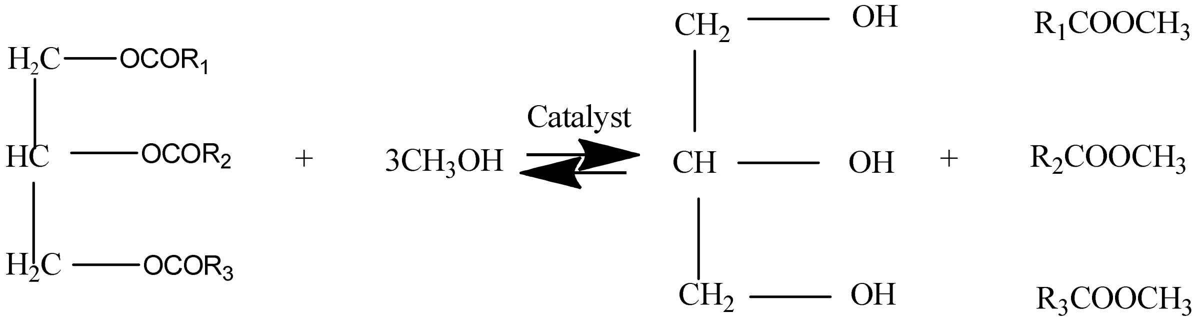
25 ml of each of the *Citrus sinensis seed* (Triglyceride) sample was placed in 250 ml conical flasks and heated to 60 °C through a water bath. A batch of potassium methoxide was created by dissolving 5.1 g (30wt. %) of KOH pellets in an agitated 250 ml beaker with 150 ml of anhydrous methanol. The solution was transferred into the warm 25 ml *Citrus sinensis seed* (triglyceride) sample with a methanol to oil ratio of 6:1. The mixture was then vigorously stirred using a magnetic stirrer at 500 revolutions per minute (RPM) for 120 minutes. To guarantee proper settling, the blend was left undisturbed in a separating funnel for 24 hours.

Upon completion of the settling process, the top layer (*Citrus sinensis seed*methyl ester sample) was poured into a beaker and then washed with distilled water to eliminate any remaining methanol, catalyst, glycerin, soap, and other contaminants. Following that, the *Citrus sinensis seed* methyl ester (FAME) sample was dehydrated by gradually increasing the temperature to a constant 100 °C. Finally, the lower layer, which is comprised of glycerol and soap was collected from the base of the funnel.

Equation 2 shows the percentage methyl ester yield of the *Citrus sinensis seed* oil sample.

$$\%\ \text{Methyl ester yield} = \frac{\text{Mass of methyl ester produced (g)}}{\text{Mass of oil sample used (g)}} \times 100 \qquad (2)$$

Equation 3 shows the product of the transesterification of the extracted *Citrus sinensis seed* oil, which is the Citrus sinensis seed methyl ester (CSSME). The product is also generally referred to as fatty acid methyl ester (FAME).



Triglyceride Methanol Glycerol Methyl Esters
(Extracted oil) (FAME)

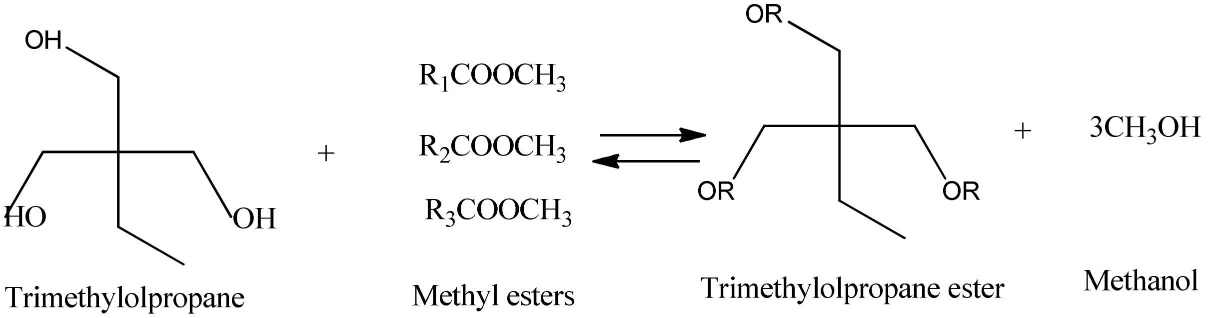
(3)

Conversely, the current method also included the process of obtaining FAME of *Citrus sinensis seed*oil. For this, a mixture of 300 g *Citrus sinensis seed*oil (Triglyceride), 100 g Methanol and 1% wt/wtOrthophosphoric Acid Catalyst were placed into a continuously stirred reactor. The reactor was outfitted with a water-cooled reflux condenser to make sure the reaction was complete. The combination was heated to 65°C and kept at that temperature for 90 minutes. Afterwards, the mixture was treated with Sodium Trioxocarbonate IV (0.2 molar solution) in order to terminate the reaction by fully neutralizing the acid.

The combination was then put into a separatory funnel and left alone for 24 hours to make sure a full division of methyl esters and glycerol phases. The glycerol phase at the lower part was collected in a sterile container and left aside. The CSSME was then heated to 65°C to eradicate any residual methanol. Lastly, the remaining catalyst in the CSSME was taken out by regularly washing it with hot distilled water at 80°C. Afterwards, the water left in the CSSME was removed by heating it in an oven at 100°C (Menkiti et al., 2017).

2.1.1. Synthesis of Bio-lubricant from CSME using trimethylolpropane (TMP)

As explained by Surapoj et al. (2018), a slight modification was made to the synthesis of the biolubricant. The result of the process was the production of *Citrus sinensis seed* methyl ester (CSSME) which was then reacted with trimethylolpropane (TMP) to form trimethylolpropane ester or *Citrus sinensis seed* biolubricant (CSSBL), as demonstrated in equation 4.



(4)

In this experiment, the transesterification set-up included a stirrer running at 1000 rpm, Kipps apparatus, a thermometer, and 50 mL three-necked round-bottom flask with a water-cooled reflux condenser. With the flow of carbon dioxide (CO_2), the TMP in the flask was heated up to 110 °C and kept at this temperature for 15 minutes to allow for moisture to escape. After that, a batch catalyzed by $CA(OH)_2$transesterification reaction between CSSME (FAME) and cooled TMP at CSSME–TMP ratios of 3:1, 4:1, 5:1, 6:1 and 7:1 was conducted using the same experimental set-up.

The transesterification experiments were conducted at temperatures of 80, 100, 120, 140 and 160 °C, in accordance with the given CSSME–TMP ratios. Samples from the respective reactions (at a given mole ratio and temperature) were monitored, collected, and analyzed, at intervals of 1, 2, 3, 4, and 5 hours. Following completion of the reaction, the mixture was cooled to room temperature before being filtered to remove the solid catalyst and obtain the *Citrus sinensis seed* biolubricant (CSSBL).

To analyze the filtered *Citrus sinensis seed* bio-based stock, a gas chromatograph (GC) was employed. In addition, before characterizing the biobased TMP ester, no unreacted methyl ester was removed. This was with the intention of boosting the wear resistance of the biobased TMP ester and at the same time, hindering the conjugation reaction that takes place at elevated temperatures (180 – 200 °C) which involves poly unsaturated fatty acid (PUFA) (Shote et al., 2018; Ishola et al., 2020)

2.1. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

FTIR analyses of the *Citrus sinensis* seeds oil (CSSO) and *Citrus sinensis* biolubricant (CSBL) samples were carried out using BUCK Scientific Infrared Spectrophotometer Model 530.

2.2. Scanning Electron Microscope (SEM)

SEM analyses of the milled *Citrus sinensis* seeds (CSS) sample was analyzed with SEM by PhenomProx produced by PhenomWorld Eindhoven, Netherlands.

2.3. X-ray Diffraction (XRD)

XRD analysis of the *Citrus sinensis* seeds (CSS) sample was carried out using EMPYREAN analytical, Netherlands.

3. Results and Discussion

3.1. Oil yield of *Citrus sinensis* seeds (CSS)

The oil yield obtained from*Citrus sinensis seed*was 53.33 wt%. The oil yield was higher when compared to the 34wt% reported for *Citrus sinensis seed* by Ezekoye et al. (2019), but lower than the 56 wt% reported for the same seed by Ibrahim and Yusuf (2015). The disparity in the oil content of CSS is due to the conditions and methods of extraction (Agu et al., 2018) and other possible factors like moisture content, seed development, fruit maturity, and geographical location differences (Berti et al., 2011). On the other hand, the oil yield obtained from CSS is within the ranges reported for other seed including *Jatrophacurcas* (40-60 wt%) (Demibras et al., 2016), *Carthamustinctorius* (51-62 wt%) (Poshetti and Tandale, 2020), and *Sterculiafoetida* (50-60 wt%) (Aktar et al., 2019). The high oil yield of *Citrus sinensis seed*shows the potential of the oil for industrial application as a non-food competing seed (Okolie et al., 2012).

3.2.Physiochemical properties of CSS

Table 1 presents the physiochemical properties of *Citrus sinensis seed*oil (CSSO).As presented in Table 1, the kinematic viscosity and acid value of *Citrus sinensis seed*oil was 46.57 mm^2s^{-1} and 3.129 mgKOH/kg, respectively. The kinematic viscosity reported in this work was higher than the 12.71 mm^2s^{-1} obtained for *Citrus sinensis seed*oil by Ezekoye et al. (2019). However, the acid value, 4.03 mgKOH/kg reported by Ezekoye et al. (2019) for *Citrus sinensis seed*oil was higher than the acid value reported for CSSO in this work. Other works such as Salimon and Abdullah (2008) and Yusuf et al. (2015) reported higher viscosity of 36 mm^2s^{-1} and 22.2 mm^2s^{-1} but lower acid value of 1.50 mgKOH/kg and 2.41 mgKOH/kg for Jatrophacurcas and Castor seed oils, respectively. The free fatty acid value for *Citrus sinensis seed*oil reported in this work was 1.565 mgKOH/kg, which was higher than 1.33 mgKOH/kg reported by Ezekoye et al. (2019) for CSSO. The refractive index for *Citrus sinensis seed*oil reported in this work was 1.4658. This value was close to the 1.457 reported for *Citrus sinensis seed*oil by Ibrahim and Yusuf (2015). The moisture content of the *Citrus sinensis seed*oil was 0.24 %, which was lower than the 4.0 % reported by Ibrahim and Yusuf (2015) for the same oil. The saponification value of the *Citrus sinensis seed*oil obtained in this work was 203.22 mgKOH/kg. This value was lower than the 93.97 mgKOH/kg and 190.32 mgKOH/mg for CSSO reported by Ezekoye et al., (2019) and Ibrahim and Yusuf (2015), respectively. The peroxide value of the *Citrus sinensis seed*oil obtained in this work was 0.89 meq/kg, which was lower than the 5.8 meq/kg reported for the same seed by Ibrahim and Yusuf (2015), but higher than the 0.82 meq/kg reported for the same seed by Ezekoye et al. (2019). The specific gravity of the *Citrus sinensis seed*oil obtained in this work was 0.914. This value was lower than the 0.931 reported by Ezekoye et al. (2019) for CSSO. The molecular weight of the *Citrus sinensis seed*oil was 834.59 g/mol. The ester value of the *Citrus sinensis seed*oil reported in this work was 99.23 %. Ezekoye et al. (2019) reported a lower ester value of 76.93 % for *Citrus sinensis seed*oil. The differences between the physiochemical properties of *Citrus sinensis seed*oil reported in this work and those of other works reported for the same and different seed oils can be attributed to the different pre-processing and extraction conditions of the seeds (Agu et al., 2022).

Table 1: Physiochemical properties of *Citrus sinensis seed*oil (CSSO)

Properties	**Values**
Total 0il yield (%)	53.33
Kinematic viscosity @ 40^0C (mm^{2}s^{-1})	46.57
Refractive index @ 33^0c	1.4658
Acid value (mgKOH/kg)	3.129
Free fatty acid value (mgKOH/kg)	1.565
Moisture (%)	0.24
Saponification (mgKOH/kg)	203.22
Peroxide value (meq/kg)	0.89
Specific gravity	0.914
Molecular weight (g/mol)	834.59
Ester value (%)	99.23

3.3. Physiochemical properties of *Citrus sinensis seed* biolubricant

Table 2 presents the physiochemical properties of the biolubricant produced from *Citrus sinensis seed*. The viscosity of a biolubricant is a measure of its resistance to flow. The higher the thickness of a biolubricant, the higher its viscosity. As shown in Table 2, the viscosity of the CSS biolubricant reported in this study was 28.22 mm^{2}s^{-1}. This value is lower than the 35.55 mm^{2}s^{-1} reported by Ocholi et al. (2018) for Sesame biolubricant. However, the viscosity of CSS biolubricant is near the range of 28.8 mm^{2}s^{-1} for ISO viscosity grades (VG) 32 for mineral biolubricants (Rudnick, 2006). This indicates the potential of industrial application for *Citrus sinensis seed* biolubricant. The density of CSS biolubricant obtained in this work was 894 kg/m^3. This value was lower than the 946 kg/m^3 reported by Nogales-Delgado et al, (2021) for high oleic safflower biolubricant. The cloud point of CSS biolubricant reported in this work was 9.5 □. This value was lower compared to the 0 □ and -5 □ reported for *Palm kernel seed*biolubricantand petrolubricant, respectively by Alang et al, (2018).

Table 2: Physiochemical properties of Citrus sinensis seed biolubricant

Properties	**Values**
Viscosity @ 40^0C (mm^{2}s^{-1})	28.22
Density (Kg/m^3)	0.894
Cloud point (^{0}C)	9.5

3.4. FTIR analysis of *Citrus sinensis seed* oil and biolubricant

Figure 1 shows the FTIR spectrum of *Citrus sinensis seed* oil. The results of the FTIR analysis was compared with known signature of identified materials (Barbara, 2004). The FTIR spectrum shows 6 detectable peaks at frequency range of 4000 to 400cm^{-1}. At the peak rangecentered at 3011.7 cm^{-1}, an indication of O–H stretching was observed, showing that water was present. The peak range centered at 2922.2 cm^{-1}indicated a C – H stretching characteristics, showingthat carbohydrates and fats were present. Further, the peak at 2855.1 cm^{-1} was an indication of C = H stretching characteristics, depicting that oxygen-containing compounds (for example, Aldehydes and Ketones)were present. In addition, the peak centered at 2150.7 cm^{-1}indicated an O – H stretching characteristics, showing that organic molecules and compounds were present. The peaks centered at 1461.1 cm^{-1} and 1379.1 cm^{-1} characterizethe presence of C = C stretching and aromatic C–N stretching, respectively. These peaks indicate that aromatic hydrocarbons and amines, respectively, are present. The peaks centered at 1744.4 cm^{-1} and 1714.6 cm^{-1} indicated a C-O stretching characteristics showing the presence of a group of triglycerides. At peaks 1237.5 and 1162.9 cm^{-1}, the presence of C–O group in the esters is shown. The peak centered at 723.1 cm^{-1}is characterized by presence of N–O stretching, indicating the presence of nitrogen-containing compounds, such as amines and amides, respectively.

Figure 2 shows the FTIR spectrum of *Citrus sinensis seed*biolubricant. At the peak range centered at 3008.0 cm^{-1}, an indication of O–H stretching was observed, showing that water was present. The peak range centered at 2922.2 cm^{-1} indicated a C – H stretching characteristics, showing that carbohydrates and fats were present. Further, the peak at 2855.1 cm^{-1} was an indication of C = H stretching characteristics, depicting that oxygen-containing compounds (for example, Aldehydes and Ketones) were present. In addition, the peak centered at 1979.2 cm^{-1} indicated a primary amide NH2 bending, indicating the presence of amides. The peaks centered at 1461.1 cm^{-1} and 1379.1 cm^{-1} characterizethe presence of C = C stretching and aromatic C–N stretching, respectively. These peaks indicate that aromatic hydrocarbons and amines, respectively, are present.The peak centered at 1744.4 cm^{-1} indicated a C-O stretching characteristics showing the presence of a group of triglycerides. At peaks 1237.5 and 1162.9 cm^{-1}, the presence of C–O group in the esters is shown. The peak centered at 723.1 cm^{-1} is characterized by presence of N–O stretching, indicating the presence of nitrogen-containing compounds, such as amines and amides, respectively.

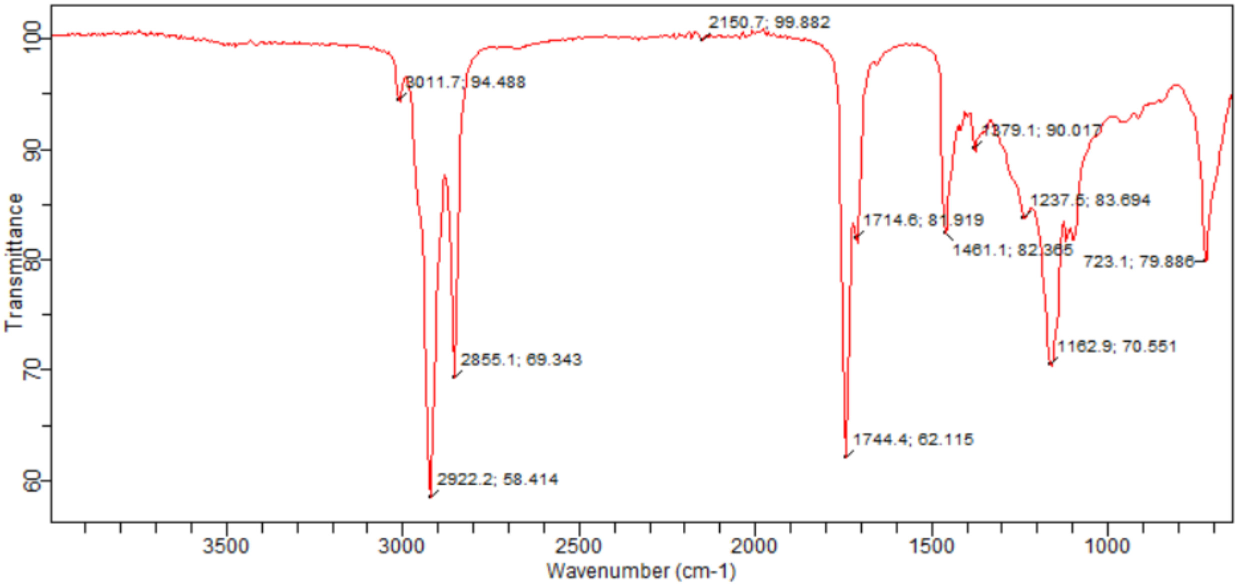
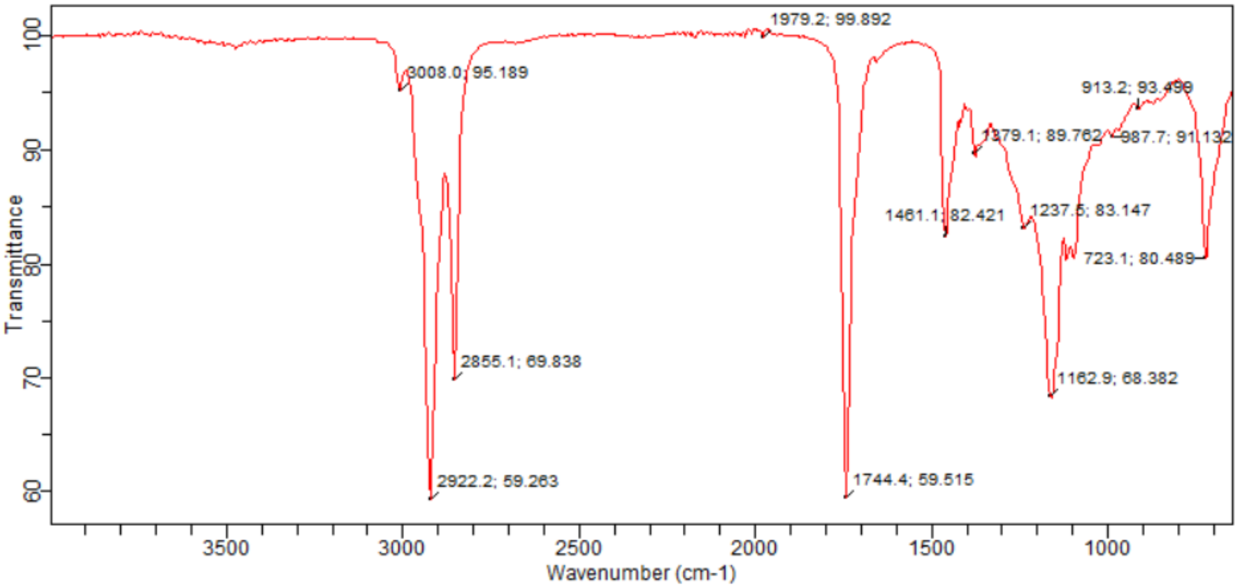
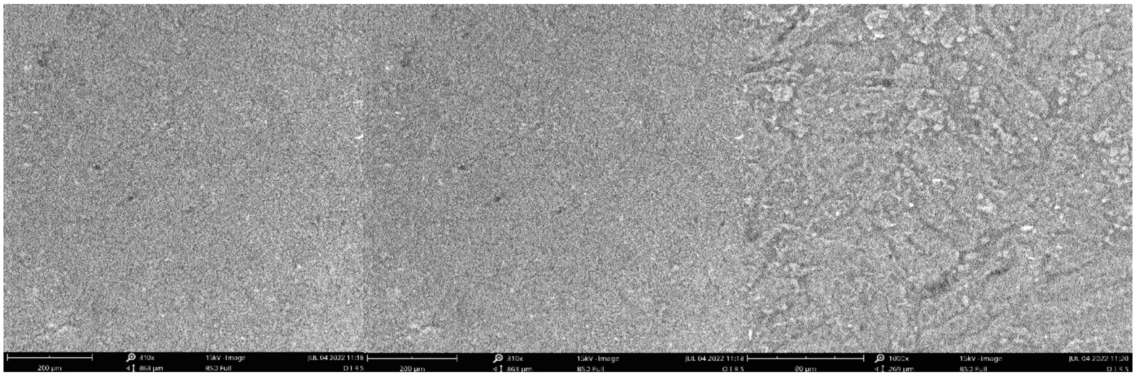


Figure 1: FTIR spectra for Citrus sinensis seed oil



3.5. SEM analysis of *Citrus sinensis seed* oil

Figure 3 (a-i) shows SEM results of the cell surface structure of *Citrus sinensis seed* oil. Figure 3 (a-b) shows the observation of a smooth and intact cell surface prior to extraction.In Figure 3 (c-e), due to the physical pretreatment of grinding, some protein bodies were released. Although the more oil and proteins were diffused at the beginning of the solvent extraction process, the external seed tissues surfaces were still smooth and intact. During the extraction process, between 30 to 90 minutes, rupture begins to take place at the cell walls of seed tissue. This is indicated in Figure 3f. As the extraction process proceeds from 90 to 150 minutes, a significant destruction of morphological structure of seed tissues was observed as shown in Figure 3 (g-i). The presence of the solvent in the cell membranes and walls made the inner structure less tightly-bound and more permeable. This enabled easier oil removal from the cell. In addition, the breaking down of the oil body membranes by the solvent molecules resulted in the release of high free oil (Rosenthal et al., 1996; Tzen, 1992).



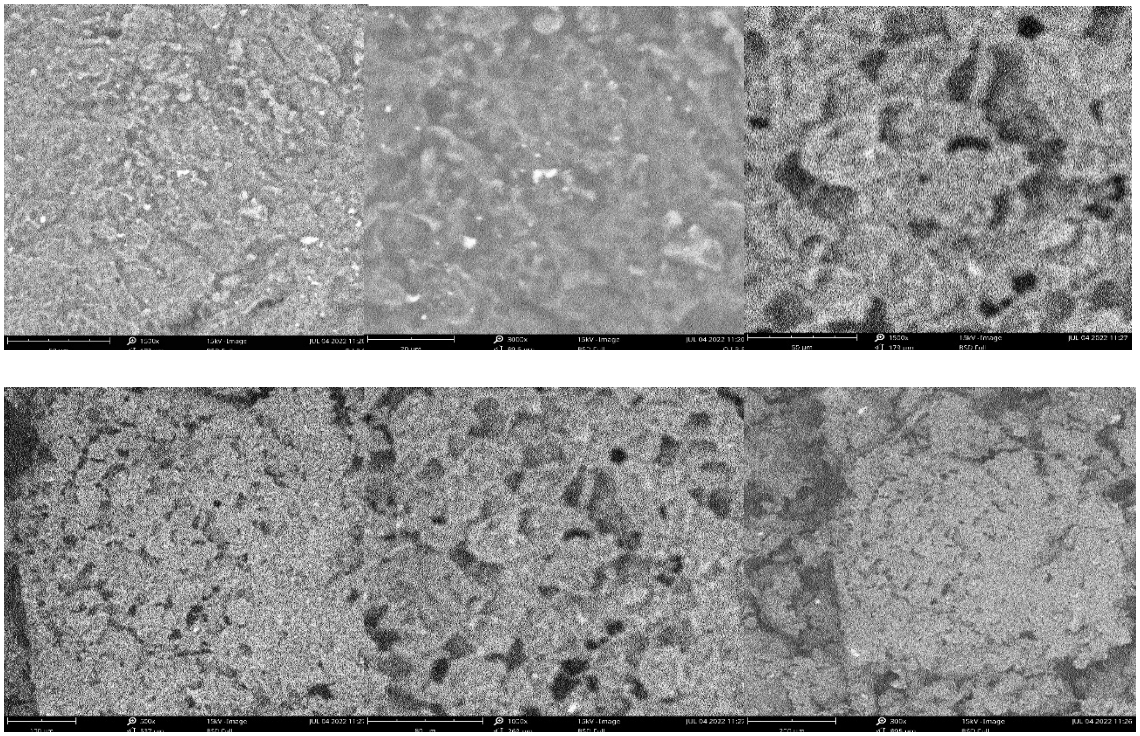


Figure 3 (a-i): SEM analysis results for *Citrus sinensis seed* oil

3.6. X-ray diffraction (XRD) spectra of *Citrus sinensis seed*

X-ray diffractometry is a method used to show the crystalline structure characteristics of substanceslikemilled nuts and seed and starch granules (Kaptso et al., 2014). Figure 4 shows the X-ray diffraction spectra from milled Citrus sinensis seed sample obtained for the extraction process. The XRD patterns in Figure 4shows the diffracting peaks of the crystalline nature of the Citrus Sinensis seed sample at different intensity and degrees. For the extraction of CSSO, the XRD spectra of the milled sampleshowednotable peaks, which appear between 22°to 24° at intensities ranging from 1800 to 2100, indicating the sample's degree of crystallinity. Agu et al. (2020) obtained a similar result for milled *Terminaliacatappa kernel* (TCK) sample. As shown in Figure 4, the XRD pattern of milled Citrus sinensis seed sample shows two major characteristic peaks. First, the peak at 22.5° with an intensity of 2150 and the second at 27.5° with an intensity of 1500.

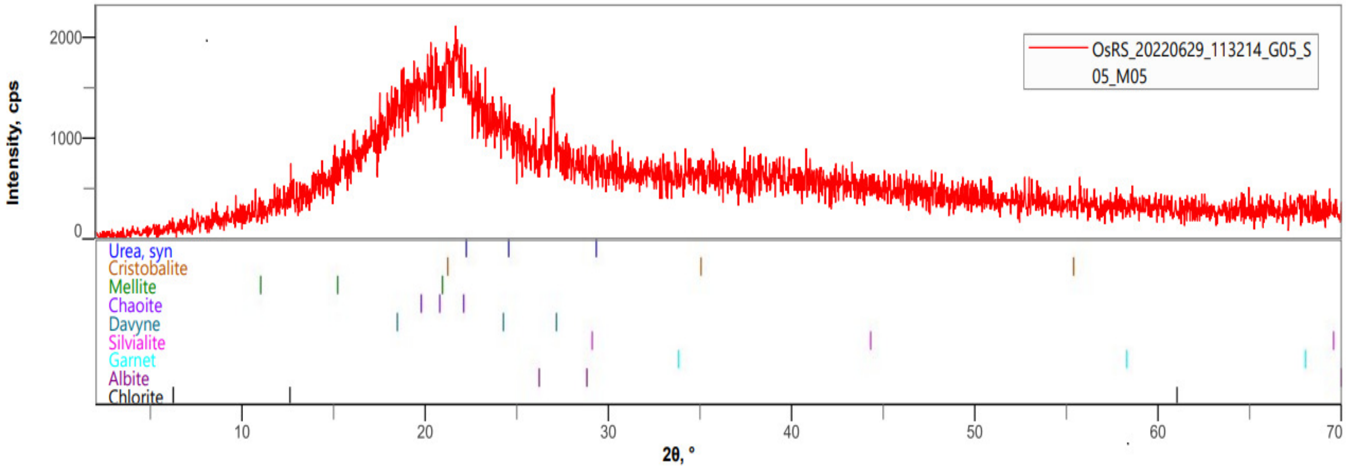


Figure 4. XRD pattern for milled *Citrus sinensis seed* sample

4. Conclusion

This work successfully achieved biolubricant production from CSSO through the process of transesterification of CSSME using TMP. The relevance of this study is justified due to the lack of studies on the production of biolubricant from *Citrus sinensis seed* oil. The physicochemical properties of CSSBL produced via the transesterification of CSSME using TMP complied with the ISO VG 32 standards compared to other samples reported in literature, indicating a potential for industrial application as biolubricant. The FTIR results indicate the presence of the C-H functional group, which is an indication of the biodegradable nature of the produced biolubricant. The XRD spectra results indicate the crystalline nature of the CSSO.

References

Agu C.M., Kadurumba C.H., Agulanna A.C., Aneke O.O., Agu I.E., Eneh J.N., 2018. Nonlinear Kinetics, Thermodynamics, and parametric studies of *Colocynthis vulgaris Shrad* seeds oil extraction. Industrial Crops and Products, 123, 386 – 400. https://doi.org/10.1016/j.indcrop.2018.06.074

Agu C.M., Menkiti M.C., Ohale P.E., Ugonabo V.I., 2020. Extraction modeling, kinetics, and thermodynamics of solvent extraction of *Irvingiagabonensis*kernel oil, for possible industrial application. Engineering Reports, e12306.https://doi.org/10.1002/eng2.12306

Agu C.M., Orakwue C.C., Ani K.A., Agulanna A.C., Dzarma G.W., 2022. Process thermodynamic, kinetics and statistical analysis of *Gmelina arborea* seed oil extraction as clean environmental friendly industrial base-oil. Case Studies in Chemical and Environmental Engineering, 6, 100216. https://doi.org/10.1016/j.cscee.2022.100216

Agu, C.M., Menkiti, M.C., Nwabanne, J.T., Onukwuli, O.D., 2019. Comparative assessment of chemically modified *Terminaliacatappa*L. kernel oil samples – A promising ecofriendly transformer fluid. Industrial Crops and Products, 140, 111727. https://doi.org/10.1016/j.indcrop.2019.111727

Akhtar, M.T., Ahmad, M., Shaheen, A., Zafar, M., Ullah, R., Asma, M., Sultana, S., Munir, M., Rashid, N., Malik, K., 2019. Comparative Study of Liquid Biodiesel FromSterculiafoetida (Bottle Tree) Using CuO-CeO2 and Fe2O3 Nano Catalysts. Front. Energy Res.,7, 4.https://doi.org/10.3389/fenrg.2019.00004

Alang, M.B., Ndikontar, M.K., Sani, Y.M., Ndifon, P.T., 2018. Synthesis and Characterisation of a Biolubricant from Cameroon Palm Kernel Seed Oil Using a Locally Produced Base Catalyst from Plantain Peelings. Green and Sustainable Chemistry, 8, 275-287. https://doi.org/10.4236/gsc.2018.83018

Anaya-Gil J., Cabarcas-Caro A., Leyva-Ricardo M., Parra-Garrido J., Gaitan-Ibarra R., Vivas-Reyes R., 2021. Artificial modification of the chemical composition of orange oil (Citrus sinensis L.) and its effect on larvicidal activity. Saudi Journal of Biological Sciences, 28, 1913 – 1918. https://doi.org/10.1016/j.sjbs.2020.12.042

AOAC. 1990. Official methods of Analysis, fifteenth ed. Association of Official Analytical Chemists, Washington, D.C, 1990.

Aydeniz-Guneser B., 2020. Cold pressed orange (*Citrus sinensis*) oil.https://doi.org/10.1016/B978-0-12-818188-1.00012-8

Barbara, S., 2004.Analytical techniques in science.Infrared spectroscopy; fundamentals and application, Wiley, London New York 2004.

Demirbas, A.,Bafail, A., Ahmad, W., Sheikh, M., 2016. Biodiesel production from non-edible plant oils.Energy Explor. Exploit., 34, 290-318.https://doi.org/10.1177/0144598716630166

Dzarma G.W., Agu C.M., Nwosu-Obieogu K., Onyedikachi L.N., Kalu O.A., Ekezie E.O., Adiele M.C., Chukwulebile A.S., 2022. Parametric study of oil extraction from African Star Apple

(*Chrysophyllumalbidum)* seeds. Cleaner Chemical Engineering, 2, 100018. https://doi.org/10.1016/j.clce.2022.100018

Efeovbokhan V.E., Alagbe E.E., Ogundowo O., Abatan O.G., Oni B.A., 2020. A Study of the Effect of Epoxidation Temperature on the Production of Biolubricant Base Stocks from Two Grades Castor Oil. International Journal of Scientific & Technology Research, 9(4), 2745 – 2749.

Egbuna S.O., Nwachukwu U.J., Agu C.M., Asadu C.O., Okolo B., 2021. Production of biolubricant samples from palm kernel oil using different chemical modification approaches. Engineering Reports, e12422. https://doi.org/10.1002/eng2.12422

Encinar J.M., Nogales-Delgado S., Sánchez N., González J.F., 2020. Biolubricants from rapeseed and castor oil transesterification by using titanium isopropoxide as a catalyst: production and characterization. Catalysts, 10, 366. https://doi.org/10.3390/catal10040366

Ezekoye V., Adinde R., Ezekoye D., Ofomatah A., 2019. Syntheses and Characterization of biodiesel from *Citrus sinensis* seed oil. Scientific African 6, e00217. https://doi.org/10.1016/j.sciaf.2019.e00217

Heikal E.K., Elmelawy M.S., Khalil S.A., Elbasuny N.M., 2017. Manufacturing of environment friendly biolubricantsfromvegetable oils. Egyptian Journal of Petroluem, 26(1), 53–59. https://doi.org/10.1016/j.ejpe.2016.03.003

Ishola, F., Adelekan, D., Mamudu, A., Abodunrin, T., Aworinde, A., Olatunji, O., Akinlabi, S., 2020. Biodiesel production from palm olein: A sustainable bioresource for Nigeria. Heliyon, 6(4), e03725. https://doi.org/10.1016/j.heliyon.2020.e03725

Kulkarni R.D., Deshpande P.S., Mahajan S.U., Mahulikar P.P., 2013. Epoxidation of mustard oil and ring opening with 2-ethylhexanol for biolubricants with enhanced thermo-oxidative and cold flow characteristics. Industrial Crops and Products, 49, 586 – 592. https://doi.org/10.1016/j.indcrop.2013.06.006

Menkiti M.C., Ocheje O., Agu C.M., 2017. Production of environmentally adapted lubricant basestock from jatrophacurcas specie seed oil. International Journal of Industrial Chemistry, https//doi.org/10.1007/s40090-017-0116-1

Menkiti, M.C., Agu, C.M., Udeigwe, T.K., 2015 Extraction of oil from *Terminaliacatappa L.*: Process parameter impacts, kinetics, and thermodynamics. Industrial Crops and Products, 77, 713 – 723. https://doi.org/10.1016/j.indcrop.2015.08.019

Nogales-Delgado, S., Encinar, J.M., González Cortés, Á., 2021. High oleic safflower oil as a feedstock for stable biodiesel and biolubricant production. Industrial Crops and Products, 170, 113701. https://doi.org/10.1016/j.indcrop.2021.113701

Ocholi, O., Menkiti, M., Auta, M., Ezemagu, I., 2017. Optimization of the operating parameters for the extractive synthesis of biolubricant from sesame seed oil via response surface methodology. *Egyptian Journal of Petroleum.* http://dx.doi.org/10.1016/j.ejpe.2017.04.001

Okolie, P.,Uaboi-Egbenni, P.,Ajekwene, P., 2012. Extraction and quality evaluation of sandbox tree seed (huracrepitan) oil. World J. Agric. Sci., 8(4), 359–365.

Poshetti, A.,Tandale, M., 2020. Experimental Study on CI Engine Performance for Optimum Blending Ratio of Blended Kusum. Biodiesel Advances in Energy Research, Springer, 2, 467–478. https://doi.org/10.1007/978-981-15-2662-6_43

Rosenthal, A., Pyle, D.L., Niranjan, K., 1996. Aqueous and enzymatic processes for edible oil extraction. Enzyme and Microbial Technology, 19(6), 402–420. https://doi.org/10.1016/S0141-0229(96)80004-F

Rudnick, L.R., 2006. Automotives Gear Lubricants, Synthetics, Mineral Oil and BioBased Lubricants: Chemistry and Technology, Taylor and Francis, Florida, 425–440.

Saidani, M., Dhifi, W., Marzouk, B., 2004. Lipid evaluation of some Tunisian citrus seeds. Journal of Food Lipids, 11(3), 242–250. https://doi.org/10.1111/j.1745-4522.2004.01136.x

Salimon J., Salih N., Yousif E., 2011. Chemically modified biolubricantbasestocks from epoxidized oleic acid: Improved low temperature properties and oxidative stability. Journal Saudi Chemical Society, 15, 195 – 201. https://doi.org/10.1016/j.jscs.2010.08.004

Salimon, J.,Abdullah, R., 2008. Physicochemical Properties of Malaysian Jatrophacurcas Seed Oil.SainsMalaysiana, 37(4), 379-382.

Sarno M., Iuliano M., Cirillo C., 2018. Optimized procedure for the preparation of an enzyme nanocatalyst to produce a bio-lubricant from waste cooking oil. Chemical Engineering Journal, 377, 120273. https://doi.org/10.1016/j.cej.2018.10.210

Sharma Y.C., Singh B., 2010. A hybrid feedstock for a very efficient preparation of biodiesel. Fuel Processing Technology 19, 1267 – 1273. https://doi.org/10.1016/j.fuproc.2010.04.008

Shote, A.S., Betiku, E., Asere, A.A., 2018. Characteristics of CO and NOx emissions from combustion of transmethylated palm kernel oil-based biodiesel blends in a compression ignition engine.J King Saud Univ Eng Sci., 31, 178-183. https://doi.org/10.1016/j.jksues.2018.02.005.

Tzen, J.T., 1992. Surface structure and properties of plant seed oil bodies. The Journal of Cell Biology, 117(2), 327–335. https://doi.org/10.1083/jcb.117.2.327

Yusuf, A.K.,Mamza,P.A.P., Ahmed, A.S.,Agunwa, U., 2015. Extraction And Characterization of Castor Seed Oil From Wild RicinusCommunislinn.International Journal of Science, Environment and Technology, 4(5), 1392 – 1404.