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Extraction and analysis of Citrus Sinensis Seed Oil (CSSO) for prospective use as bio lubricant

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Abstract
This study investigated oil extraction of citrus sinensis seed oil (CSSO) from Citrus sinensis seed for the production of bio-lubricant. Citrus sinensis seedoil (CSSO) was extracted using Soxhlet extraction method with n-hexane as solvent. The physiochemical properties of the CSSO were examined. Fourier transform infrared (FTIR) was used in the spectroscopy analysis to identify the functional groups. Central Composite Design (CCD) through Response Surface Methodology (RSM) was used to examine the statistical significance of the process parameters. The suitable optimum variables for the extraction process were temperature (65), particle size (0.5), and time (120), with the desirability value of 0.978. The model goodness of fitwas 0.9087 while the model lack of fit and p-value were 40.44 and 0.1005, respectively. The results from the physicochemical properties of the methyl ester from CSS were specific gravity (0.94), kinematic viscosity (46.57mm2 /s) at 40°C, acid value (3.129mgKOH/g), moisture content (0.24%), refractive index (1.4258) at 33°C, saponification value (203.22mgKOH/g), ester value (99.23%), and free fatty acid (1.565mgKOH/g). The spectroscopic analysis showed a number of functional groups which are present in conventional bio-lubricant. The study highlighted the potential suitability of CSSO as bio-lubricant production.

Keywords: ANOVA, FTIR, bio-lubricant, Citrus Sinensis Seed Oil (CSSO) orange seed oil,

1. Introduction

The environmental issues caused by petroleum based products have attracted significant concern across the globe. For decades, petroleum based oil products have been used for a number of industrial energy applications (Himashree et al., 2020; Khaled et al., 2018).However, the environmental toxicity and potential carcinogen of petroleum based oil requires urgent alternative (Himashree et al., 2020). In view of this, oil production from alternative sources (preferable non-edible seeds) has attracted global acceptance. For a suitable substitute to petroleum base oil, selected seeds need to meet regulatory standard with environmental and human compatibility. The biodegradability and non-toxicity are some of the comparative advantage of bio oil to petroleum base oil. However, the optimum temperature performance and other experimental process conditions need to be evaluated to ascertain the feasibility of bio based oils.

Due to gradual depletion of none renewable minerals, researches are now being focused in the area of renewable raw material sources (Sharma and Singh, 2010; Anaya-Gil et al., 2021). Presently, the global price of crude oil, which is the main energy source has 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; Khaled et al., 2018). 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 (Neelima et al., (2017).

The industrial applicability of bio-oils for production of bio-lubricant has increased. In other words, the demand for oil bearing seeds and nuts for extracting vegetable oils for this purpose have also increased (Bull and Obunwo, 2014; Neelima et al., 2020). 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), *Terminalia catappa L.* kernel (Menkiti et al., 2015), *Gmelina arborea*(Agu et al. 2022), and *Chrysophyllum albidum*(Dzarma et al., 2022). It is worthy to note that some of these seeds/nuts are food competing, making it crucial to investigate the bio-lubricant potentials of none food competing ones like the sweet orange (*Citrus sinensis)* seeds. *Citrus sinensis* is a member of citrus and it belongs to the Rutaceae family and Aurantioideae sub family. Sweet orange is considered one of the most important fruit with medical value due to the presence of many antioxidants and vitamin C. The orange fruit can be affected by climatic factors such as temperature, precipitation, and humidity. In general, its seeds contain essential oil which can serve a suitable alternative as a bio-lubricant. Phenolic compounds in citrus seeds, recently attracted importance especially flavonoids due to the free radicals and anti-oxidants activity; which is of immense importance to human health (Imeh and Khokhar, 2002).

The main aim of this study is to determine the suitability of Citrus sinensis seed oil (CSSO) as a bio-lubricant by evaluating its physiochemical properties. This study is designed to explore alternative sources of bio-lubricant to ease the increased pressure and demands on petroleum based bio-lubricant. Functional groups and elemental composition of CSSO were also determined using the Fourier transform infrared spectroscopy. Furthermore, the central composite design through the response surface methodology (CCD-RSM) was to examine the statistical significance of the process parameters.

Material and methods

Sample preparation

The outermost coatings of *Citrus sinensis* seeds (CSS) were carefully removed, while the kernels were separated, cleaned and gotten rid of moisture 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.

Extraction of *Citrus sinensis* seeds (CSS) oil

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 150mins. 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).

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

Physiochemical characterization of CSSO

Moisture content

For moisture content (MC) determination, 2g of the sample was placed in an oven for 90 minutes at 100°C after which the weight before and after drying was also measured. The loss in weight was equal to the MC of sample. The percentage MC in the sample was calculated using equation (2):

$$\text{MC}\,\% = \frac{\text{loss in weight}}{\text{oven dry} - \text{dry weight of sample}} \text{x}\ 100 \qquad (2)$$

Viscosity
A viscometer tubes HV M472 obtained from Walter Herzog (Germany) were used to measure the viscosity. The viscosity and was calculated using ASTM method D445–97 (ASTM, 2011c). All measurements were made in triplicate, and the average values were reported with their standard deviations (±SD).

Specific gravity
The density of the *Citrus sinensis* seeds oil (CSSO)was determined at 20 °C based on the ASTM method D1298–99 (ASTM, 2011e) using a glass hydrometer. The specific gravity (SG) is determined from the ratio of the density of CSSO to the density of water using equation (3):

$$S.G = \frac{\rho_{OSO}}{\rho_{water}} \quad (3)$$

Where S.G is the specific gravity, ρ_{OSO} is the density of CSSO (kg/m³) and ρ_{water} is the density of water (997kg/m³).

Refractive Index (R.I)
In this experiment, a refractometer was used to measure the R.I. the equipment uses a high-resolution optical sensor to measure the total reflection of a light beam that is in contact with a sample. For the default reading the sample stage on the equipment was covered with distilled water before it is covered with CSSO and reading were taken.

Acid Value
The weight of the cooled CSSO was measured in a 250ml conical flask. 50 mL of freshly neutralized hot ethyl alcohol and about 1 ml of phenolphthalein indicator solution was also added. The mixture were heated in a water bath at 75 to 80°C and titrated against potassium hydroxide (KOH) while shaking vigorously during titration. Using the phenolphthalein indicator, the end point was from colorless to light pink(Persisting for 15 sec.). The CSSO acid value was estimated as shown in equation (4).

$$Acid\ value = 56.1\frac{V \times N}{W} \quad (4)$$

V = Volume in mL of standard KOH used, N = Normality of the KOH solution; and W = Weight in gm of the CSSO

Density
Density was determined using equation (5)

$$density = \frac{mass\ of\ CSSO}{volume\ of\ CSSO} \quad (5)$$

Saponification value
Saponification value was measured by adding 20 ml ethanolic potassium hydroxide (0.5N) to 1 g of oil, the mixture was boiled about an hour, cooled, and several drops of phenolphthalein were added and titrated by H_2SO_4 (0.5N), till pink color disappearance. Saponification value was calculated using equation (6) while ester value is calculated using equation (7):

$$Saponification\ value\ = \frac{(A-B)\ \times N\ \times 56.1}{w} \quad (6)$$

$$Ester\ value = saponification\ value - Acid\ value \quad (7)$$

Where:
A =H2SO, for blank, mL
B =HZSO, for sample, mL
W =weight of sample, g

N =normality H_2SO_4 solution
56.1 =equivalent weight of potassium hydroxide

Instrumental characterization

Fourier Transform Infrared Spectroscopy (FTIR)

Spectroscopic analyses FTIR were carried out on the CSSO to evaluate the distribution of functional groups present. The FTIR spectra of produced CSSO were recorded in the absorbance mode, between4000 and 400 cm^{-1}, on pellets made from a mixture of CSSO/KBr, using a Perkin Elmer Spectrum BX spectrophotometer. The identified organic compounds show characteristic absorption peaks emanating from vibrational transitions of the CSSO. These absorption peaks are characteristic of the inherent compound in CSSO. The identification of these absorptions peaks and proper assignment was made according the previously published data.

Experimental design methodology

The significance and interactive effects of the process variables on oil yield of CSSO were investigated using the Central Composite Design of Response Surface Methodology (CCD-RSM). The CCD-RSM was used to predict the optimum values of the process variables through the numeric optimization process. The independent process variables investigated were temperature (A), particle size (B) and time (C). The experimental range and levels as generated by CCD-RSM are shown in Table 1. The design matrix with the combination and responses of the independent variables are presented in Table 2, while Table 3 shows the RSM predicted responses. The mathematical model relating the process variable with the response is presented in equation (8)

$$y = \beta o + \sum_{i=1}^{n} \beta iXi + \sum_{i=1}^{n} \beta iiXi^2 + \sum_{i=1}^{n-1} \sum_{j2}^{n} \beta ijXiXj + \mathrm{e} \quad (8)$$

From equation (8), Y is the response (% oil yield), βi, βii, and βij represents the regression coefficients for the linear, quadratic and interaction terms of the model, respectively. Ɛ is the random error term that allows uncertainties between the experimental and predicted values (Onu, et al; 2023; Henry et al, 2021). The probability levels ($p < 0.05$) and interactive effects of the independent process variables were investigated using the ANOVA in Design Expert 7.0 statistical software. Furthermore, numerical optimizations of the process variables were also investigated, to determine the optimum values of the considered process variables.

Table 1: Factors levels of independent variables for oil extraction. α =1.68179

		Levels				
Independent Factors	**Symbol**	**-α**	**Low (-)**	**Medium (0)**	**High (+)**	**+α**
Temp, (°C)	X_1	51.5911	55	60	65	68.4090
Particle size (mm)	X_2	0.15910	0.5	1.0	1.5	1.84090
Time (Min	X_3	39.5463	60	90	120	140.454

Table 2: Experimental design matrix of factors combination with RSM predicted and actual responses

run	time (x_1)	temp (x_2)	particle size (x_3)	%csso yield	RSM predicted
1	90	60	1	50.2	50.2643
2	120	65	0.5	58.5	58.1639
3	120	55	1.5	52.8	51.6012
4	90	60	0.159104	57.6	55.9226
5	90	51.59104	1	48	47.3314
6	60	65	1.5	43	43.9549

7	90	60	1	50.2	50.2643
8	120	65	1.5	53	52.2573
9	120	55	0.5	54.2	54.2578
10	60	55	0.5	44.7	46.4553
11	90	68.40896	1	51	50.2494
12	90	60	1	50.1	50.2643
13	60	65	0.5	47	49.2114
14	60	55	1.5	43.1	44.4488
15	39.54622	60	1	45.3	42.0653
16	90	60	1	49.7	50.2643
17	90	60	1	50.9	50.2643
18	90	60	1.840896	48.9	49.1824
19	140.4538	60	1	53.8	55.6125
20	90	60	1	50.3	50.2643

Results and discussion

Physiochemical characterization

Table 4shows the results of the physicochemical properties of the oil from CSSO. The oil yield obtained (53.33%) were in agreement those in literature. Using solvent extraction technique, Aydeniz-Guneser, (2020) reported the yield of cold pressed oil as 51.80% Saidani et al. (2004) reported a higher oil yield for sweet orange (51.8%) compared to the 34% of bitter oranges. In another study, the oil yields in bitter and sour orange seeds evaluated by a Twisselmann-type extractor were 56.5% and 57.4%, respectively (Matthaus & Ozcan, 2012). However, factors such as geographical origin and climatic conditions can cause changes in the oil content of citrus seeds (Aydeniz-Guneser, 2020).Kinematic viscosity is a measures the internal resistance of the CSSO bio-lubricant and the fluidity property. From Table 4, the Kinematic viscosity at 40^0C was 46.57 and was within the required range as high viscosity may disturb the bio-lubricant flow rate (Khaled et al., 2018).

The Refractive index (RI) measures the uniform compositions of CSSO. It is used to evaluate the distribution of *naphrhenic*, *paraffinic* and *aromatic* carbon atoms in oils and lubricants. Acid value measures the number of milligrams of potassium hydroxide required to neutralize the free fatty acid in one gram of a fat. Free fatty acid (FFA) measures the grams of free fatty acids in 100g of oil(Khan et al., 2013; Neagu et al., 2013). In this work, the acid value and FFA were 3.129 and 1.565 mgKOH/Kg, respectively (Table 4).The saponification value of CSSO bio-lubricant measures the weight of potassium hydroxide in milligrams needed to saponify one gram of oil, it was 203.22mgKOH/Kg. This value is higher than sweet orange fixed oil (183 mg/g) and many vegetable oils (Esteban et al., 2012; Mamma and Christakopoulos, 2008).

Table 3: Physiochemical properties of CSSO

Properties	Values
Total oil yield (%)	53.33
Kinematic viscosity @ 40^0C (mm^2s^{-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

Fourier Transform Infrared Spectroscopy (FT-IR)

Table 5, shows the results from the FTIR spectroscopic analysis used to identify functional groups present in CSSO. The presence of functional groups provides information on suitability as well as the efficiency of CSSO for bio-lubricant production (Ezekoye et al., 2019).The sample of CSSO for bio-lubricant was scanned within mid-infrared region of 3500 to1000 cm^{-1}using a Shimadzu FTIR Spectrometer. The FTIR analysis revealed that the functional groups present in CSSO are within characteristics of esters (C=O), Alkene (C=C), Alkynes (C≡C) and Alkanes (C–H) carbonyl (C-O) and alcohol (OH) bands(Yadav,2013).The band absorption at peak 3011.7 - 2922.2 cm^{-1} absorption spectrum shows that the biodiesel contains low moisture content, evident in the physiochemical properties in Table 4.Table 5 also revealed the absorption within 2855.1, 2150.7, and 1744.4cm^{-1} of symmetric stretching vibrations were representatives of alkane, alkynes and carbonyl bands. Ezekoye et al., (2019) reported that these bands indicate double bond bending vibrations at low energy indicating the presence of olefins (alkenes) functional groups. The characteristic peaks in the regionof1744.4 - 1714.6cm^{-1} stretching vibrations revealed the presence of carbonyl ester functional groups in the oil. Functional groups with these bands are prioritized when assessing the qualities of bio-oils as a suitable alternative (Adeniyi, et al. 2020; Bounaas et al., 2018; Ezekoye et al., 2019). The bands in the region of 1461.1 - 1379.1cm^{-1} absorption spectrum with asymmetric and symmetric vibrations show alkane (C = H) and alkene (C = C) groups in bio-oils. In the FTIR of CSSO, the region of 1237.5 - 1162.9$cm^{-1}$was attributed to esters and aromatic band functional groups respectively. The peak at 723.1cm^{-1} out of planebendingvibrations showed alkene chain (Adeniyi, et al. 2020). The FTIR spectrum of *Citrus sinensis* seeds oil (CSSO) is show in figure 1.

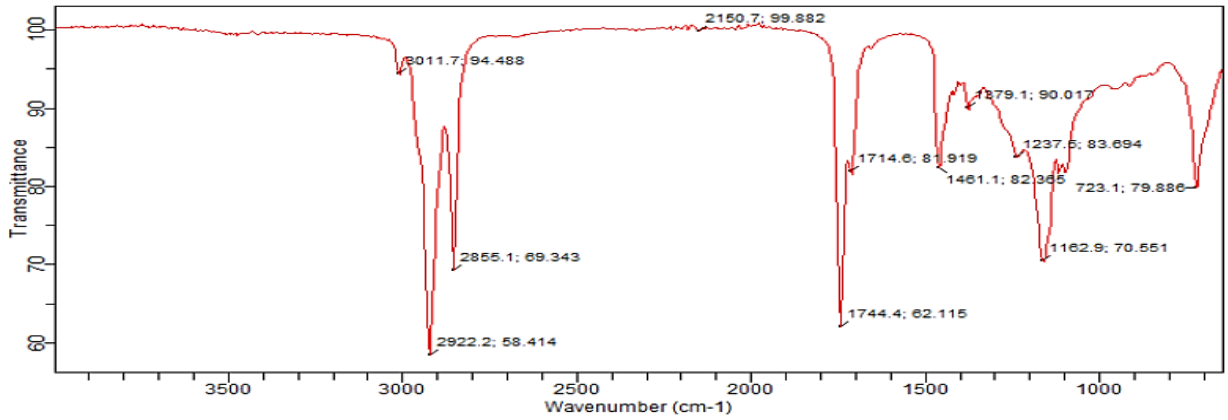

Figure 1: FTIR spectrum *Citrus sinensis* seeds oil (CSSO)

Table 4: FTIR absorbance spectra and functional groups

Wavenumber (cm^{-1})	Types of vibration	functional groups
3011.7	stretching	intermolecular hydrogen OH bonding; alcohol
2922.2	Asymmetric	C=H (Alkane band)
2855.1	symmetric	C=H (Alkane band)
2150.7	stretching	C ≡ C (Alkynes band)
1744.4	stretching	C - O (Carbonyl band)
1714.6	stretching	C=O (Ester in FAME)

1461.1	Asymmetric	C = H(Alkane band)
1379.1	symmetric	C= C (Alkenes band)
1237.5	stretching	C-O-C (Esters)
1162.9	Asymmetric	C - H (Aromatic)
723.1	out of plane bending	C=H (alkene)

Analysis of variance (ANOVA)

Table 6shows the ANOVA result for the oil yield of CSSO. From Table 6, the model's F-value was 11.05. This is an indication that the majority of the variations in the response could be explained by the quadratic model. The statistical significance of the model and its regression coefficient were ascertained from the model's P-values (Hao et al., 2021). In this case, the model P-value was < 0.0001, which indicated that the experimental data were in good agreement with the observed response. Equation (9) shows the quadratic model relating the response (oil yield of CSSO) with the independent process factors variable. However, the statistical significance (P > 0.05) of the process variables (temperature (A), particle size (B) and time (C)), were also investigated and presented in the ANOVA (Table 6). The Table shows the variables with high statistical significance (P< 0.05) on the oil yield of CSSO process. From Table 6, the linear term of A(temperature), the interactive terms of AB (temperature*particle size) and the quadratic terms of A^2 and C^2 (temperature² and time²) were non-significant. As such, they were removed from equation(9). The final significant model equation is presented in equation (10). Within the range of experimental values for the process variables, equation (10) could be used to predict the methyl esteryield of CSSO.

Final Equation in Actual Factors:

YIELD CSSO (%) = -53.43486 +2.78568*Temp +10.16478*Particle size +0.13038*Time -0.32500*Temp *Particle size +1.91667E-003*Temp *Time -0.010833*Particle size *Time -0.020521*Temp ^2 +3.17686*Particle size ^2 - 5.57415E-004*Time ^2 (9)

Significant model equation in actual Factors:

YIELD CSSO (%) = -53.43486 +10.16478*Particle size (mm) +0.13038*Time (Min) +1.91667E-003*Temp (°C)*Time (Min) -0.010833*Particle size (mm)*Time (Min)+3.17686*Particle size (mm)^2 (10)

The model goodness of fit and how well it replicated the observed outcome was investigated using the R^2 value. The result indicated that the model R^2 value was 0.9087, indicating that 90.87% of the observed outcome was satisfactorily explained by the model (Onu et al. 2022). Also, the model goodness of fit was evaluated through the lack of fit value. The model lack of fit and p-value were 40.44 and 0.1005, respectively, indicating that the lack of fit is not-significant relative to the pure error (Ijeoma et al. 2021). Previous works (Hao et al., 2021) reported that the adequacy and statistical significance of the quadratic model were evaluated through the not-significant lack of fit.

Table: 5 ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	310.53	9	34.5	11.05	0.0004	significant
A-Temp °C	9.98	1	9.98	3.2	0.1041	
B-Particle size (mm)	53.66	1	53.66	17.19	0.002	
C-Time (Min)	221.37	1	221.37	70.91	< 0.0001	
AB	5.28	1	5.28	1.69	0.2225	
AC	0.66	1	0.66	0.21	0.00352	

BC	0.21	1	0.21	0.068	0.0008	
A^2	3.85	1	3.85	1.23	0.2927	
B^2	9.23	1	9.23	2.96	0.00163	
C^2	3.62	1	3.62	1.16	0.3066	
Residual	31.22	10	3.12			
Lack of Fit	30.47	5	6.09	40.44	0.1005	non-significant
Pure Error	0.75	5	0.15			
Cor Total	341.75	19				

Std. Dev.	1.77	R-Squared	0.9087
Mean	50.11	Adj R-Squared	0.8264
C.V. %	3.53	Pred R-Squared	0.8187
PRESS	232.83	Adeq Precision	12.885

Numerical optimization process

The numerical optimization process of the CCD was employed to optimize the independent process variables to maximize oil yield of CSSO. The optimization process finds the optimum values of the process variables which will maximize the desired function (% CSSO oil yield). Table 7 shows the weight, and importance of the variable, which was within the experimental range. The suitable optimum variables values are also presented in the solution in Table 7. These values were temperature (65), particle size (0.5), and time (120), with the desirability value of 0.978. Additional experiments were conducted to validate the RSM prediction (58.1639). The experiments were conducted in triplicate using the optimum solutions of the process variables as shown in Table 7, and the average value recorded. The validated experimental result for oil yield of CSSO was 54.11% ± 0.122. This was reasonably in good agreement with the RSM predicted values. Therefore, this confirmed the efficacy of the RSM model in predicting oil yield of CSSO.

Table 6: Numerical optimization for the extraction of methyl ester from CSSO

Constraints

Lower Name	Upper Goal	Lower Limit	Upper Limit	Weight	Weight	Importance
Temp °C	is in range	55	65	1	1	3
Particle size (mm)	is in range	0.5	1.5	1	1	3
Time (Min)	is in range	60	120	1	1	3
YIELD CSSO (%)	maximize	43	58.5	1	1	3

Solutions

Number	**Temp °C**	**Particle size (mm)**	**Time (Min)**	**YIELD CSSO (%)**	**Desirability**	
1	65	0.5	120	58.1639	0.978	Selected
2	65	0.5	117.89	57.9175	0.962	
3	65	0.5	117.21	57.8364	0.957	
4	63.18	0.5	120	57.7588	0.952	
5	65	0.53	117.21	57.5901	0.941	
6	64.95	0.5	113.49	57.3776	0.928	
7	60.93	0.5	120	57.0703	0.908	

Conclusion

This work showed the prospects for bio-lubricant production from CSSO through the soxhlet extraction procedure. The physiochemical properties of the CSSO were comparable with established standards indicating its potentials for industrial application. The ANOVA results showed that the Citrus sinensis seed particle size (mm) and time (minutes) of extraction were statistical significant. The optimum conditions for the extraction of methyl ester from CSSO were as follows: temperature of 65^0C, particle size of 0.5mm and extraction time of120minutes. These conditions resulted in the CSSO production yield of 58.1639%**.** The functional group of the CSSO indicated high level of ester. However, the oil yield (53.33%) showed the need for further improvement on the extraction route through the use of proper enhancement additives.

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