Asian Journal of Chemistry; *Vol. 31, No. 4 (2019), 839-844*

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2019.21762

Investigation on Thermo-Oxidative Stability of Karanja Oil Derived Biolubricant Base Oil

UMESH CHANDRA SHARMA[1,*], ABHISHEK KUMAR CHANDRA[1] and SADHANA SACHAN[2]

[1]Department of Chemical Engineering, University Institute of Engineering and Technology, C.S.J.M. University, Kanpur-208024, India
[2]Department of Chemical Engineering, Motilal Nehru National Institute of Technology, Allahabad-211004, India

*Corresponding author: E-mail: uc_sharma@hotmail.com

Received: 15 October 2018; *Accepted*: 11 December 2018; *Published online*: 27 February 2019; AJC-19295

Vegetable oils lack acceptable thermo-oxidative stability due to the presence of tertiary β-hydrogen in glycerol backbone of triglyceride molecule. Chemical modification methods may significantly improve the thermo-oxidative stability of vegetable oils derived biolubricants without hindering their environmentally benign characteristics. This study was aimed at evaluation of thermo-oxidative stability of non-edible karanja oil derived biolubricant base oil. The biolubricant karanja oil trimethylolpropane ester (KOTMPE) was synthesized by conventional two step transesterification process. Thermal stability of synthesized product was assessed by thermogravimetric analysis in non-isothermal mode under nitrogen atmosphere, whereas the oxidation stability was analyzed using Rancimat method. Kinetics of thermal degradation of biolubricant was also investigated by thermogravimetric analysis to obtain order of thermal degradation, activation energy and the frequency factor. The results revealed excellent thermo-oxidative stability for synthesized product at high temperatures with ample scope for further improvement by blending with appropriate additives as demanded by specific applications.

Keywords: Karanja, Thermogravimetric analysis, Rancimat induction period, Activation energy, Frequency factor.

INTRODUCTION

Vegetable oils derived biolubricants possess multiple acceptable characteristics like superior lubricity, high viscosity index, high flash point, low volatility, excellent tribological and anti-corrosive properties as well as environmental sustainability rooted in their high biodegradability, low toxicity and renewability [1]. The main drawbacks of vegetable oils are their low thermo-oxidative stability and poor cold flow behaviour largely due to presence of unsaturated fatty acids that prevents their direct application as biolubricants or industrial fluids [2,3].

A lubricant should have high thermo-oxidative stability for successful commercial application. The thermal stability of lubricants is particularly important for high temperature applications (>100-120 ºC) such as automotive lubricants, fire-resistant hydraulic fluids, jet engine oils and metal working and quenching fluids [4] during which lubricant performance may go down significantly by polymerization or by evolution of undesirable compounds [5]. Likewise, oxidative degradation has been identified as an important constraint for lubricants in service and accounts for multiple problems [6].

A lubricant with poor thermo-oxidative stability is susceptible to oxidation when exposed to air or high temperature machine environment during application. Thermo-oxidative degradation results in increased acidity and viscosity, base oil decomposition, additive depletion, sludge formation, filter plugging, oil darkening, rapid aging, reduced shelf life and machine corrosion [6], which severely dampen the desired lubricating performance. Factors such as heat, light, water, metal catalysts and acids increase the oxidation process [7]. To avert all these problems, a lubricant should possess superior thermo-oxidative stability [6].

All vegetable oils are essentially glyceryl esters of fatty acids called triglycerides or triacylglycerols containing saturated and unsaturated carbon chain in fatty acid structure. Unsaturated carbon-carbon double bonds (C=C) in the oleic (C18:1), linoleic (C18:2) and linolenic acid (C18:3) moieties in a triglyceride molecule are susceptible to different oxidation reactions. Saturated fatty acids exhibit comparatively high oxidative stability, which decreases with increasing unsaturation in the fatty acid chain. Other factors affecting the oxidation stability of vegetable oils are fatty acid chain length and the presence of bis-allylic protons [8]. Oxidative degradation of vegetable oils leads to formation of polar oxy compounds through successive initiation, propagation, branching and termination reactions [9]. The auto-oxidation usually culminates in an insoluble sludge formation and increase in oil viscosity, acidity, rancidity, volatility and corrosion [10].

The auto-oxidation mechanism of vegetable oils has been studied substantially by several researchers. A partial list includes Frankel [11-13], Porter *et al*. [14], Angelo [15], Wasowicz *et al*. [16], Schneider [17], Nie [7], Salimon *et al*. [18], Salih *et al*. [8], Králová [19], Ahmed *et al*. [20] and Ghnimi *et al*. [21]. A conventional representation of the mechanism is shown in Fig. 1.

Initiation	RH	$\xrightarrow{\textit{Initiator}}$	R• + H•
Propagation	R• + O_2	$\overset{\textit{Fast}}{\longleftrightarrow}$	ROO•
	ROO• + RH	$\xrightarrow{\textit{Slow}}$	ROOH + R•
Branching	ROOH	→	RO• + OH•
	RO• + RH + O_2	→	ROH + ROO•
	OH• + RH + O_2	→	H_2O + ROO•
Termination	ROO• + ROO•	→	ROOR + O_2
	ROO• + R•	→	ROOR
	R• + R•	→	R-R
Peroxide decomposition	ROOH	→	Multiple low molecular weight compounds
Peroxide polymerization	ROOH	→	Multiple high molecular weight compounds

Extrinsic factors = Light, water, oxygen
Intrinsic factors = Metal catalysts, acids, heat
RH = unsaturated fatty acid molecule of triglyceride, R• = free fatty acid radical, H• = free hydrogen radical, ROO• = peroxy radical, RO• = alkoxy radical, OH• = hydroxyl radical, ROH = alcohol molecule, ROOH = fatty acid hydrogen peroxide.

Fig. 1. Auto-oxidation mechanism of vegetable oils

Thermogravimetric analysis (TGA) has been effectively applied for long to determine the thermal stability behaviours of polymers and oils [4], but its application to lubricating oils is comparatively new [1]. TGA is a fast, reliable and low-cost technique applied for thermal stability analysis of oil by measuring the changes in its weight and enthalpy as a function of temperature and heating rate [4,22]. Besides, TGA has the advantage of being a highly precise and sensitive technique requiring only a small amount of sample [1]. Differential scanning calorimetry (DSC) is a relatively simple but effective thermo-analytical technique that is used for analyzing the effect of temperature on the material properties. DSC is capable of generating reproducible results on multiple analyses of given test material [23]. The peaks in a DSC thermogram indicate the physico-chemical changes occurring in a test sample during the course of heating or cooling [24]. The exothermic peaks represent chemical decomposition and oxidation of material, whereas the endothermic peaks represent the physical properties such as melting and boiling of material [18]. Rancimat test is an established method to determine the oxidation stability of oil products. Researchers have investigated the thermo-oxidative behaviours of variety of vegetable oils and their derived alkyl and polyol esters [2,4,22-33]. These studies found that the vegetable oils with more saturation in fatty acid structure show better oxidative stability.

The main objective of this study was to investigate the thermo-oxidative stability of non-edible karanja oil derived triester lubricant. Such studies are essential to ascertain the application of synthesized product at high-temperature operating conditions. Kinetic study was performed to evaluate the rate of thermal degradation, activation energy and frequency factor.

EXPERIMENTAL

Karanja oil trimethylolpropane ester (KOTMPE) biolubricant was synthesized from non-edible karanja oil *via* esterification and transesterification protocols. The details can be found elsewhere in previous works of Sharma *et al*. [34,35]. The thermal stability behaviour of KOTMPE was analyzed by Mettler Toledo TGA instrument, whereas the oxidation stability was determined using Rancimat instrument as per EN 14112 standard method.

Thermogravimetric analysis: Thermogravimetric analysis of KOTMPE was performed in computer controlled Mettler Toledo TG/SDTA851e model thermo gravimetric analyzer in non-isothermal mode. Sample size of around 42 mg was taken in an open alumina pan and heated in inert nitrogen atmosphere. The conventional heating rate of 10 ºC/min was followed in the study and temperature was varied from room temperature to 800 ºC with nitrogen flow rate of 50 mL/min. The resulting TGA curve was used to analyze the onset and offset temperatures of the test sample. The TGA degradation onset temperature specifies the resistance of the sample against thermal degradation and is determined by extrapolating the horizontal baseline of TGA curve at 1 % degradation and the intercept of this line with tangent to the downward portion of the curve. The higher onset temperature for product decomposition indicates the higher thermal stability. The maximum decomposition temperature approximates the temperature at which the maximum weight loss in the sample occurred [36].

Oxidative stability analysis: The oxidation stability of KOTMPE was measured in terms of induction period expressed in units of time (h) evaluated according to EN 14112 standard test method using Metrohm 893 Rancimat equipment. A schematic diagram of the test procedure is shown in Fig. 2. Test sample of 3 g KOTMPE was taken in a glass reaction vessel kept at 110 ºC constant heating block temperature. The oxidation was stimulated by passing a stream of purified air at a constant flow rate of 10 l/h through the sample. The volatile organic acids released during the oxidation process, along with air stream, were passed to the measuring vessel containing 50 mL of deionized water and an electrode for measuring the solution conductivity. The electrode was connected to a computer controlled measuring and recording device. The accumulation of organic acids in deionized water increased the solution conductivity. The continuous measurement of the solution conductivity over time gave an oxidation curve. The point of inflection at oxidation curve is called the induction period (IP) or oxidative stability index (OSI). The end of the induction period was characterized with rapid increase in solution conductivity that was caused by dissociation of volatile organic acids produced in the oxidation process and their absorption in deionized water [22,27,37].

Kinetic analysis: The data obtained from non-isothermal thermogravimetric analysis of KOTMPE biolubricant were used to study the kinetics of thermal degradation of test biolubri-

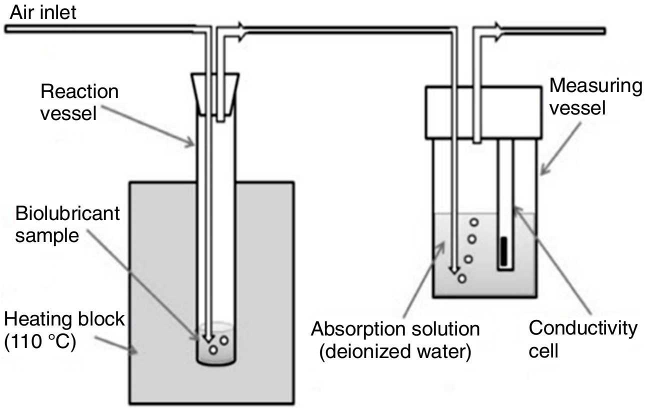

Fig. 2. Rancimat test method

cant under heating rate of 10 ºC/min and nitrogen flow rate of 50 mL/min.

The rate of thermal degradation (dx/dt) for biolubricant is given as follows:

$$\frac{dx}{dt} = kf(x) = k(1-x)^n \tag{1}$$

where n is the order of thermal degradation, k is the degradation rate constant, and x is the fractional weight loss given as follows:

$$x = \frac{w_o - w_t}{w_o - w_\infty} \tag{2}$$

where w_o, w_t and w_∞ are the initial, present and final weights of biolubricant sample, respectively.

Based on TGA thermogram (Fig. 3), thermal degradation of biolubricant was found to be of the first order, *i.e.* n = 1. The equation (1) now becomes

$$\frac{dx}{dt} = k(1-x) \tag{3}$$

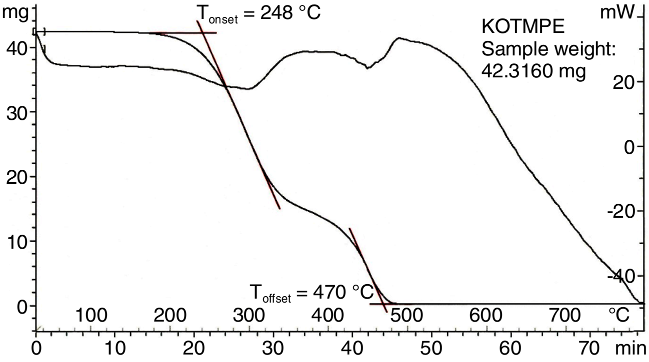

Fig. 3. TGA/DSC thermogram of KOTMPE in N_2 atmosphere

Now for non-isothermal analysis, eqn 3 is modified to include the biolubricant heating rate.

$$\frac{dx}{dT}\cdot\frac{dT}{dt} = k(1-x) \tag{4}$$

where dT/dt is the biolubricant heating rate expressed as B for the sake of simplification.

The degradation rate constant k is expressed by the following Arrhenius equation.

$$k = A \exp(-E_a/RT) \tag{5}$$

where A is called the frequency factor and E_a is called the activation energy of the reaction. R is the ideal gas law constant (8.314 J/molK).

Substituting eqn 5 into eqn 4 gives

$$\frac{dx}{dT} = \frac{A}{B}\exp\left(\frac{-E_a}{RT}\right)(1-x)$$

or
$$\frac{1}{1-x}\frac{dx}{dT} = \frac{A}{B}\exp\left(\frac{-E_a}{RT}\right) \tag{6}$$

The eqn 6 is now rearranged to the form of a straight line equation (y = mx + c) to evaluate the non-isothermal kinetic parameters by the Arrhenius plot method.

$$\ln\left(\frac{1}{1-x}\frac{dx}{dT}\right) = \ln\frac{A}{B} - \frac{E_a}{RT}$$

or
$$\ln\left(\frac{1}{1-x}\frac{dx}{dT}\right) = \left(-\frac{E_a}{R}\right)\frac{1}{T} + \ln\frac{A}{B} \tag{7}$$

A plot of ln[1/(1-x)dx/dT] *versus* 1/T should give a straight line of slope $-E_a/R$, from which the kinetic parameters A and E_a can be easily calculated.

RESULTS AND DISCUSSION

Thermal analysis: TGA/DSC thermograms of KOTMPE in inert nitrogen atmosphere are shown in Fig. 3. It is clear that both thermograms exhibit two steps weight loss. TGA thermogram showed that 1% weight loss in KOTMPE sample occurred at 180.36 ºC. The 50 % weight loss came off at 312.53 ºC and 90 % weight loss took effect at 451.11 ºC. The onset and the offset decomposition temperatures were graphically obtained at 248 and 470 ºC, respectively. The maximum decomposition temperature cropped up at 445.73 ºC with 0.07448 mg weight loss. The temperature plateau starting at 485.69 ºC showed no further significant weight loss.

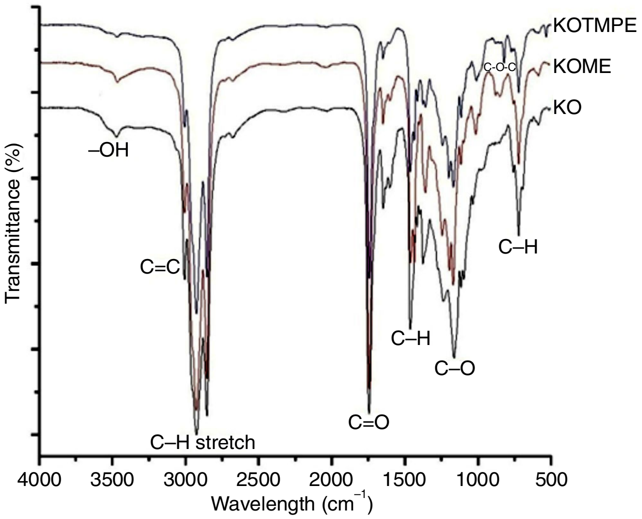

Fig. 4. FTIR spectra of KO, KOME and KOTMPE

Table-1 shows the experimental values of T_{onset} in nitrogen environment obtained in current study on KOTMPE biolubricant base oil and from similar studies carried out by other researchers with different lubricants samples.

TABLE-1
THERMAL STABILITY ANALYSIS OF KOTMPE

Sample	T_{Onset} in nitrogen (°C)*	Ref.
KOTMPE biolubricant base oil	248	Present study
WCOME epoxide	187	[38]
Servo hydraulic lubricant	260	[2]
COME epoxide	340	[2]

*Heating rate 10 °C/min

The weight loss profile for KOTMPE is given in Table-2. Nik *et al*. [4] suggested that the changes in specimen weight may be due to formation and disintegration of the physical and chemical bonds at elevated temperatures. Table-2 shows a marked difference in thermal stability of test biolubricant at 50 % weight loss and onwards. This behaviour is accredited to removal of unsaturated bonds in fatty acid chains of KOTMPE, which lead to improved thermal stability of polyol triester [2].

TABLE-2
WEIGHT LOSS DATA OF KOTMPE UNDER N_2 ATMOSPHERE

Heating rate (°C/min)	Temperature for weight loss (°C)			
	1 %	10 %	50 %	90 %
10	180	241	312	451

The improved thermal stability of KOTMPE was confirmed by the presence of ester group in polyol triester as confirmed by FTIR spectroscopy. Karanja oil methyl ester (KOME) reacted with trimethylol propane (TMP) using sulphuric acid as catalyst produced polyol triester and water as byproduct. FTIR spectra of karanja oil (KO), KOME and KOTMPE are shown in Fig. 4. The FTIR peaks at 3473 and 3464 cm^{-1} in spectra of KO and KOME belong to alcohol group (-OH) (3500-3100 cm^{-1}) stretching, respectively. The absence of alcohol group in KOTMPE spectrum indicated the completion of esterification reaction [38]. The peaks at wavelength 3006 cm^{-1} belonged to aliphatic C=C double bond bending vibration, whereas the peaks at 2925-2854 cm^{-1} indicated the stretching vibration of aliphatic CH_2 and CH_3 in three test samples. The peaks at 1746-1743 cm^{-1} indicated the stretching vibration of ester carbonyl (C=O) in fluids. The complete disappearance of C=C double bonds at 1604 cm^{-1} in karanja oil and appearance of C-O-C bands in KOME and KOTMPE at 852 and 822 cm^{-1}, respectively signified that most of the double bonds in feed were converted. The peaks at 1196 and 1201 cm^{-1} in the spectra of KOME and KOTMPE, respectively showed the C-O bond as the result of ester formation. The peaks at 1118 and 1116 cm^{-1} of KO, KOME and KOTMPE were referred to as C-O stretching ester. The spectra also displayed absorption bands at 723 cm^{-1} characteristic of aliphatic C-H group vibration [39]. The esterification rate calculated by acid values of the system before and after the reaction showed 87.35 % conversion [4].

Oxidative stability: European standards for biodiesel, EN 14213 for domestic heating fuel and EN 14214 for automotive diesel fuel, required that Rancimat induction period for the test fuels at 110 °C should be greater than or equal to 4 and 6 h, respectively [40]. Rancimat induction period of synthesized KOTMPE biolubricant at 110 °C was determined to be 6 h. Table-3 shows the experimental data on Rancimat induction period of KOTMPE carried out in present study along with data available in literature from similar studies with other vegetable oils.

TABLE-3
RANCIMAT INDUCTION PERIOD OF SOME VEGETABLE OIL DERIVED SAMPLES

Sample	Rancimat IP (h)	Ref.
Karanja oil TMP ester	6.0	Present study
Corn oil TMP ester	7.2	[7]
Sunflower oil methyl ester	0.61	[41]
Pongamia oil methyl ester	1.83	[22]
Soybean oil methyl ester	3.3	[41]
Sesame/Mustard methyl ester (B50)	5.48	[37]
Canola oil methyl ester	7.1	[41]
Jatropha oil	7.34	[42]
Partially hydrogenated palm oil	22.8	[43]
Refined jojoba oil	31.4	[44]
Crude jojoba oil	34.5	[44]
Refined meadowfoam oil	67.3	[44]
Crude meadowfoam oil	246.9	[44]

Researchers found that fatty acid methyl esters and subsequent trimethylol propane esters were less stable than parent vegetable oils. The lower stability of methyl ester molecules was partly due to small size of methyl ester molecule (one-third of triacylglycerol molecule) and partly due to its less viscosity, whereas the lower stability of trimethylol propane ester was attributed to presence of excess methyl ester. Strong alkali catalysts used at high temperatures during the two-stage transesterification process added to low oxidation stability of fatty acid methyl esters and trimethylol propane esters [7]. Crude unrefined vegetable oils were more stable than refined oils due to presence of natural antioxidants like tocopherols in unrefined vegetable oils [45].

High unsaturation in fatty acid composition of vegetable oils is responsible for low thermo-oxidative stability and poor low-temperature properties [2]. However, the unsaturated fatty acids in vegetable oils are reported to display better lubrication characteristics than saturated fatty acids [43]. The hydroxyl groups present in vegetable oils are more susceptive to free radicals formation steering the oxidative degradation mechanism. Therefore, the oxidative stability of vegetable oils derived products increases with decreasing number of hydroxyl groups and increasing number of mid and end chain ester substituents in synthesized products [8].

Kinetics of thermal degradation: Fig. 5 presents the Arrhenius plot for KOTMPE biolubricant drawn from non-isothermal thermogravimetric analysis data. Fig. 5 depicts a linear relationship between ln[1/(1-x)dx/dT] and 1/T characterizing the thermal degradation of test biolubricant as a first order reaction. For this sample, the activation energy and the frequency factor were calculated to be 97.27 kJ/mol and 1.35 × 10^9 min^{-1}, respectively. The study shows that the synthesized KOTMPE biolubricant has good thermal stability even without additives.

Conclusion

Thermo-oxidative stability of synthesized KOTMPE biolubricant was determined using TGA and EN 14112 Rancimat standard test method. A sample size of 42.3160 mg was taken

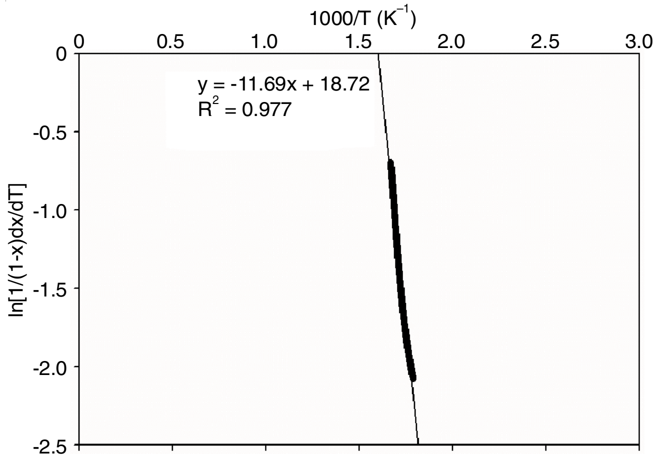

Fig. 5. Arrhenius plot for thermal degradation of KOTMPE biolubricant

and thermal analysis was conducted at a heating rate of 10 ºC/min from room temperature to 800 ºC in inert nitrogen atmosphere at supply rate of 50 mL/min. Present study also revealed that 1, 50 and 90 % weight loss in synthesized biolubricant took effect at 180.36, 312.53, and 451.11 ºC, respectively. The onset and offset decomposition temperatures appeared at 248 and 470 ºC, respectively, whereas the maximum decomposition temperature cropped up at 445.73 ºC with 0.07448 mg weight loss. The high thermal stability of synthesized product was accredited to absence of unsaturated bonds in fatty acid chains of KOTMPE as confirmed by FTIR spectrum. The oxidative stability of biolubricant was figured at 6 h, according to Rancimat test method that was within the prescribed limit for vegetable oils derived products. The kinetics of non-isothermal degradation of biolubricant was also evaluated in this study. The thermal degradation was found to be of the first order with activation energy of 97.27 kJ/mol and the frequency factor of 1.35×10^9 min^{-1}. The study affirmed the TGA as a quick and reliable analytical technique for thermal stability analysis of biolubricants. The thermo-oxidative stability of synthesized biolubricant was found quite satisfactory that can be improved further by addition of suitable additives depending on end use of finished product.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. N.H. Jayadas, K.P. Nair and G. Ajithkumar, Proceedings of the World Tribology Congress III, vol. 1, p. 539 (2005).
2. V.B. Borugadda and V.V. Goud, *Energy Procedia*, **54**, 75 (2014); https://doi.org/10.1016/j.egypro.2014.07.249.
3. C. Liu, J. Liu, L. Ma and L. Rong, *J. Chem.*, **2014**, 802732 (2014); https://doi.org/10.1155/2014/802732.
4. W.B. Wan Nik, F.N. Ani and H.H. Masjuki, *Energy Convers. Manage.*, **46**, 2198 (2005); https://doi.org/10.1016/j.enconman.2004.10.008.
5. P.K. Sripada, M.Sc. Thesis, University of Saskatchewan, Saskatoon: Canada (2012).
6. N. Salih, J. Salimon, B.M. Abdullah and E. Yousif, *Arab. J. Chem.*, **10**, S2273 (2017); https://doi.org/10.1016/j.arabjc.2013.08.002.
7. J. Nie, M.Sc. Thesis, University of Saskatchewan, Saskatoon: Canada (2012).
8. N. Salih, J. Salimon, E. Yousif and B.M. Abdullah, *Chem. Cent. J.*, **7**, 128 (2013); https://doi.org/10.1186/1752-153X-7-128.
9. N. Salih, J. Salimon and E. Yousif, *Ind. Crops Prod.*, **34**, 1089 (2011); https://doi.org/10.1016/j.indcrop.2011.03.025.
10. Z. Liu, B.K. Sharma, S.Z. Erhan, A. Biswas, R. Wang and T.P. Schuman, *Thermochim. Acta*, **601**, 9 (2015); https://doi.org/10.1016/j.tca.2014.12.010.
11. E.N. Frankel, *Prog. Lipid Res.*, **19**, 1 (1980); https://doi.org/10.1016/0163-7827(80)90006-5.
12. E.N. Frankel, *J. Am. Oil Chem. Soc.*, **61**, 1908 (1984); https://doi.org/10.1007/BF02540830.
13. E.N. Frankel, *J. Sci. Food Agric.*, **54**, 495 (1991); https://doi.org/10.1002/jsfa.2740540402.
14. N.A. Porter, S.E. Caldwell and K.A. Mills, *Lipids*, **30**, 277 (1995); https://doi.org/10.1007/BF02536034.
15. A.J. St. Angelo, J. Vercellotti, T. Jacks and M. Legendre, *Crit. Rev. Food Sci. Nutr.*, **36**, 175 (1996); https://doi.org/10.1080/10408399609527723.
16. E. Wasowicz, A. Gramza, M. Hes, H.H. Jeleñ, J. Korczak, M. Malecka, S. Mildner-Szkudlarz, M. Rudziñska, U. Samotyja and R. Zawirska-Wojtasiak, *Pol. J. Food Nutr. Sci.*, **13/54**, 87 (2004).
17. C. Schneider, *Mol. Nutr. Food Res.*, **53**, 315 (2009); https://doi.org/10.1002/mnfr.200800131.
18. J. Salimon, N. Salih and E. Yousif, *Ind. Crops Prod.*, **38**, 107 (2012); https://doi.org/10.1016/j.indcrop.2012.01.019.
19. M. Králová, *Maso Int. J. Food Sci. Technol.*, **2**, 125 (2015).
20. M. Ahmed, J. Pickova, T. Ahmad, M. Liaquat, A. Farid and M. Jahangir, *Sarhad J. Agric.*, **32**, 230 (2016); https://doi.org/10.17582/journal.sja/2016.32.3.230.238.
21. S. Ghnimi, E. Budilarto and A. Kamal-Eldin, *Compr. Rev. Food Sci. Food Saf.*, **16**, 1206 (2017); https://doi.org/10.1111/1541-4337.12300.
22. G. Dwivedi and M.P. Sharma, *Egypt. J. Pet.*, **25**, 33 (2016); https://doi.org/10.1016/j.ejpe.2015.06.008.
23. N.H. Jayadas and K.P. Nair, *Tribol. Int.*, **39**, 873 (2006); https://doi.org/10.1016/j.triboint.2005.06.006.
24. S. Rani, M.L. Joy and K.P. Nair, *Ind. Crops Prod.*, **65**, 328 (2015); https://doi.org/10.1016/j.indcrop.2014.12.020.
25. A. Aravind, M.L. Joy and K.P. Nair, *Ind. Crops Prod.*, **74**, 14 (2015); https://doi.org/10.1016/j.indcrop.2015.04.014.
26. C.J. Reeves, P.L. Menezes, T.C. Jen and M.R. Lovell, *Tribol. Int.*, **90**, 123 (2015); https://doi.org/10.1016/j.triboint.2015.04.021.
27. S. Jain and M.P. Sharma, *Fuel*, **93**, 252 (2012); https://doi.org/10.1016/j.fuel.2011.09.002.
28. V.B. Borugadda and V.V. Goud, *Waste Biomass Valoriz.*, **7**, 23 (2016); https://doi.org/10.1007/s12649-015-9434-8.
29. E.K. Heikal, M.S. Elmelawy, S.A. Khalil and N.M. Elbasuny, *Egypt. J. Pet.*, **26**, 53 (2017); https://doi.org/10.1016/j.ejpe.2016.03.003.
30. B.K. Sharma, A. Adhvaryu and S.Z. Erhan, *Tribol. Int.*, **42**, 353 (2009); https://doi.org/10.1016/j.triboint.2008.07.004.
31. M.B. Dantas, M.M. Conceicao, V.J. Fernandes Jr., N.A. Santos, R. Rosenhaim, A.L.B. Marques, I.M.G. Santos and A.G. Souza, *J. Therm. Anal. Calorim.*, **87**, 835 (2007); https://doi.org/10.1007/s10973-006-7780-2.
32. P. Chand, C.V. Reddy, J.G. Verkade, T. Wang and D. Grewell, *Energy Fuels*, **23**, 989 (2009); https://doi.org/10.1021/ef800668u.
33. L.M.S. Freire, T.C. Bicudo, R. Rosenhaim, F.S.M. Sinfrônio, J.R. Botelho, J.R. Carvalho Filho, I.M.G. Santos, V.J. Fernandes, N.R. Antoniosi Filho and A.G. Souza, *J. Therm. Anal. Calorim.*, **96**, 1029 (2009); https://doi.org/10.1007/s10973-009-0055-y.
34. U.C. Sharma, S. Sachan and R.K. Trivedi, *J. Oleo Sci.*, **67**, 105 (2018); https://doi.org/10.5650/jos.ess17140.
35. U.C. Sharma, S. Sachan and S. Sinha, *Asian J. Chem.*, **30**, 790 (2018); https://doi.org/10.14233/ajchem.2018.20997.
36. K.V. Padmaja, B.V.S.K. Rao, R.K. Reddy, P.S. Bhaskar, A.K. Singh and R.B.N. Prasad, *Ind. Crops Prod.*, **35**, 237 (2012); https://doi.org/10.1016/j.indcrop.2011.07.005.

37. A. Goyal, N.S. Hans, H.S. Paras and P.K. Yadav, *Int. J. Res. Appl. Sci. Eng. Technol.*, **5**, 2250 (2017); https://doi.org/10.22214/ijraset.2017.8323.
38. V.B. Borugadda and V.V. Goud, *J. Clean. Prod.*, **112**, 4515 (2016); https://doi.org/10.1016/j.jclepro.2015.06.046.
39. J. Salimon, N. Salih and B.M. Abdullah, *Int. J. Chem. Eng.*, **2012**, 896598 (2012); https://doi.org/10.1155/2012/896598.
40. S.R. Westbrook, National Renewable Energy Laboratory Subcontract Report NREL/SR-540-38983, NREL, Battelle, p. 22 (2005).
41. W.W. Focke, I. Westhuizen, A.B.L. Grobler, K.T. Nshoane, J.K. Reddy and A.S. Luyt, *Fuel*, **94**, 227 (2012); https://doi.org/10.1016/j.fuel.2011.11.061.
42. H.M. Mobarak, H.H. Masjuki, E.N. Mohamad, M.A. Kalam, H.K. Rashedul, M.M. Rashed and M. Habibullah, *Appl. Surf. Sci.*, **317**, 581 (2014); https://doi.org/10.1016/j.apsusc.2014.08.168.
43. B. Shomchoam and B. Yoosuk, *Ind. Crops Prod.*, **62**, 395 (2014); https://doi.org/10.1016/j.indcrop.2014.09.022.
44. T.A. Isbell, T.P. Abbott and K.D. Carlson, *Ind. Crops Prod.*, **9**, 115 (1999); https://doi.org/10.1016/S0926-6690(98)00022-3.
45. R.O. Dunn, *J. Am. Oil Chem. Soc.*, **82**, 381 (2005); https://doi.org/10.1007/s11746-005-1081-6.