Preparation and properties of bio-lubricants of neopentylglycol esters from various acids

Lakkoju Babi and Vemulapalli Vandana*
Department of Chemistry, GITAM Institute of science, GITAM (Deemed to be University), Visakhapatnam-530045, INDIA
*taarush@gmail.com

Abstract

In this work, two different neopentyl glycol (NPG) esters have been synthesized from NPG with 10-undecylenic acid (UDA) and calophyllum fatty acid (CFA) by the esterification process by using para toluene sulfonic acid as a catalyst. The esterification reaction progress has been determined by collecting measured water by using the Dean Stack apparatus.

The prepared ester structures have been characterized by NMR, IR and the general physico-chemical behaviors such as density, viscosity, flash point, pour point and copper strip corrosion were determined. Moreover, these prepared ester properties have been compared to commercial ISO VG grade lubes.

Keywords: Neopentyl glycol, esterification, physico-chemical behavior.

Introduction

Lubricants are identified as a friction reducer between contacting metal surfaces. Lubricants are essential for all machinery works for the entire world. We knew that all types of lubricants were prepared/extracted from crude petroleum oils. The overutilization of lubricants leads to decreases in the reserves of crude petroleum oil. Simultaneously, the crude oil prices are increasing at a rapid pace.[28] Mineral-based lubricants are environmentally unacceptable products due to their non-degradable and toxic nature.[1,23] These mineral-based lubricants have contaminated the air, soil and water source in the environment. The environmental concern is an urgent need to develop pollution-free and environmentally friendly lubricants as the alternative for mineral-based lubricants.[9]

Vegetable oils are the potential source to be an alternative for mineral oils due to their biodegradable, renewable and good lubrication performance.[4,26] Non-edible oils are potential renewable resources for making bio lubricants possessing numerous industrial applications, they offer better or at least the same performance as petroleum oil-based products besides being less expensive.[8]

Chemical modifications of various oils such as karanja oil,[6] pongamia oil,[5] castor esters,[14] soybean oil and high oleic sunflower oils[7] were reported to be excellent bio-lubricants.

Lubricant properties of vegetable oils were enhanced by converting them to various polyol esters. Polyol esters from vegetable oil have been produced in various ways.[11] Polyol esters synthesized are eco-friendly and biodegradable which are fire resistant and have good lubricating properties.[20] The polyol ester lubricants were derived from sal seed oil.[16]

Rubber fatty acid and thumba oil esters of alcohols 2-ethylhexanol, neopentyl glycol, trimethylolpropane and pentaerythritol are potential as hydraulic fluids.[15,17] Polyol esters of 10-undecenoic acid and undecanoic acid are potential lubricant base stock.[21] Rapeseed oil[22] and lard neopentyl glycol and trimethylolpropane esters showed higher thermo-oxidative stability due to the low content of polyunsaturated acids.[12] Pure synthetic esters of TMP-oleate and TMP-C_8-C_{10} exhibited high wear rates with a lot of abrasive marks on the surface in a sliding contact experiment.[27] Trimethylolpropane esters were prepared from jatropha methyl ester,[2,18] palm and palm kernel oil,[29,30] palm oil methyl ester,[31] rapeseed oil,[10] waste cooking oil fatty acid,[19] calophyllum inophyllum fatty acid,[3,24] by transesterification or esterification process.

Calophyllum inophyllum based TMP ester exhibited superior tribological properties and was used as a biodegradable lubricant.[13,24] In the present study, non-edible oil ester was showing better lubricant properties. Keeping this view, calophyllum inophyllum diol ester was developed and compared with synthetic diol ester from 10-undecylenic acid and commercial oils. NPG esters of CFA and UDA were synthesized as a renewable lubricant base stock and evaluated for their basic lubricant properties.

Material and Methods

Raw materials: Neopentyl glycol (NPG), 10-undecylenic acid (UDA), calophyllum fatty acid (CFA), para toluene sulfonic acid (pTSA), toluene, hexane, ethyl acetate, anhydrous sodium sulfate, sodium bicarbonate and silica gel were used directly without further purification.

Spectral methods

Infrared (IR) spectral analysis: The prepared neopentylglycol esters were analyzed by 1600 FT-IR Perkin-Elmer spectrometer, Norwalk, CT. The liquid sample was analyzed.

^{1}HNMR spectral analysis: The prepared neopentylglycol esters were analyzed by Brucker-Avance 400 MHz proton nuclear magnetic resonance (^{1}HNMR) spectrometer in $CDCl_3$. Chemical shift relative to TMS as internal standard is given as δ value in ppm.

Physico-chemical and lubricant behavior of synthesized esters: The physico-chemical behaviors of synthesized NPG esters were determined by standard AOCS and ASTM methods as follows:

Physico-chemical characteristics	
Density (according to pycnometer) at	25 ^{0}C
Acid value	AOCS Cd 3d -63
Kinematic viscosity (cSt) at	40 ^{0}C 100 ^{0}C
This method was carried out according to ASTM D 445	
Flash point (^{0}C) according to Fire point (^{0}C) according to	ASTM D 92 ASTM D 92
Cloud point (^{0}C) according to Pour point (^{0}C) according to	ASTM D 2500 ASTM D 97
Copper strip corrosion	ASTM D 130
Viscosity index (VI)	ASTM D 2270

Experimental methods

Calophyllum inophyllum oil extraction: 500 g of finely powdered calophyllum dried kernels were extracted using a Soxhlet extractor with hexane (1500 mL) as a solvent for 12 h at 60-65^{0}C. Hexane was removed under reduced vacuum after 12 h. 200 g crude calophyllum inophyllum oil was obtained by drying under reduced pressure. The crude oil was used directly without further purification and its physicochemical and basic lubricant properties were evaluated.

Preparation of Calophyllum fatty acid (CFA): 54 g of NaOH in 675 mL of water and 300 g of calophyllum inophyllum were taken in a beaker, stirred continuously for four hours at 80-90 ^{0}C. The reaction continued until the triglyceride spot disappeared under TLC monitoring [(hexane and ethyl acetate (90:10 v/v) as mobile phase)]. After that the reaction mixture was cooled and neutralized with concentrated HCl, extracted with ethyl acetate and washed twice with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. 270 g of calophyllum fatty acid (CFA) was obtained.

The fatty acid composition of calophyllum inophyllum oil was analyzed by gas chromatography (GC) by converting fatty acid to its methyl ester. 5 g of calophyllum inophyllum oil and sodium methoxide (0.05 g, 1% weight of reactant) were dissolved in 15 mL of methanol and stirred continuously at 60-65^{o}C. The reaction was monitored by TLC using 9:1 v/v hexane: ethyl acetate as solvent. After completing the reaction, the solvent was removed by rota evaporator, neutralized with dilute HCl and extracted with ethyl acetate. The ethyl acetate layer was concentrated to afford 4.2 g of calophyllum inophyllum fatty methyl ester.

Preparation of the neopentyl glycol esters: In this study, two different NPG esters have been synthesized by esterification of NPG and acids like CFA and UDA. Following work conditions have been adopted:[19]

- Molar ratio: 1:2.5 (alcohol: acid).
- Temperature: 120-130 ^{0}C.
- Catalyst: 1% wt. (based on total reactants).
- Solvent: toluene (azotropic solvent).
- Time: 4-5 hr.

10-Undecylenic acid (UDA): A three-necked glass-reactor was fitted with a magnetic stirrer, Dean Stark apparatus and an effective cooling condenser. 70.6 g of NPG and 250 g of UDA were charged and 100ml toluene was added as a solvent. Catalyze the reaction with 3.2 g of pTSA (calculated on weight percentage of reactants). The reaction mixture has maintained the temperature at 120-130 ^{0}C. In the Dean Stark apparatus, the collected water was measured periodically checking TLC results in the reaction progress. The heating was stopped after the completion of the reaction and cooled to room temperature. To remove the toluene by rotary evaporator, the reaction mixture was washed twice with saturated $NaHCO_3$ solution and followed by water. The organic layer was dried over anhydrous Na_2SO_4 and dried under vacuum. Pure UDA based NPG ester was collected by silica gel column chromatography and characterized by spectral analysis.

Calophyllum fatty acid (CFA): A three-necked glass-reactor was fitted with a magnetic stirrer, Dean Stark apparatus and an effective cooling condenser. 30 g of NPG and 170 g of UDA were charged and 100 mL toluene was added as a solvent. Catalyze the reaction with 2 g of pTSA (calculated on weight percentage of reactants). The reaction mixture has maintained the temperature at 120-130 ^{0}C. In the Dean Stark apparatus, the collected water was measured periodically checking TLC results in the reaction progress. The heating was stopped after the completion of the reaction and cooled to room temperature. To remove the toluene by rotary evaporator. The reaction mixture was washed twice with saturated $NaHCO_3$ solution followed by water. The organic layer was dried over anhydrous Na_2SO_4 and dried under vacuum. Pure CFA based NPG ester was collected by silica gel column chromatography and characterized by spectral analysis.

Results and Discussion

Preparation of Calophyllum fatty acid: The seeds of calophyllum inophyllum were collected from GITAM (Deemed to be University) campus, dried and crushed to afford non-edible oil. Calophyllum oil was extracted with hexane as a solvent by the Soxhlet extraction process. The extracted crude oil was greenish-yellow with a disagreeable odor, rich in free fatty acid (high oleic and linoleic acid) composition and viscosity of 38.17 cSt at 40^{0}C. The oil got darkened during the storage Physico-chemical behavior[25] is shown in table 1.

Calophyllum fatty acid was synthesized by alkali hydrolysis of calophyllum oil. Thus, the obtained fatty acid was converted to their methyl esters and the fatty acid composition was determined by GC (Figure 1). Calophyllum inophyllum oil contains palmitic acid (15.23%), stearic acid

(15.93%), oleic acid (37.57%) and linoleic acid (27.78%) as tabulated in table 2.

Preparation of neopentylglycol esters: The acids like UDA (derivative of ricinoleic acid) and CFA (extracted from Calophyllum inophyllum) were used to prepare esters with NPG by esterification. Para toluene sulfonic acid was used to enhance the esterification reaction at 120-130 ^{0}C. The help of the Dean-Stark apparatus and toluene solvent simplifies the removal of water periodically which assures the irreversibility of the esterification reaction. The reaction progress was determined regularly by collecting the quantity of water and converting high polar acid to a less polar ester by checking TLC.

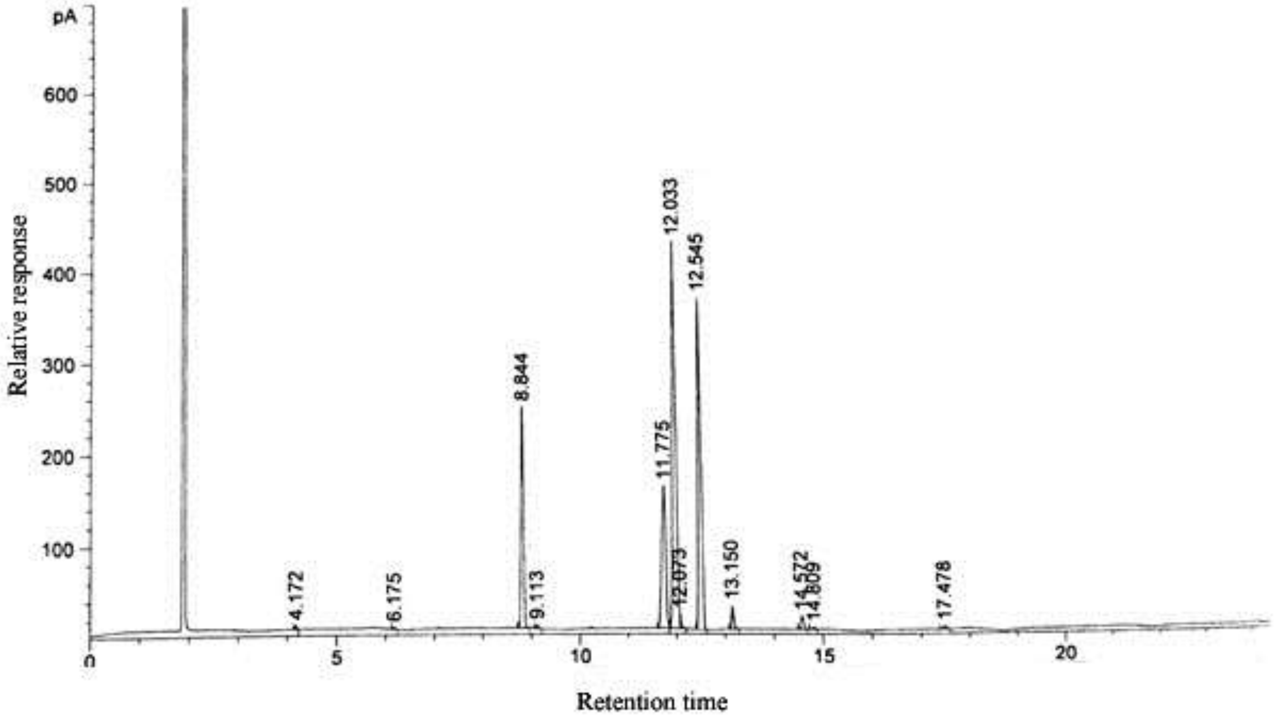


Figure 1: Gas Chromatography for fatty acid composition in Calophyllum inophyllum.

Table 1
Physico-chemical properties of Calophyllum inophyllum oil

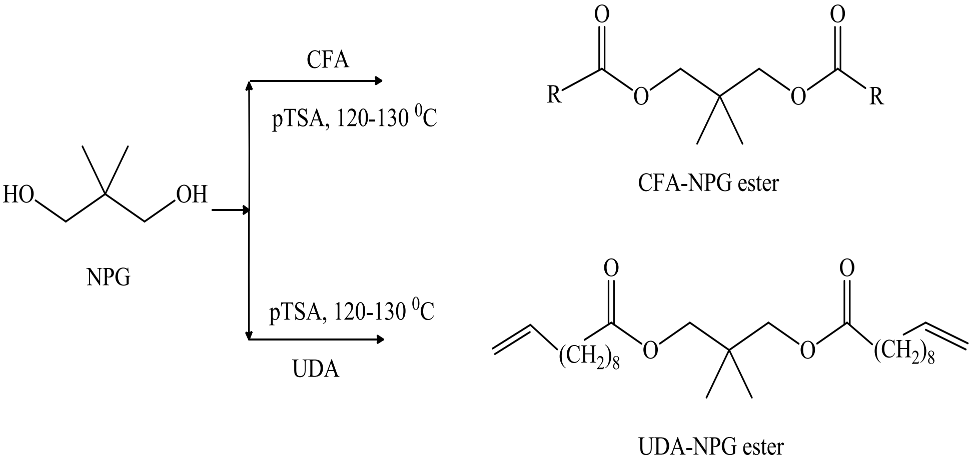
S.N.	Properties	Value
1	Color	Greenish-yellow
2	Odor	Disagreeable
3	Free fatty acid (mg KOH/g)	44
4	Acid number (mg KOH/g)	0.23
5	Density at 15°C (g/cc)	0.910
6	Specific gravity	0.935
7	Moisture (%)	0.35
8	Viscosity at 40°C (cSt)	38.17
9	Flash point (°C)	185
10	Fire point (°C)	189

Table 2
Fatty acid composition of Calophyllum inophyllum oil.

S.N.	Fatty acid	Composition (%)
1	Palmitic (16.0)	15.23
2	Stearic(18.0)	15.93
3	Oleic(18:1)	37.57
4	Linoleic(18:2)	27.78
5	Others	3.50
6	Saturated	31.16
7	Unsaturated	68.84

Table 3
The conversion of esterification reaction with time

Time (in hours)	CFA- NPG ester (% conversion)	UDA-NPG ester (% conversion)
1.0	38.5	45.3
2.0	49.6	54.1
3.0	56.4	66.2
4.0	78.5	82.7
5.0	89.1	93.5



Scheme 1: Preparation of NPG esters from various acids

The reaction's conversation efficacy was determined using a molar ratio of 1:2.5 (alcohol: acid), catalyst (1% wt per reactants) at 120-130 ^{0}C. Over 89% of the conversation was observed within the 4-5 h for prepared neopentyl glycol esters, as shown in table 3 and illustrated by figure 2. The heating was stopped after the completion of the reaction and cooled to room temperature. The rotary evaporator was used to get rid of toluene. The organic layer was washed twice with saturated $NaHCO_3$ solution followed by water. The organic layer was dried over anhydrous Na_2SO_4 and dried under vacuum. Pure neopentyl glycol esters were collected by silica gel column chromatography (Scheme 1).

The calculated average molecular weights of the CFA and UDA-NPG esters were 633.04 and 436.67 respectively. The CFA-NPG ester was having higher molecular weight, elemental density then UDA-NPG ester.

Spectra analysis: The synthesized neopentylglycol esters from oleic acid and 10-undecylenic acid samples were analyzed using ^{1}HNMR and IR techniques shown in table 4 and table 5. The absorption bands are recorded and represented in figures 2 to 5.

^{1}HNMR spectral analysis: From the table 4, figure 3 and figure 4, two peaks (0.9-1.0 ppm) with approximately the same area corresponding to the CH_3 of NPG esters appear in the ^{1}H NMR spectrum, which indicates that there are only two kinds of the chemical environment of H in synthesized compounds. The ^{1}H NMR spectrum of neopentylglycol esters exhibits a characteristic signal at 3.9-4.0 ppm which could be assigned to the O-CH_2 in the ester group. Moreover, there is a peak at 2.2-2.4 ppm representing the CO-C$\underline{H_2}$ group. It indicates for the ester linkage in CFA and UDA-NPG esters. The multiplet peaks were observed between 4.9-5.8 ppm in the NMR spectrum represent the C=CH which suggests unsaturation in the synthesized esters compounds.

IR spectral analysis: From the table 5, figure 5 and figure 6, the C-H stretching vibrations of the CH_3 group in CFA and UDA-NPG esters were observed at 2927 cm^{-1} and 2928 cm^{-1} respectively. Stretching vibrations of the CH_2 group of CFA and UDA-NPG esters were observed at 2855 cm^{-1} and 2856 cm^{-1} respectively. A medium intensity band of C-H stretching vibration was observed at 3005 cm^{-1} in case of CFA-NPG ester, 3077 cm^{-1} and 3021 cm^{-1} in case of UDA-NPG ester representing the alkene C-H group's stretching. The medium intensity absorption band was the observed region between 1600-1680 cm^{-1} representing the C=C stretching vibrations.

These two absorption bands indicate the presence of unsaturation in CFA and UDA-NPG esters. A very strong and sharp intensity absorption band was observed at 1736 cm^{-1} in case of CFA-NPG ester, 1741 cm^{-1} in case of UDA-NPG ester representing for the stretching vibration of C=O. A strong intensity absorption band was observed at 1214 cm^{-1} in case of CFA-NPG ester, 1168 cm^{-1} in case of UDA-NPG ester for C-O stretching vibration. These absorption bands represent the confirmation of the ester group.

Table 4
^{1}HNMR spectral analysis of NPG esters

Ester group assignment	CFA-NPG ester	UDA-NPG ester
1. CH_3, s	0.8-1.0 ppm	0.9-1.0 ppm
2. CH_2, m	1.2-1.7 ppm	1.2-1.7 ppm
3. $C=C-CH_2$ m	1.9-2.1 ppm	2.0-2.1 ppm
4. $CO-CH_2$, m	2.2-2.3 ppm	2.3-2.4 ppm
5. $O-CH_2$, s	4.1 ppm	3.9 ppm
6. CH=CH, m	5.3-5.4 ppm	4.9-5.1 and 5.7-5.9 ppm

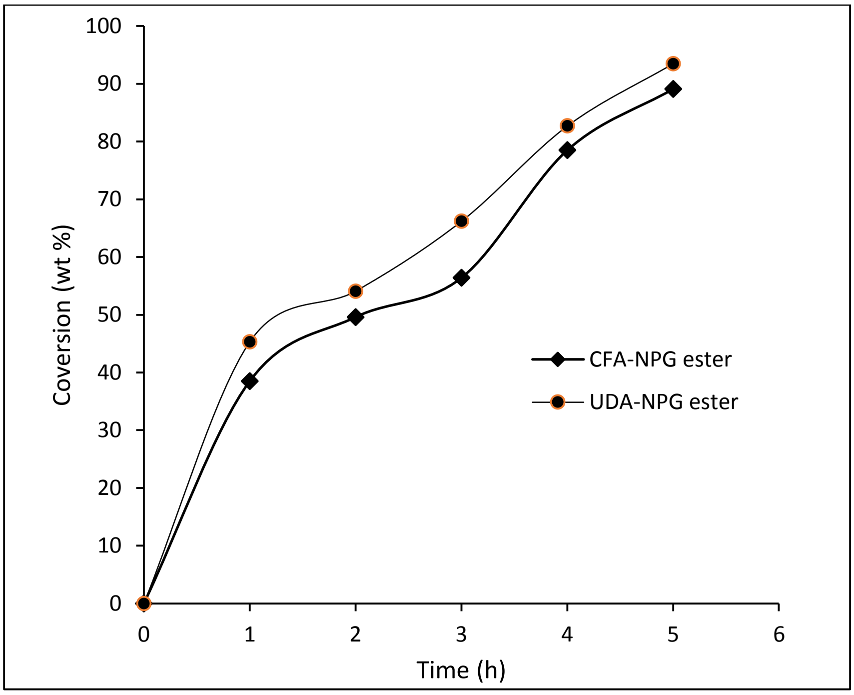


Figure 2: The conversion (collected water) versus esterification of the reaction time

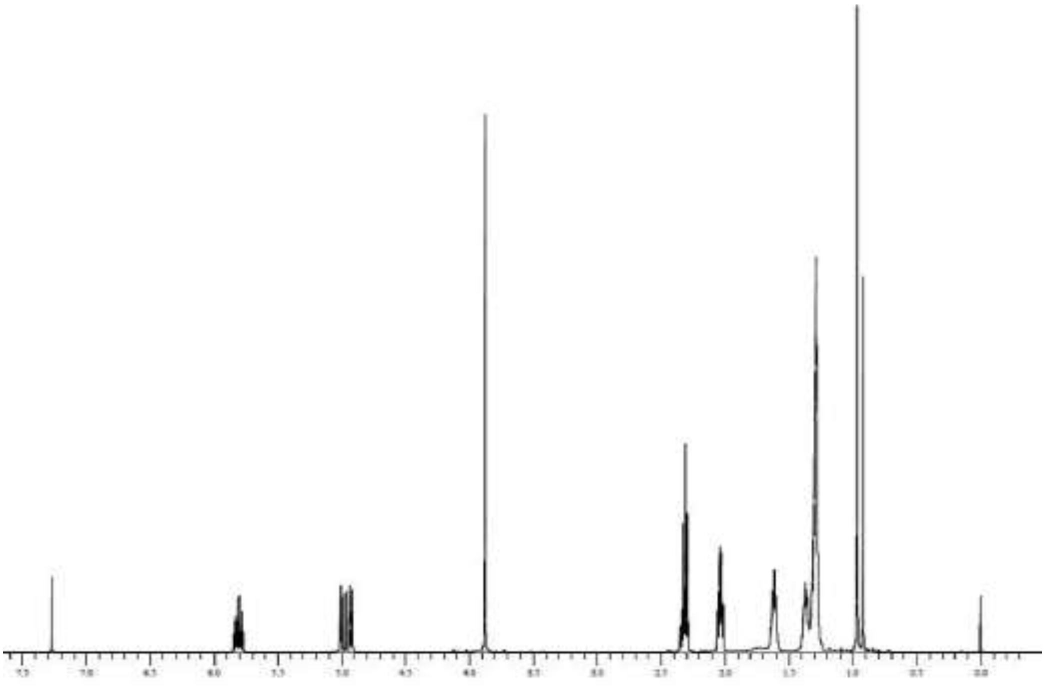


Figure 3: ^{1}HNMR of UDA-NPG ester.

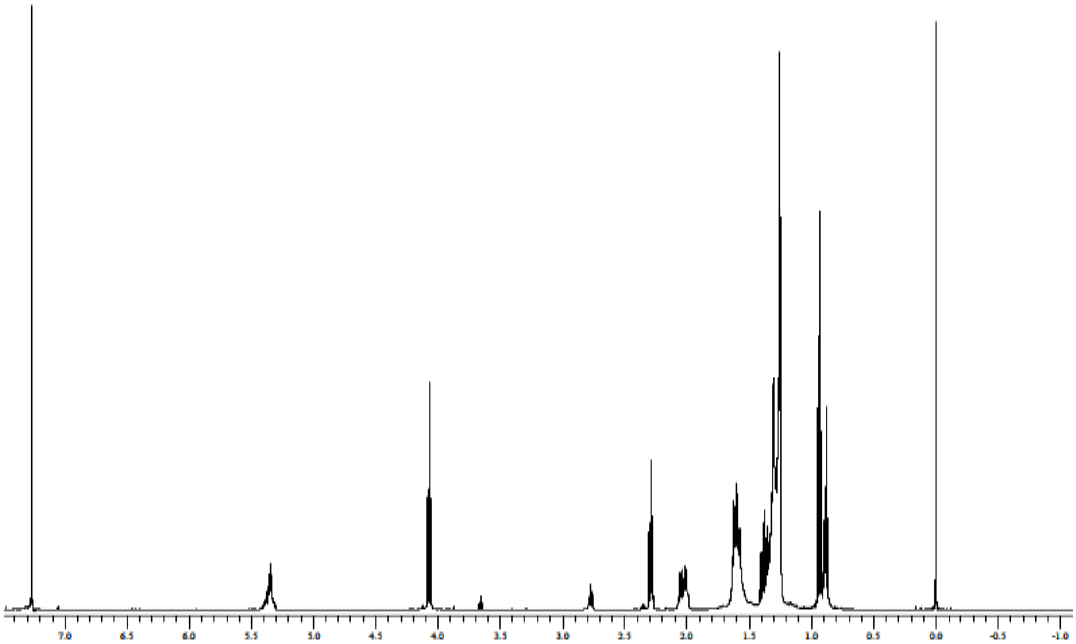


Figure 4: ^{1}HNMR of CFA-NPG ester.

Table 5
IR spectral analysis of neopentylglycol esters

Ester group assignment	CFA-NPG ester	UDA-NPG ester
1. C-H Str. Vib. a C=CH b. CH_3 c. CH_2	 3005 cm^{-1} 2927 cm^{-1} 2855 cm^{-1}	 3077 & 3021 cm^{-1} 2928 cm^{-1} 2856^{-1}
2. C-H Ben. Vib. c. CH_3 d. CH_2	1447 cm^{-1} 1369 cm^{-1}	1464 cm^{-1} 1379^{-1}
3. C=O Str. Vib.	1736 cm^{-1}	1741^{-1}
4C-O Str. Vib.	1214 cm^{-1}	1168 cm^{-1}

The ^{1}HNMR and IR spectral analysis represent for the structural conformation and ester formation of the CFA and UDA-NPG esters.

Physico- chemical aspects of synthesized esters: In this study, some of the physico-chemical and lubricant behaviors of the CFA and UDA-NPG esters were analyzed and compared with each other along with commercial oil like HP spindle oil. All properties were characterized and reported in table 6.

Density versus molecular weight: From the table 6, results indicate that the densities of NPG esters increase with molecular weight. It clearly illustrated that the linear relationship as shown in figure 7. UDA-NPG ester and CFA-NPG ester densities were 0.928 and 0.962 g/cm^3 respectively which offered better densities than HP spindle oils.

Kinematic viscosity: The viscosities of CFA and UDA-NPG esters were characterized at different temperatures at 40 ^{0}C and 100 ^{0}C. The viscosities at 40 ^{0}C are 13.65 and 10.51 cSt, at 100 ^{0}C are 3.96 and 3.31 cSt for CFA and UDA-NPG esters respectively. The kinematic viscosity was increasing linearly with an increase of density as well as molecular weight.

Table 6 and figure 8 indicate the linear relation between the kinematic viscosity, density and molecular weight of CFA and UDA-NPG ester. These viscosities matched the standard ISO grade oils VG 10 and 12.

The linear relation of synthesized esters was tested at different temperatures (40^0 and 100^{0}C). The variations of these viscosities at different temperatures are helpful to achieve viscosity index (VI) and it suggested the excellent lubricity of prepared esters. The viscosity index of prepared esters is showing better than the HP spindle oils.

Flash and fire points: Table 6 indicates that the flash and fire points of CFA-NPG ester (198 and 202 ^{0}C) were lower than UDA-NPG ester (254 and 263 ^{0}C). Due to their structural arrangement of unsaturation in the case of CFA-NPG ester, the doublet was present in the center of the carbon skeleton; at higher temperatures, it leads to the molecule breakdown. But in the case of UDA-NPG ester, the terminal unsaturation was present in its skeleton structure.

Cloud and pour points: The cloud and pour points of NPG esters were -3.8 and -16 ^{0}C for CFA-NPG ester, -8.4 and -35.5 ^{0}C for UDA-NPG ester respectively. CFA-NPG ester was showing a higher pour point due to its structural rigidity.

Finally, the prepared esters show a higher flash point and lower pour point than HP spindle oil and obese the ISO VG 10, 12 properties. Table 6 indicates that the prepared esters were less corrective, showing 1a on the copper strip corrosion test.

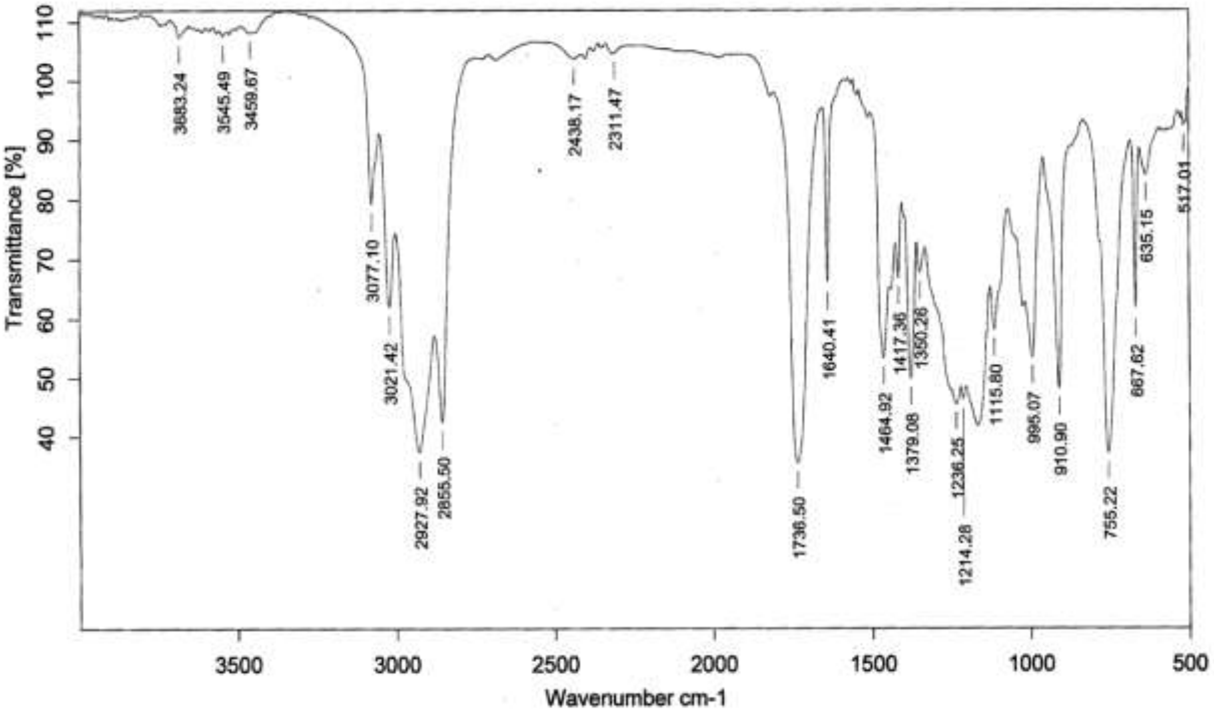


Figure 5: IR of UDA-NPG ester

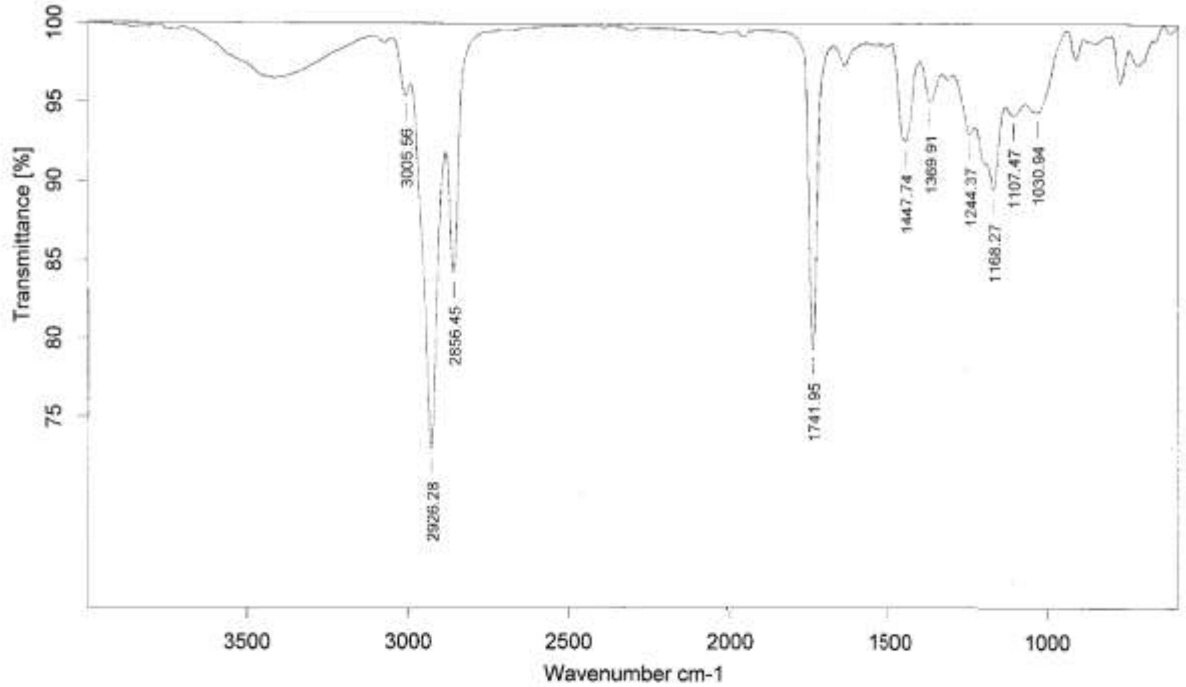


Figure 6: IR of CFA-NPG ester

In our observation the synthesized neopentylglycol esters from oleic acid and 10-undecenoic acids met the standard ISO VG 10 and 12 grade properties and showing better properties as compared to commercial oil of HP spindle oil like spintek (10 and 12) oils. These synthetic esters were recommended to textile industries as lubrication oil on machine and spindle bearing etc.

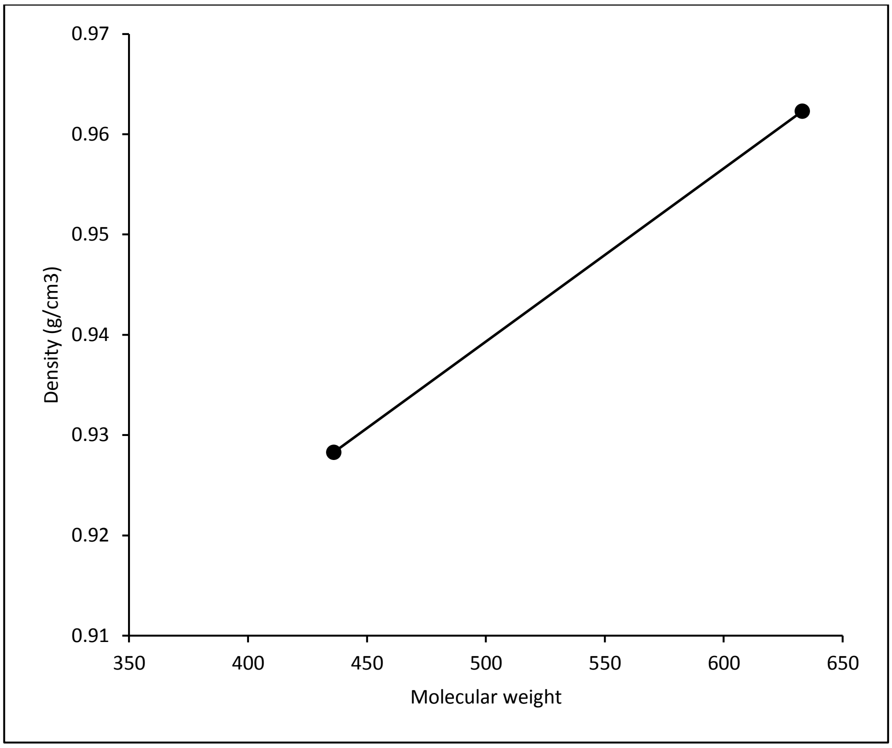


Figure 7: Density versus the molecular weight of NPG esters.

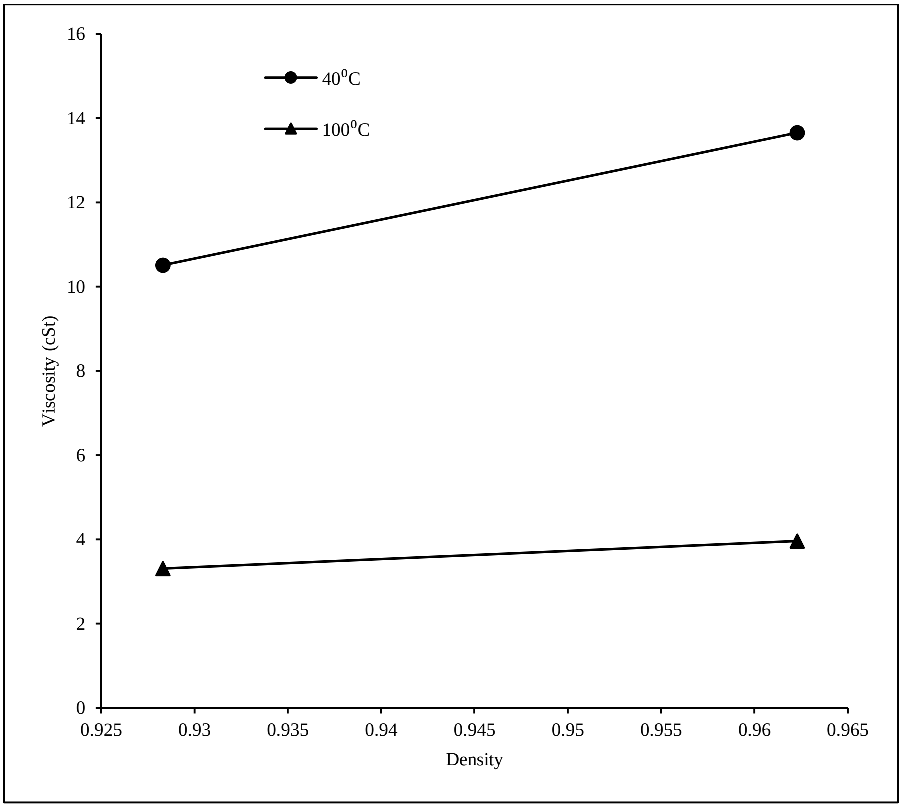


Figure 8: Kinematic viscosity versus density neopentylglycol esters

Table 6
Physico-chemical characteristics of neopentylglycol esters and compared to HP spindle oils

Properties	**Neopentylglycol esters**		**HP spindle oils**	
	CFA	**UDA**	**Spintek (VG -10)**	**Spintek (VG-12)**
Density (g/cm^3) 25 ^{0}C	0.9623	0.9283	0.860	0.860
Acid value (mg KOH/g)	0.20	0.31	-	-
Kinematic Viscosity				
at 40^{0}C (mm^2/s)	13.65	10.51	10	12
at 100^{0}C (mm^2/s)	3.96	3.31	-	-
Viscosity index (VI)	208.6	212.8	85	85
Flash point (^{0}C)	198	254	150	168
Fire point (^{0}C)	202	263	-	-
Cloud point (^{0}C)	-3.8	-8.4	-	-
Pour point (^{0}C)	-16	-35.5	-6	-6
Copper strip corrosion	1a	1a	-	-

Conclusion

Neopentylglycol dioleate and diundecenoate esters have been synthesized by opitumal esterification reaction conditions: molar ratio 1:2.5 (alcohol, acid), pTSA catalyst (1% wt based on reactents), temperature 120-130 ^{0}C and toluene. The reaction progress and convertion was determined by TLC and collecting of water. Over 89% of conversion was obtained in 4-5 h.

The structure has been characterized by molecular weight, elemental analysis, ^{1}HNMR and IR spectral analysis. Physico-chemical properties have been characterized by measuring density, acid value, kinematic viscosity (40, 100 ^{0}C), flash, fire, cloud, pour points and copper strip corrosion. These synthesized esters meet the standard ISO VG 10 and 12 grade properties and showing better properties as compared to commercial oil of HP spindle oil like spintek (10 and 12) oils. These synthetic esters were recommended to textile industries as lubrication oil on machine and spindle bearing etc.

Acknowledgement

We thank the Department of Chemistry, GITAM (Deemed to be University) for giving an opportunity to carry out research. This work was ostensibly supported by the Department of Science and Technology under the Technology System Development Programme (TSDP) Government of India, project no "DST/TSG/AF/2014/01". Department of Lipid Science and Technology, Hyderabad IICT is acknowledged for ^{1}H NMR, GC and IR spectral data.

References

1. Aluyor E.O. and Ori-Jesu M., Biodegradation of mineral oils–A review, *African Journal of Biotechnology*, **8(6)**, 915-920 **(2009)**

2. Arbain H.N. and Salimon J., Synthesis and characterization of ester trimethylolpropane based Jatropha curcas oil as bio lubricant base stocks, *Journal of Science and Technology*, **2(2)**, 47-58 **(2009)**

3. Atabani A.E., Irfan A.B., Mahlia T.M.I., Masjuki H.H. and Mofijur M., Fuel properties of croton megalocarpus, Calophyllum inophyllum and cocosnucifera (coconut) methyl esters and their performance in a multi cylinder diesel engine, *Energy Technology*, **1(11)**, 685-694 **(2013)**

4. Asadauskas S. and Erhan S.Z., Depression of pour points of vegetable oils by blending with diluents used for biodegradable lubricants, *J. Am. Oil Chem. Soc.*, **76(3)**, 313–316 **(1999)**

5. Bekal S. and Bhat N.R., Bio-lubricant as an alternative to mineral oil for a CI engine—an experimental investigation with pongamia oil as a lubricant, *Taylor & Francis Group, LLC, Energy Sources*, **34(11)**, 1016–1026 **(2012)**

6. Chauhan P.S. and Chhibber V.K., Chemical modification in karanja oil for bio lubricant industrial applications, *Journal of Drug Delivery and Therapeutics*, **3(3)**, 117-122 **(2013)**

7. Erhan S.Z. and Asadauskas S., Lubricant base stocks from vegetable oils, *Industrial Crops Production*, **11(2-3)**, 277–282 **(2000)**

8. Erhan S.Z., Brajendra K.S. and Joseph M.P., Oxidation and low temperature stability of vegetable oil-based lubricants, *Industrial Crops and Products*, **24(3)**, 292-299 **(2006)**

9. Erhan S.Z., Sharma B.K., Liu Z. and Adhvaryu A., Lubricant base stock potential of chemically modified vegetable oils, *Journal of Agricultural and Food Chemistry*, **56(19)**, 8919-8925 **(2008)**

10. Esauosukainen Yu-Yen L., Merja L., Tommi T. and Pekka L., Transesterification of trimethylol propane and rapeseed oil methyl ester to environmentally acceptable lubricants, *J. Am. Oil Chem. Soc.*, **75(11)**, 1557-1563 **(1998)**

11. Eychenne V., Mouloungui Z. and Gaset A., Total and partial erucate of pentaerythritol. Infrared spectroscopy study of relationship between structure, reactivity and thermal properties, *J. Am. Oil Chem. Soc*, **75(2)**, 293-299 **(1998)**

12. Gryglewicz S., Piechocki W. and Gryglewicz G., Preparation of polyol esters based on vegetable and animal fats, *Bio resource Technology,* **87(1)**, 35–39 **(2003)**

13. Habibullah M., Masjuki H.H., Kalam M.A., Gulzar M., Arslan A. and Zahid R., Tribological characteristics of Calophyllum inophyllum–based TMP (trimethylolpropane) ester as energy-

saving and biodegradable lubricant, *Tribology Transactions*, **58(6)**, 1002–1011 (**2015)**

14. José A.C.S., Alberto C.H. and Denise M.G.F., A potential biodegradable lubricant from castor biodiesel esters, *Lubrication Science*, **25(1)**, 53-61 **(2013)**

15. Kamalakar K., Prasad R.B.N. and Karuna M.S.L., Rubber seed oil-based biolubricant base stock: A potential source for hydraulic oils, *Industrial Crops and Products*, **51**, 249-257 **(2013)**

16. Kamalakar K., Mohini Y., Rao B.V.S.K., Karuna M.S.L. and Prasad, R.B.N., Sal fatty acid based bio lubricant base-stocks: A potential source for high temperature applications, *JLST*, **45(3)**, 79-85 **(2013)**

17. Kamalakar K., Saimanoj G.N.V.T., Prasad R.B.N. and Karuna M.S.L., Thumb (Citrulluscolocynthis L.) seed oil: a potential bio-lubricant base-stock, *Grasasy Aceites*, **66(1)**, e055 **(2015)**

18. Kamil N.M.R., Suzana Y. and Umer R., Optimization of polyol ester production by transesterification of Jatropha-based methyl ester with trimethylolpropane Taguchi design of experiment, *Fuel*, **90(6)**, 2343–2345 **(2011)**

19. Lakkoju B. and Vemulapalli V., Synthesis and characterization of triol based bio-lubricant from waste cooking oil, In AIP Conference Proceedings, AIP Publishing LLC, **2297(1)**, 020002 **(2020)**

20. Nagendramma P., Savita K. and Bisht R.P.S., Study of synthesized ecofriendly and biodegradable esters: fire resistance and lubricating properties, *Lubrication Science,* **22(3)**, 103-110 **(2010)**

21. Padmaja K.V., Rao B.V.S.K., Reddy R.K., Bhaskar P.S., Singh A.K. and Prasad R.B.N., 10-Undecenoic acid-based polyol esters as potential lubricant base stocks, *Industrial Crops and Products*, **35(1)**, 237– 240 **(2012)**

22. Paeglis T., Karabeško P., Mierin I., Seržane R., Stre¯le M., Tupureina V. and Jure M., Compostions of hydraulic fluids based on rapeseed oil and its derivatives, In 8th international scientific conference: Engineering for Rural Development, Jelgava, 171–175 **(2009)**

23. Soni S. and Agarwal M., Lubricants from renewable energy sources–a review, *Green Chemistry Letters and Reviews,* **7(4)**, 359-382 **(2014)**

24. Srinivas V., Chebattina K.R.R., Pranay G.V.S., Lakkoju B. and Vandana V., Tribological properties of polyol ester–commercial motorbike engine oil blends, *Journal of King Saud University-Engineering Sciences*, DOI: 10.1088/1757-899X/653/1/012013 **(2020)**

25. Vandana V., Kodanda R.R.C.H., Somnath G. and Babia L., Synthesis of Calophyllum inophyllum esters as biofuel feed stock, *JOJ Material Science*, **2(2)**, 555–583 **(2017)**

26. Waara P., Jesper H., Thomas N. and Åke B., Additive influence on wear and friction performance of environmentally adapted lubricants, *Tribology International*, **34(8)**, 547-556 **(2001)**

27. Waara P., Thomas N. and Braham P., Tribochemical wear of rail steels lubricated with synthetic ester-based model lubricants, *Tribology Letters*, **17(3)**, 561-568 **(2004)**

28. Willing A., Lubricants based on renewable resources–an environmentally compatible alternative to mineral oil products, *Chemosphere*, **43(1)**, 89-98 **(2001)**

29 Yunus R., Fakhru'l-Razi A., Ooi T.L., Iyuke S.E. and Idris A., Preparation and characterization of trimethylol propane esters from palm kernel oil methyl esters, *Journal of Oil Palm Research*, **15(2)**, 42-49 **(2003)**

30. Yunus R., Fakhru'l-Razi A., Ooi T.L., Iyuke S.E., Rozita O. and Idris A., Synthesis of palm oil based trimethylol propane esters with improved pour points, *Industrial Engineering Chem. Res*., **44(22)**, 8178-8183 **(2005)**

31. Yunus R., Fakhru'l-Razi A., Ooi, T.L., Idris A., Biak D.R.A. and Iyuke S.E., Kinetics of transesterification of palm-based methyl esters with trimethylol propane, *J. Am. Oil Chem. Soc*., **81(5)**, 497–503 **(2004)**.

(Received 10th February 2021, accepted 21st April 2021)