RESEARCHERID
THOMSON REUTERS

[Ahmed *et al.*, 5(11): November, 2018] ISSN 2349-0292
Impact Factor 3.802

GLOBAL JOURNAL OF ADVANCED ENGINEERING TECHNOLOGIES AND SCIENCES

SYNTHESIS OF SOME POLYOL ESTERS DERIVED FROM DIBASIC ACIDS AND THEIR EVALUATION AS SYNTHETIC LUBRICATING BASE OILS

Mohamed E. Haseeb, Ahmed M. Al-Sabbagh, Amal M. Nassar, Nehal S. Ahmed*, Ismail A. EL-Magly, Galal H. Sayed

* Department of Petroleum Applications, Egyptian Petroleum Research Institute, Egypt
Chemistry Department, Faculty of Science, Ain Shams University, Egypt

DOI: 10.5281/zenodo.1482332

ABSTRACT

The present work is generally directed to synthesis complex esters based on dibasic acids for lubricating oil. Eight complex esters were synthesized in two steps as two groups. In the first group two monoesters were prepared by reaction of malonic acid with amyl alcohol or 2-ethyl hexanol individually .The second group two monoesters were prepared based on adipic acid by the same reaction with the same alcohols. The four prepared monoesters were reacted with neopentyl glycol or trimethylol propane individually to prepare eight complex esters. The prepared complex esters were elucidated by using FTIR, H1-NMR and MS. The thermal stability of these esters was characterized by TGA. The optimum degree of esterification was followed by measuring (TAN). Evaluation of the prepared complex ester as synthetic lubricant was carried on the term of Viscosity Index(VI),Pour Point(PP) and Flash Point(FP) From the obtained data , it was found that some prepared complex esters exhibited the behavior of synthetic lubricating base oils. By comparing results of prepared complex esters and the commercial product, it was found that the complex esters achieved better values than commercial product in viscosity index, flash point and achieved the same values in pour point.

KEYWORDS: Synthetic lubricants, complex esters, thermal analysis, viscosity index, and pour point.

INTRODUCTION

The base oils may be divided into three types, one of them is mineral oils which are components obtained from petroleum crude oils after different types of refining, bio lubricants which are chemical modification of some vegetable oils and synthetic lubricants which are chemical products. The first true synthetic lubricants, derived from silicones and polyolefins were developed in the United States in the early 1930's. World War II accelerated synthetic lubricant development [1]. The current interest in synthetic lubricants follows from environmental regulations issued by international, federal and state bodies which stress bio degradability, non-toxicity, environmental friendliness and recyclability. In addition, equipment manufacturers are requiring lubricants with longer service lives, lower volatilities and increased energy efficiency; such lubricants are in some cases, required to function in more severe temperature and pressure regimes. Synthetic lubricants are chemical products obtained by chemical reaction of lower molecular weight to provide a fluid of suitable molecular weight designed to provide certain predictable properties. Examples include poly alpha-olefins, diesters, polyol esters and silicone fluids [2-4]. Additives are blended into the synthetic or mineral oil base fluids to impart properties needed for specific applications[5] . Synthetic base fluids are often well-defined materials. In formulated products they may offer: (utility over wide temperature ranges, good stability, long service life and unique performance traits). Synthetic lubricants have both desirable and undesirable properties. Hence, matching the correct lubricant with the intended application is important [6]. The wide variety of synthetic lubricants available in the market place attests to the fact that one type of synthetic lubricant will not work for all applications. Synthetic ester based lubricants are used in a large number of applications including, for example, automotive , aviation oils, refrigeration oils, metal working fluids, gear oils, turbo oils and hydraulic fluids [7-9]. In the present work eight complex esters should be synthesized by two steps the first step is to prepare mono esters via esterification reaction of malonic acid and adipic acid with amyl alcohol or 2-ethyl hexanol individually. The second step is to prepare the complex esters complex esters via esterification of each mono ester with neopentyl glycol or trimethylol propane individually .The lubricating performance of the prepared esters should be evaluated.

ISSN 2349-0292
Impact Factor 3.802

MATERIALS AND METHODS

Preparation of mono Esters.

Esterification has been carried out in a-Dean-Starck apparatus by reacting 1 mole of malonic acid or adipic acid with 1 mole of amyl alcohol or 2-ethyl hexanol individually. The reactions were carried out in a resin kittle in presence of 1 % amberlyst 15 as a catalyst, and xylene as an azeotropic solvent. Esterification reactions were carried out under a slow stream of deoxygenated nitrogen. The reaction was heated gradually to 160°C ± 5°C. The extent of reaction was followed by monitoring the amount of withdrawn water, to give four mono esters and designation are shown in Table 1.

Table 1. The Designation of Prepared Mono Ester

Designation	Prepared mono ester composition
MA	Malonic acid +amyl alchol
MH	Malonic acid+2-ethyl hexanol
AA	Adipic acid+amyl alchol
AH	Adipic acid+2-ethyl hexanol

Synthesis of Complex Esters.

Complex esters were prepared by esterficiation of the prepared mono esters with neopentyl glycol in the ratio (2 mole: 1 mole) or with trimethylol propane in the ratio (3 mole: 1 mole) .The reaction was carried out in a Dean-starck apparatus equipped with stirrer, efficient condenser ended by a trap of bottomed tap, thermometer, and an inlet for introduction of dry nitrogen. The percentage weight of catalyst 1 % Amberlyst 15 was charged. The reaction was heated gradually from the room temperature up to 160°C ± 5°C. The extent of reaction was followed by monitoring the amount of librated water using xylene as azeotropic agent, and then they were purified by washing with an aqueous solution of sodium carbonate(10% by weight) followed by washing several times with distilled water. The rotary evaporator was used under vacuum to get rid of xylene [10-11],to give eight complex esters and designation are shown in Table 2.

Table 2. The Designation of Prepared Complex Ester

Designation	Prepared complex ester composition
MAN	Malonic acid +amyl alchol+neopentyl glycol
MAT	Malonic acid +amyl alchol+trimethylol propane
AAN	Adipic acid +amyl alchol+neopentyl glycol
AAT	adipic acid +amyl alchol+trimethylol propane
MHN	Malonic acid+2-ethyl hexanol+neopentyl glycol
MHT	Malonic acid+2-ethyl hexanol+trimethylol propane
AHN	Adipic acid+2-ethyl hexanol+neopentyl glycol
AHT	Adipic acid+2-ethyl hexanol+trimethylol propane

The justification of these esters was predicted using FTIR, H1NMRand Mass Spectroscopy .The TGA was carried out for the prepared esters, to study their thermal stability. Otherwise the rheological properties were determined using Simultaneous Q-600 TGA (USA) to evaluate the flow properties of these esters. The total acid number was

determined to follow the degree of esterification reaction. The evaluation of these complex esters as synthetic lubricants was carried out and their results should be compared with commercially used materials.

RESULTS AND DISCUSSION

The compositions of the prepared monoesters were confirmed by F.T.I.R. spectroscopy. The spectrum in Fig.(1) for mono ester of AAT shows that; appearance of carboxylic acid band at around 1700 cm^{-1} and appearance of the ester group band at 1720±10 cm^{-1},the ether band appeared at 1250 ±100cm^{-1}.The band for methyl group that appears near 1370-1465 cm^{-1}The band for (-C-H) aliphatic appears near 2840 $cm^{-1}$and 2950 cm^{-1}.Apperance of broad band covering awide range between 2800$cm^{-1}$and 3500 cm^{-1} for the OH- stretch of carboxylic acid . Disappeare of the strong band at 3600 cm^{-1} indicates that all hydroxyl groups of alcohols were consumed in the esterification reaction [12]

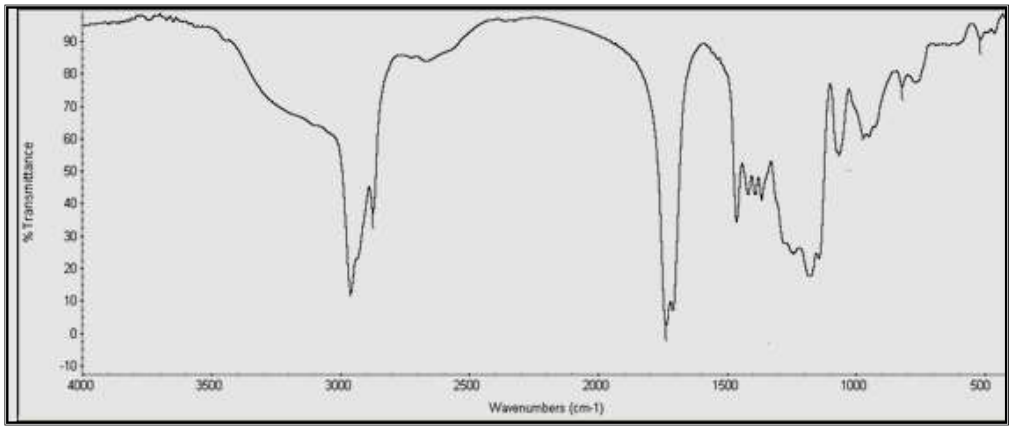

Fig.(1):F.T.I.R. Spectrum of Mono Ester

The prepared complex esters were also elucidated by using F.T.I.R. spectroscopy.In Fig.(2) it was found disappearance of broad band at 1700 cm^{-1} which characteristic absorption bands of the carboxylic acid, indicated that all hydroxyl groups of acids were consumed in the esterification reaction [13]. Disappeare of the strong band at 3600 cm^{-1} indicated that all hydroxyl groups of alcohols were consumed in the esterification reaction.

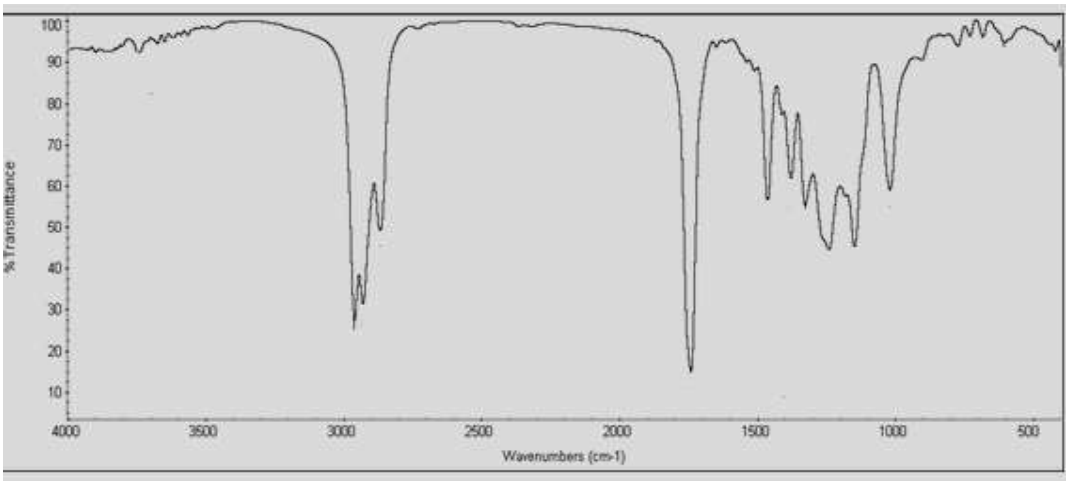

Fig.(2):F.T.I.R. Spectrum of Complex Ester

.

The H^1NMR was also used to justify the chemical structure of the prepared esters. The mono ester AH and the complex ester AHT were selected to investigate the H^1 chemical shifts. Fig.(3) shows that the chemical shift of mono ester as following; where (a)H^1-CH_3,triplet at 0.9ppm,(b) H^1- CH_2, sextet at1.4 ppm,(C) H^1- CH_2COOR esters, triplet at 2.5 ppm,(d) H^1- CH_2.OOC-R esters doublet at 3.7 ppm and (e) H^1-COOH carboxylic acid, singlet at12 ppm.Fig.(4) shows that the chemical shift of complex ester as following; where (a) H^1- CH3, triplet at 0.9ppm , (b) H^1- CH2, sextet at1.4 ppm, (C) H^1-CH_2COOR esters, singlet at 2.5 ppm, (d) H^1- CH2-OOCR esters,

doublet at 3.7 ppm and disappeare of RCOOH carboxylic acid which confirms the completeness of esterification process for the compound AHT.

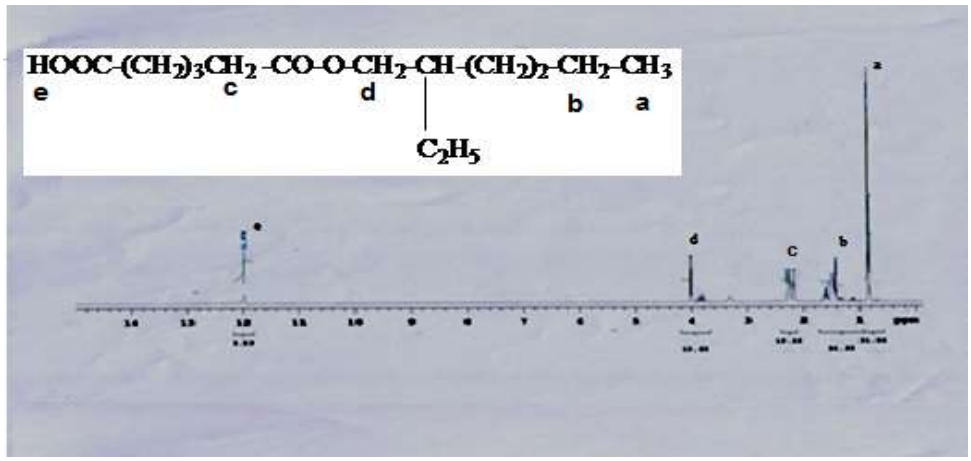

Fig.(3):H[1]-NMR Spectrum of Mono Ester AH

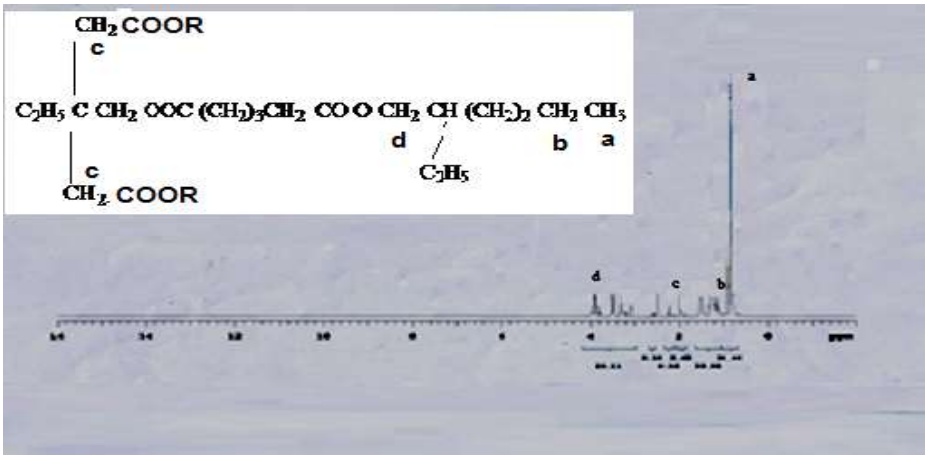

Fig. (4):H1-NMR Spectrum of Complex Ester AHT

Mass Spectroscopy of the Prepared Complex Esters.

The compositions of the prepared monoesters were confirmed by Mass Spectroscopy. The complex esters MHN and AHN were selected to investigate the mass spectrum which indicates that, the experimental molecular weight of the prepared esters are close to the theoretical which confirms the esterification reaction occurs successfully. Fig.(5) shows that the following fragments of complex ester MHN as follows; $C_2H_5^+$ fragment at M/Z=28, $CH(CH_2)_3CH_3^+$ fragment at M/Z=71, C_2H_5 CH-$(CH_2)_3CH_3^+$ fragment at M/Z=105,$CH_3(CH_2)_3CH(C_2H_5)$-CH_2-O^+fragment at M/Z=139, $CH_3(CH_2)_3CH(C_2H_5)$-CH_2-$OCOCH_2COOCH_2^+$ fragment at M/Z=199, $CH_3(CH_2)_3CH(C_2H_5)$-CH_2-$OCOCH_2COOCH_2C(CH_3)_2CH_2OCO^+$ fragment at M/Z=285 and $CH_3(CH_2)_3CH(C_2H_5)CH_2OCOCH_2$.$COOCH_2C(CH_3)_2CH_2OCOCH_2COOCH_2CHC_2H_5(CH_2)_3CH_3^+$ fragment at M/Z=501. Fig .(6) shows that the following fragments of complex ester AHN as follows; $C_2H_5^+$ fragment at M/Z=28, $(CH_2)_3CH_3^+$ fragment at M/Z=57, $CH_3(CH_2)_3CHC_2H_5^+$ fragment at M/Z=105, $(CH_2)_4COOCH_2CH^+$ fragment at M/Z=129, $(CH_2)4COOCH_2CHC_2H_5^+$ fragment at M/Z=150, $CH_3(CH_2)_3CHC_2H_5CH_2$.$OCO(CH_2)_4CO^+$ fragment at M/Z=241and $CH_3(CH_2)_3CHC_2H_5CH_2OCO(CH_2)_4COOCH_2C(CH_3)_2$-$CH_2OOC(CH_2)_4COOCH_2CHC_2H_5(CH_2)_3CH_3^+$ fragment at M/Z=600.

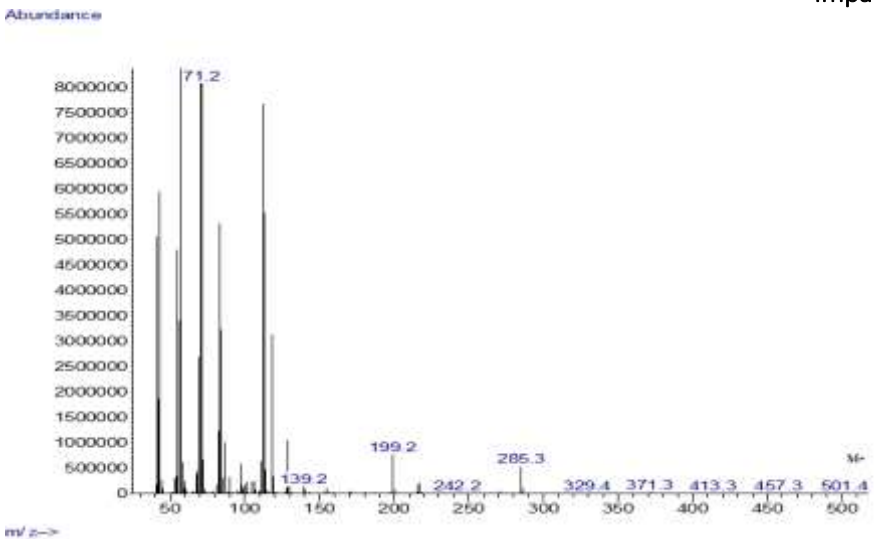

Fig. (5): Mass Spectrum of Complex Ester MHN

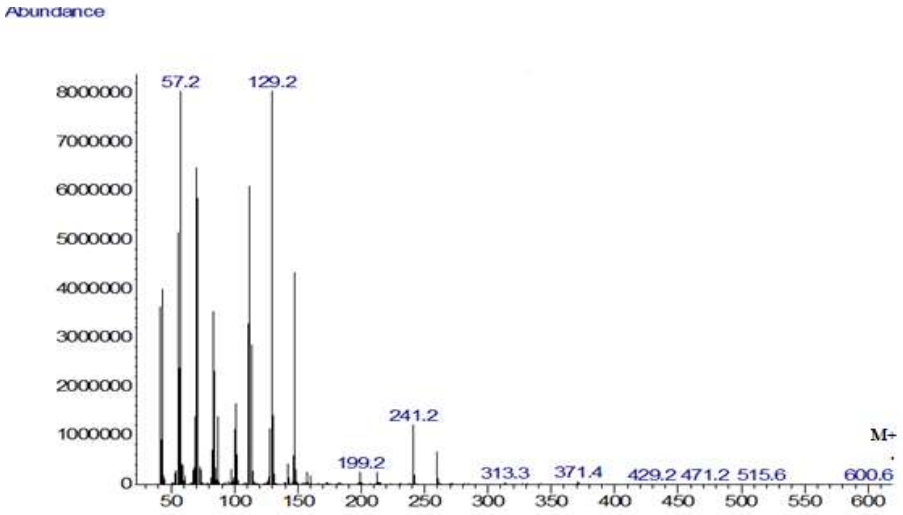

Fig.6: Mass Spectrum of Complex Ester AHN

Thermal Stability of The Prepared Complex Esters.

The thermal stability of the prepared complex esters was investigated, in Figs. (7&8). The prepared compounds degraded in the temperature range between 200 ºC and 500ºC. Fig .(7) shows that the primary degradation step occurs at 250ºC, with weight loss of 28.64 %,which may be related to fragments $CH_3(CH_2)_3CH(C_2H_5)$-CH_2-O coming from mass spectrometry of complex ester MHN, The complete degradation occurs at 500ºC, with weight loss of 71.47% , which may be related to fragments $CH_3(CH_2)_3CH(C_2H_5)$-CH_2-$OCOCH_2COOCH_2C(CH_3)_2CH_2OCOCH_2COO$. Fig.(8) shows that the primary degradation step occurs at 280ºC, with weight loss of 47.57 %,which may be related to fragments $CH_3(CH_2)_3CHC_2H_5CH_2OCO(CH_2)_4COOCH_2$ coming from mass spectrometry of complex ester AHN, The complete degradation occurs at 500ºC with weight loss of 51.86%, which may be related to fragments $CH_3(CH_2)_3CHC_2H_5CH_2OCO(CH_2)_4COOCH_2C(CH_3)_2$. Therefore, the thermogravimetric study has shown a good thermal stability for the prepared complex esters, and this confirms the suitability of using the prepared complex esters as synthetic lubricating base oil it can be used at high temperature without degradation.

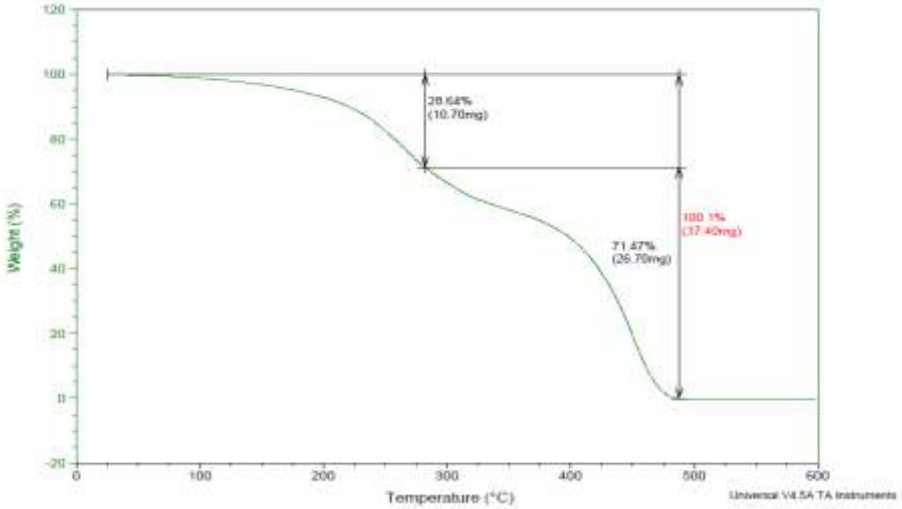

Fig.(7): TGA of Complex Ester MHN

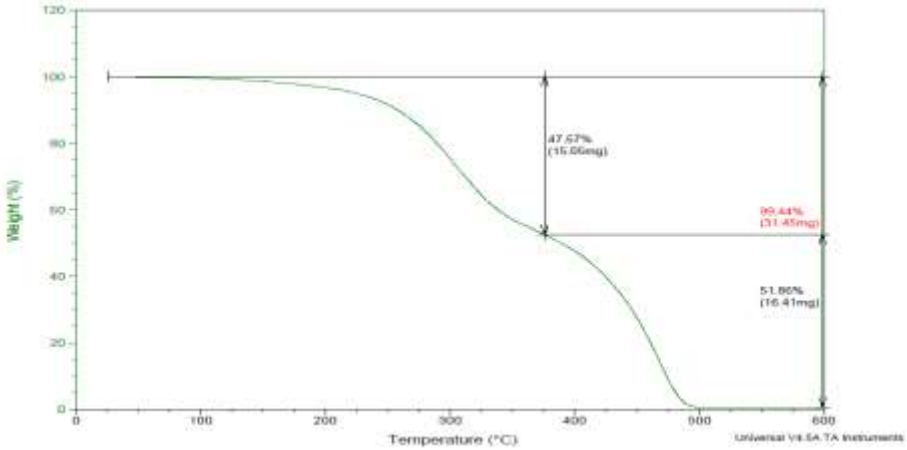

Fig.(8): TGA of Complex Ester AHN

Rheological Properties of The Prepared Compounds

The rheological behavior of oils and their products is generally simple Newtonian fluid (viscosity is independent of shear rate). Shear rate is measure of the rate of shear deformation. Shear stress is an applied force per unit area needed to produce deformation in a fluid. A Newtonian liquid is one that flows immediately on application of even the smallest force and for which the rate of flow is directly proportional to the force applied [14-16]. All the prepared complex esters are Newtonian fluid behavior as shown in Figs.(9&10).

ISSN 2349-0292
Impact Factor 3.802

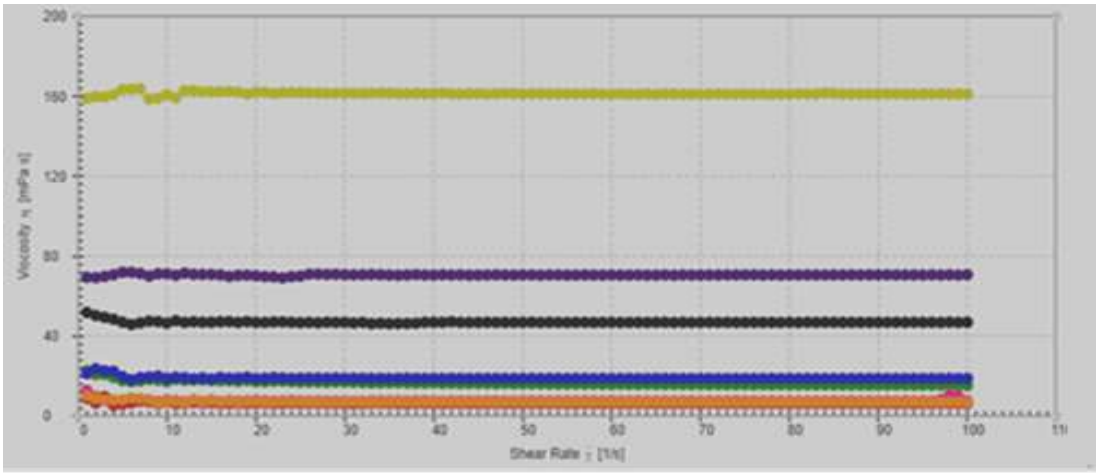

Fig.(9):Flow Curve of Complex Esters

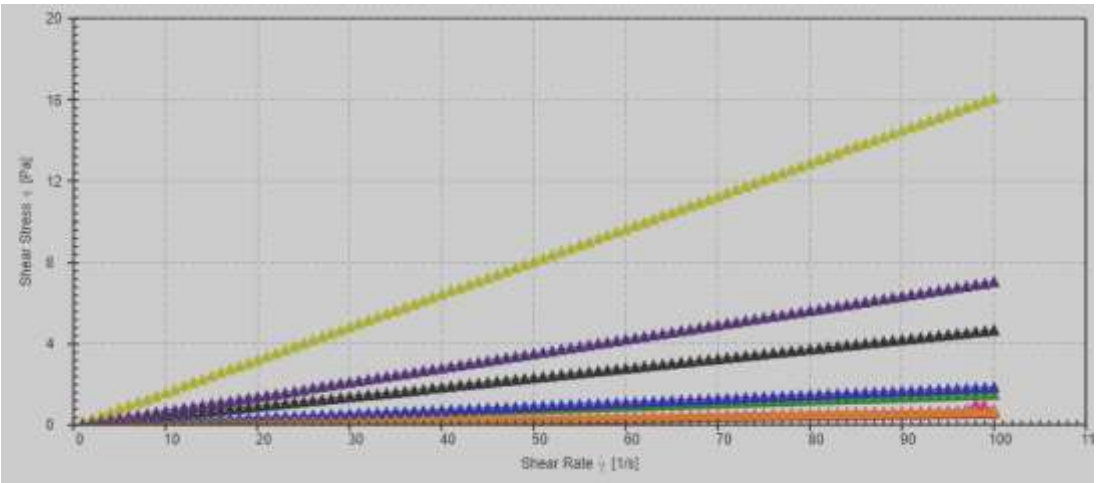

Fig.(10):Flow Curve of Complex Esters

Physical Properties of the Prepared Complex Ester.

In this study some physical properties of the prepared complex esters have been considered and some correlations have been established for the aim of characterizing the prepared complex esters as follows from Table.(2), the density shows a regular variation with each series values diminishing as the length of the aliphatic alchohol increases [17]. All values of the flash points are above 200oC, for a given polyol the flash point increased with increasing dibasic acid chain length,This effect was more pronounced in the case of NPG esters and least in the case of TMP esters [18].Kinematic viscosity and viscosity index give information about lubricant resistance to flow under gravity and effect of elevate temperature on flow, lubricant viscosity changes with increasing temperature. In Table.(2), it was found that the viscosity index of the complex ester which prepared from adipic acid is higher than that prepared from malonic acid and the viscosity index increases with increasing the number of carbon atoms of monoester and the viscosity index of the complex ester which prepared from trimethylol propane is higher than that prepared from neopentylglycol this is probably due to the fact that there are three alkyl groups in the structure of TMP esters but only two alkyl groups in the molecules of NPG esters . As regarding the pour point, the values registered present very attractive values, the best value recorded being less than -500C, and The pour point of prepared complex ester which prepared from malonic acid is lower than that prepared from adipic acid. It is assumed that the polarity of the ester molecules function their attraction to the positive charged metal surface creating a film which requires additional energy (load) to wipe them off the result is stronger film which

translates into higher lubricity and lower energy consumption in lubricant applications. In this study the prepared complex esters have been examined in the laboratory according to some of the available tests mentioned [19].

Table 3. Physico-Chemical Characteristics of Prepared Complex Esters

Designation	Prepared complex ester composition	pour point pp°c ASTM-D98-87	Vis.at40°C ASTM D-2270-87	Vis.at100°C ASTM D-2270-87	Viscosity Index ASTM D-2270-87	Flash point °C ASTMD 92,D93	Density gm/cm³ ASTM D92-13	TAN, mg KOH/ gm ASTM-D664
MAN	Malonic acid +amyl alchol+NPG	≤-50	4.78	1.53	48.6	213	0.8923	0.2
MAT	Malonic acid +amyl alchol+TMP	≤-50	9.98	2.56	77.02	219	1.0284	0.5
AAN	Adipic acid +amyl alchol+NPG	-48	13.20	3.34	127.429	219	0.9525	NIL
AAT	adipic acid +amyl alchol+TMP	-48	71.02	11.71	160.41	240	0.9923	NIL
MHN	Malonic acid+2-ethyl hexanol+NPG	≤-50	4.977	1.6	70.8	231	0.8875	0.2
MHT	Malonic acid+2-ethyl hexanol+TMP	≤-50	5.77	1.8	80.3	240	0.9646	0.2
AHN	Adipic acid+2-ethyl hexanol+NPG	-42	33.84	6.2	127.4	261	0.9524	NIL
AHT	Adipic acid+2-ethyl hexanol+TMP	-48	113	17	165	267	1.0345	NIL

CONCLUSION

Eight complex esters were synthesized and elucidated by using FTIR, 1H-NMR, and mass spectroscopy. Using untraditional catalyst Amberlyst (ion exchange resin) to reduce the acidity of the prepared esters and its ability to recover. The TGA was used to detected the thermal stability of the prepared compounds and it was found that all compounds are more or less stable at high temperature. All prepared complex ester exhibited the behavior of synthetic lubricating base oil and achieved better values than commercial product in viscosity index, flash point and achieved the same values in pour point.

REFERENCES

[1] Beyer C. and Jeditte R., "New Methacrylate Based Synthetic Lubricant" ;Lubrication Engineering 48, 450-455 **(1992).**
[2] Bernard. J. H, Steven .R. S and Jacobson. B; Fundamental of Fluid Film Lubrication Second Edition, Marcel Dekker,inc,New york, **(2004).**
[3] Garwood.W. E. *;* "Synthetic Lubricant" ; US Patent 2(937),129 **(1960).**
[4] Pirro. D.M.and Wessol .A.A., Lubrication fundamental, Marcel Dekker,inc,New york, (2001).
[5] Amal M. N, Nehal S. A, Hamdy S. A and Ahmed F. E; Journal of Tribology International, 93(31), 297-305, **(2016).**
[6] Rasha .S.K,Nehal.S.A and Amal .M.N, petroleum and coal journal, 59, 6, 736-746,**(2017).**
[7] Chang T.-S. ,Yunus R., Rashid U,. Choong TSY, Awang Biak DR and Syam AM. J. Oleo Sci., 64,143-151,**(2015).**
[8] Erhan SZ, Sharma BK, Liu Z and Adhvaryu A. Journal of Agricultural Food Chemistry.; 56.8919-892,. **(2008)**
[9] Margaret .M. W,Suzzy C. Ho and Reg F ; Practical Advances in Petroleum Processing**,(2007).**
[10] El-Magly. I.A, Nagib .H.K and Mokhtar .W.M ;Egyptian Journal of Petroleum,22(1), 169-177,**(2013).**
[11] Rasha S. K., Nehal S. A., Amal M. N. ," Study the efficiency of some compounds as lubricating oil additives; Applied Petrochemical Research", 3, 1-8 , **(2013)**.
[12] Jinli .Z, Chuanjie .Wu, Wei. L, Yiping .W and Hui .C ; Journal of Fuel, 83(3), 315-326, **(2004).**

[13] Nehal.S .A, Amel.M .N ;Tribology-Lubricants and Lubrication, Chang-Hung Kuo **,(2011).**
[14] Al-Sabagh AM., Sabaa MW, Saad GR., Khidr TT and Khalil TM., Egyptian Journal of Petroleum; 21, 19–30,**(2012).**
[15] Chhabra R P. Non-Newtonian Fluids: An Introduction. In Rheology of Complex Fluids. Deshpande AP. Kumer SPB. Krishnan. JM. Eds.; Springer Science business Media: New York.**(2010)**.
[16] S. Zzeyania.B, Mikoua .M. , Najab .J.and Elachhab .A; Tribology International.114, 27–32, **(2017).**
[17] Mirci E. L., Boran S., Pode V. and Resiga D., journal of synthetic lubrication, 24, 51-63 **(2007)**.
[18] Mirci E. L., Resiga D. and Pode V., journal of synthetic lubrication, 22, 341-354 **(2010)**.
[19] Venkataramani S. P., Kalra L. S., Raman V. S. and Srivastava C. H., journal of synthetic lubrication, 5, 271-289 **(1989)**.