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"Study The Efficiency of Some Esters Based on 2- Ethyl Hexanoic Acid as Synthetic Lubricants"

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Abstract

Esters have many important properties, such as biodegradation, low toxicity, good thermal stability and excellent solvability, because these features are definitely the most versatile of the various types of base fluids currently available and can be modified to provide unique physical and chemical properties that can be designed to meet the lubricant industry's challenges. In this article, Reaction was prepared by various branched synthetic esters of 2- ethyl hexanoic acid with different 2 groups of alcohols, the first one (1-hexanol, 2- ethyl hexanol,1-octanol, 1- dodecanol and 1- hexadecanol), and the second group (neopentyl glycol, trimethylol propane and pentaerythritol). All the preparation compound form were confirmed by examine the physical and chemical properties as (Nuclear Magnetic Resonance, Infra-Red Spectroscopy, Total Acid Number, Density, Thermo Gravimetric Analysis TGA, Specific gravity, Reflective index, Molecular weights estimation and flash point). As a synthetic lubricating oil, the performance of these compounds was studied. Prepared compounds have been found to contain low pour point (PP), high viscosity level (VI) and Newtonian fluid for rheological behavior.

Keywords: Synthetic oil; branched ester; pour point; rheology and viscosity index.

1. Introduction

Synthetic oils provide an environmentally friendly fe ature. In extreme temperatures synthetic oil is used as a replacement for petroleum oil. lubricating oil, sometimes referred to simply as A lubricant, is a kind of friction-reducing oil, wearing and heating in contact with mechanic components. Lubrication oil is used in vehicles, where engine oil and fluid transmission are classified explicitly. Two particular categories of lube oil are available: Mineral and Synthetic, mineral oil are lubricating oil that are refined with natural crude oil, synthetic oils are manufacturing lubricating oils. The low costs for oil extraction of crude oil make the most commonly used type today is the mineral lubricating oils. Mineral oils can also be produced with different viscosities, so they can be used in A variety of applications [1]. The 2018 Annual Oil and Lube News survey showing that more than half of car owners choose to make synthetic or synthesized mixes when their oil is changed according to Will Hixson, Speaker for the Automotive Oil Change Association [2]. Synthetics have several advantages over traditional engine oil. They're designed to be more efficient at: (1) Oil breakdown resistant which makes it last longer than traditional oil. (2) endure higher temperatures than traditional oil, this associates to keep engines running longer. (3) Flowing in cold temperatures, thereby reducing engine wear during frigid startups. A drawback is there: synthetic motor oil will cost 2-4 times more than regular oil, so you don't want it, unless the manual of your owner sets out synthetic [2]. In addition, the most common use are synthetic esters. This is because it's outstanding and strong lubricants in many applications where other oils struggle in the lubricants industry for most of the 20th century. In terms of engine oils, chilled oil, compressor oil, chain lubricants, fats, metalworking fluids, hydraulic fluids, transmission fluids and much more, synthetic esters offer high performance lubrication. Esters can be mixed with Polyalphaoleifn (PAO) or mineral oils to improve screening swell, solvency, volatility reduction and energy efficiency [3,4]. Thanks to their biodegradability and low toxicity, many esters are used in environmentally appropriate lubricants. Polyol esters (POE's) are very thermally and oxidatively stable and often work with very low temperatures. The esters also gain a high polarity on metal surfaces, improving the lubricity while maintaining additional desirable diester properties [5,6]. Polyols can be tailored for almost any application from cooling lubes to oven chain lubes. In the present research, the different branched synthetic

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esters were synthesized by way of reaction 2- ethyl hexanoic acid with different 2 groups of alcohols, the first one (1-hexanol, 2- ethyl hexanol,1-octanol, 1-dodecanol and 1- hexadecanol), and the second group (neopentyl glycol, trimethylol propane and pentaerythritol), then study the efficiency of them as synthetic oil.

2. Experimental

2.1. Preparation of Branched Synthetic Ester:

The different branched synthetic esters were synthesized by way of reaction 2- ethyl hexanoic acid with various 2 groups of alcohols, the first one with (1-hexanol, 2- ethyl hexanol,1-octanol, 1- dodecanol and 1- hexadecanol) to give product A, B, C, D and E esters compounds and the second group with (neopentyl glycol, trimethylol propane and pentaerythritol) to give product F, G and H esters compounds . In the flask of 1wt % percent catalyst and xylene was carried out in the resin bottle as a solvent the reactions. Slow flow of deoxygenated nitrogen conducted esterification reactions; reactions were troubled with 500 rpm mechanical stirrer. The mixed reactants with the same xylene weight were then slowly heated with a controlled thermostat temperature in rooms up to 140 ° ± 0.5 ° C [5,6]. The range of reaction was controlled by monitoring the amount of liberated water give products as shown in Table (1).

Table (1). The mean molecular weights of prepared compounds

Designation of the prepared esters	Molecular formula	Mean molecular weight (gm/ mole)	
		theoretical	Experimental
A	$C_{13}H_{28}O_2$	**228.38**	**228.21**
B	$C_{16}H_{32}O_2$	**256.43**	**256.1**
C	$C_{16}H_{32}O_2$	**256.24**	**255.7**
D	$C_{20}H_{40}O_2$	**312.54**	**312.2**
E	$C_{24}H_{48}O_2$	**368.65**	**367.8**
F	$C_{21}H_{40}O_4$	**356.55**	**355.2**
G	$C_{30}H_{56}O_6$	**512.77**	**512.6**
H	$C_{37}H_{68}O_8$	**640.94**	**640.5**

2.2. Prepared Branched Esters Purification:

The synthesizes esters are cleaned by wash in a funnel separating using a 10% solution of sodium carbonate to remove unreacted acid. The filtered ester was then washed many times with distilled water to clear any traces of sodium carbonate, then the ester was left overnight on a calcium chloride anhydrous for remove excess water. Filtration was then taken away from anhydrous calcium chloride and rotary extracting xylene.

2.3 The Chemical Structure of Prepared Esters Confirmation

Analysis test	Propose	Properties of instrumental
I.R. spectroscopic analysis	Determination of function group	Model Mattson Infinity Top 961 Spectrometer F.T.I.R.
^{1}HNMR Spectroscopic Analysis	determine the structure of organic molecules	Spectrometer: Magnets: 400 Megahertz, console: Variant mercury plus, sample: Variant 5 mm.
Gas Chromatography (GC-mass).	Determination of Molecular Weights	Column name: DB-5MS (0.25nm x 30cm, 0.1µm film) and flammable ionizing detector, Agilent technology type 5977A MSD, 7890B GC device. As a carrier gas, pure nitrogen was used. At a fixed rate of 20°C/min, the temperature range for the oven ranged from 40 to 320°C. The injector sensor temperature was 300°C.
	Determination of the Yield	Track the quantity of water released for products

2.4 Study the Physicochemical Properties of Prepared Compounds:

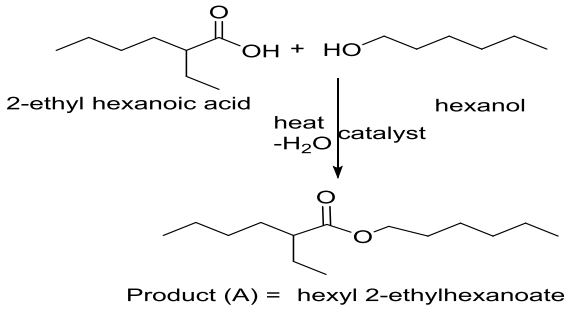
Properties	Test method	Properties of instrumental or procedure
Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA)	ASTM D 6375-99A	Evaporation loss of lubricating oil by TGA 55 Rate:20^{o}C min^{-1} Temperature :600^{o}C Under : Nitrogen gas
Total Acid Number (TAN)	ASTM D 664	Model Type Mehrshom CLO-05.
Density	ASTM D 1298	Density at 15 ^{o}C (g/ml)
Reflective Index	ASTM D 1747	
Specific Gravity	ASTM D 4052	Model Type Meler Toledo DEUO. Density meter at 15 ^{o}C
Flash Point	ASTM D 92	Cleveland open cup tester
The kinematic viscosity at 40°C	ASTM D 445	KV1000 Kinematic Viscosity Bath
The kinematic viscosity at 100°C	ASTM D 445	
Viscosity Index	ASTM D 22-70	
Pour Point	ASTM-D 97	Seta Cloud and Pour Point Cryostat
Rheological and Tribological Properties		Model Type the Modular Compact Rheometer 502 (Anton Paar).

3. Results and Discussions:

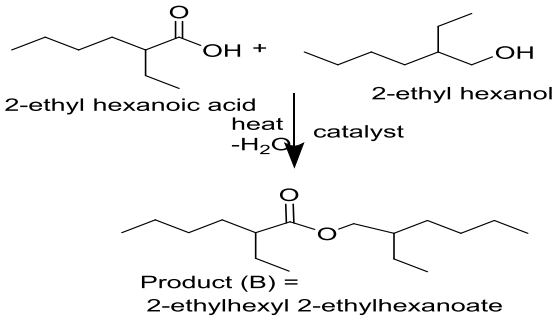
3.1. Preparation of Branched Synthetic Ester:

a. First Group of Ester

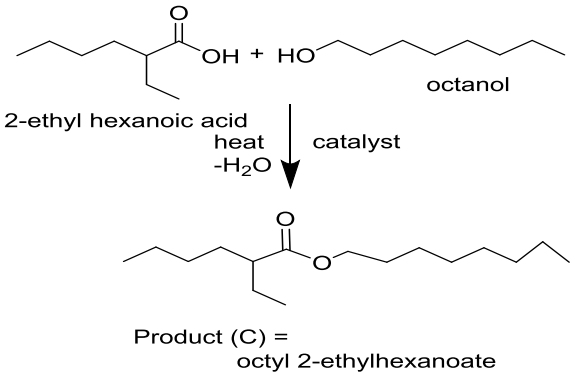
Reaction of 1 mole of 2- ethyl hexanoic acid with 1 mole of (hexanol, 2-ethyl hexanol, octanol, dodecyl alcohol and hexadecyl alcohol). Esterification reactions were carried out and the extent of the reaction was monitored for release of the products (A, B, C, D and E) by the amount of released water. as shown in the following reaction.



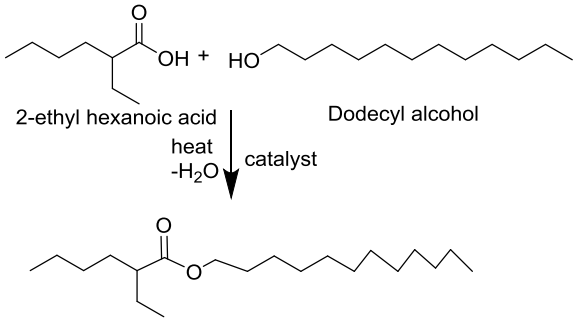
Product (A) = hexyl 2-ethylhexanoate



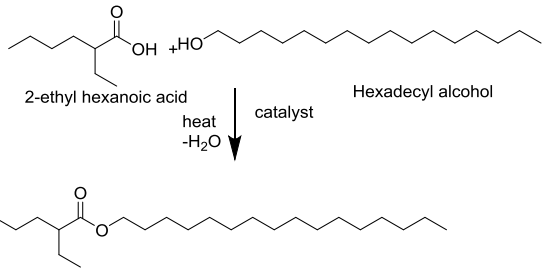
Product (B) =
2-ethylhexyl 2-ethylhexanoate



Product (C) =
octyl 2-ethylhexanoate



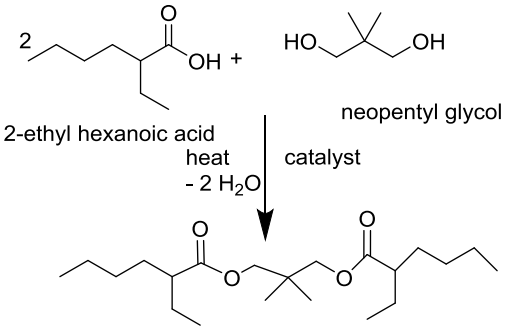
Product (D) = dodecyl 2-ethylhexanoate



Product (E) = hexadecyl 2-ethylhexanoate

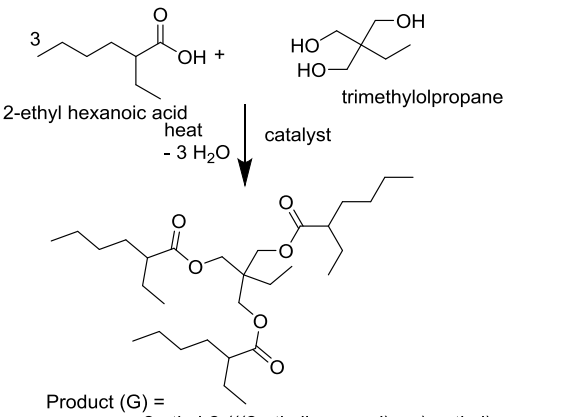
b. Second Group of Ester

Reaction of 2 mole of 2- ethyl hexanoic acid with 1 mole of neopentyl glycol. Esterification reactions were carried out and the extent of the reaction was monitored for release of the product (F) by the amount of released water, as seen below in the following reaction.



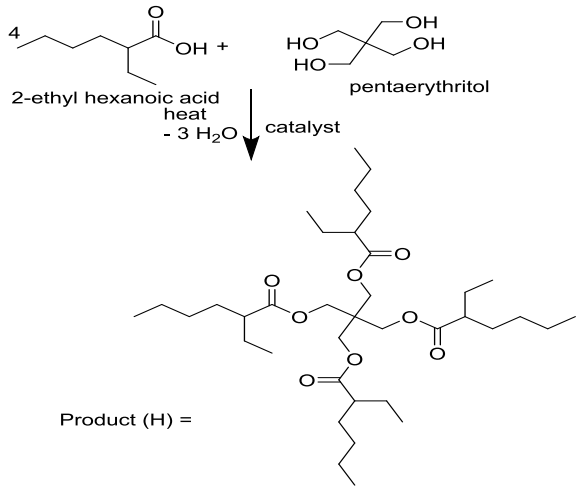
Product (F) =
2,2-dimethylpropane-1,3-diyl bis(2-ethylhexanoate)

Reaction of 3 mole of 2- ethyl hexanoic acid with 1 mole of trimethylol propane Esterification reactions were carried out and the extent of the reaction was monitored for release of the product (G) by the amount of released water, as seen below in the following reaction.



Product (G) =
2-ethyl-2-(((2-ethylhexanoyl)oxy)methyl)propane-1,3-diyl bis(2-ethylhexanoate)

Reaction of 4 mole of 2- ethyl hexanoic acid with 1 mole of pentaerythritol. Esterification reactions were carried out and the extent of the reaction was monitored for release of the product (H) by the amount of released water, as seen below in the following reaction



2,2-bis(((2-ethylhexanoyl)oxy)methyl)propane-1,3-diyl bis(2-ethylhexanoate)

The completion of esterification reactions was elucidated with **I.R. spectroscopy**. All esters have a spectrum of I.R similar to that offered by I.R. Figures (1-2) display the following: absence of vigorous absorption band at 3200 cm^{-1} of aliphatic (–OH) group, the characteristic capacity bands of the carboxylic acids. These bands are broad peak extending from 3300cm^{-1} to 2500cm^{-1} due to hydrogen bonded (–-OH) and the (C-H) stretching vibrations. Manifestation of the ester group bands at 1735 cm^{-1} ± 10 cm^{-1} and 1265 cm^{-1} ± 100 cm^{-1} due to (C= O) and (C-O-C) stretching respectively. The band for (C –H) aliphatic seems near 2870cm^{-1} & 2950cm^{-1}. This indicates that the esterification process success in carrying out [7].

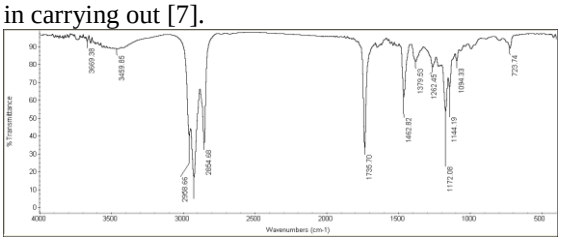


Fig. (1). IR spectrum of the prepared compound (E).

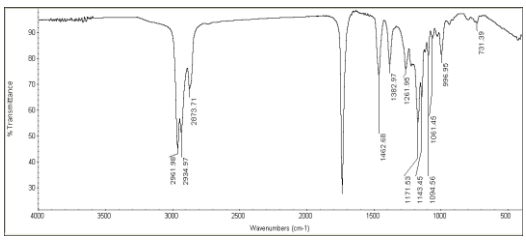


Fig. (2). IR spectrum of the prepared compound (F).

^{1}HNMR study, showing in Figures (3-4), will demonstrate the chemical structure of the compounds. The signal was therefore selected for esterification at 3.9 ppm (as specified to groups of O-CH_2), the signal at 2-2.5 ppm (as allocated to groups of O = C-CH_2) and the signal at 1.5–2 ppm (allocated to aliphatic protons) [7].

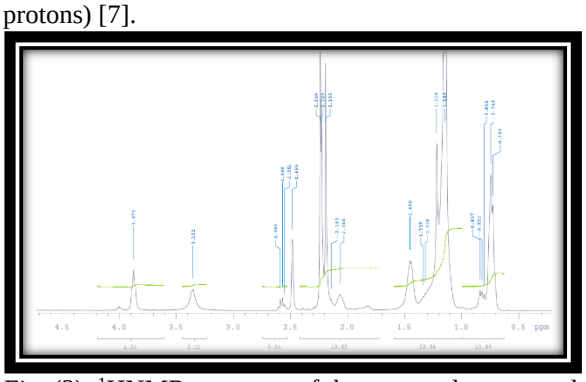


Fig. (3). ^{1}HNMR spectrum of the prepared compound (E).

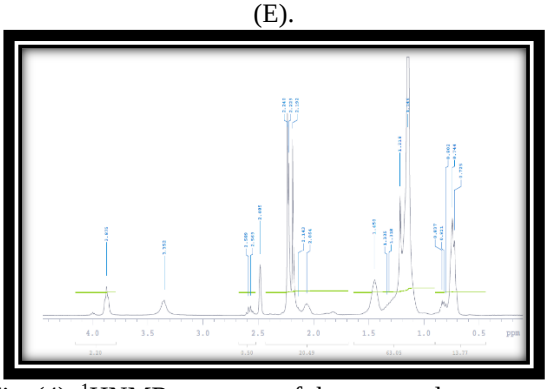


Fig. (4). ^{1}HNMR spectrum of the prepared compound (F).

The average **molecular weights** of prepared compounds with the use of Gas Chromatography are presented in Table (1), as demonstrated in theoretical and experimental average molecular weight equivalent to all compounds, and found the smallest one is (A) ester and the largest one is (H). Figures (5-6) show **mass spectrum** for the prepared compound (E-F). the molecular mass values are between 228 to 640 mass units, which represent a normal range that falls in the used domain of synthetic oils.

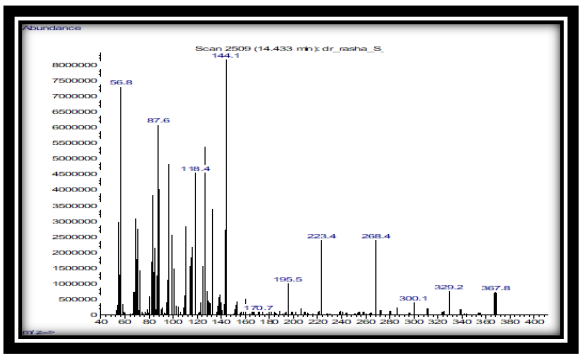


Fig. (5). Mass spectra of the prepared compound (E).

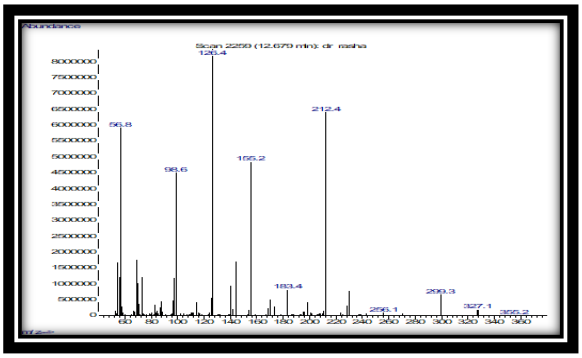


Fig. (6). Mass spectra of the prepared compound (F).

The **Yield** of all prepared compounds determined by monitoring the quantity of liberated water to give products and it is equal 98% except (F) prepared ester 75%.

Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) displayed good thermal stability for prepared compounds as in those compounds' temperature ranges from 175° to 330 ° C determined in all Figures (7-22). The higher the beginning temperature of lube decomposition base stock. the higher its thermal stability so compound (H) is the highest thermal stability [8].

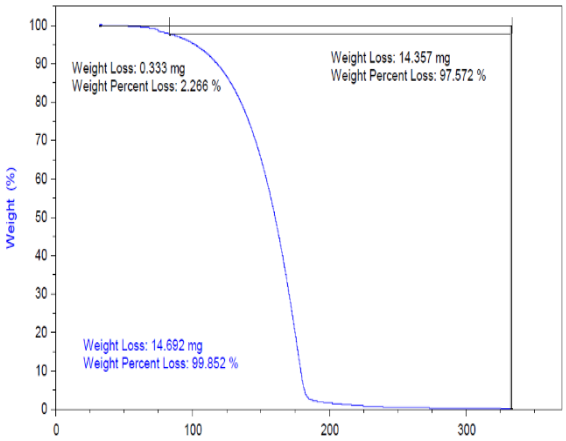


Fig. (7). TGA analysis of the prepared compound (A).

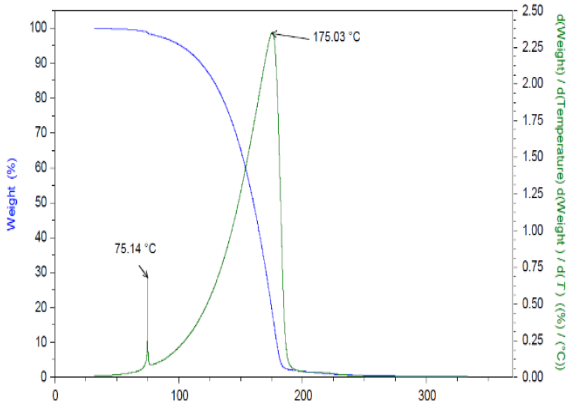


Fig. (8). DTG analysis of the prepared compound (A).

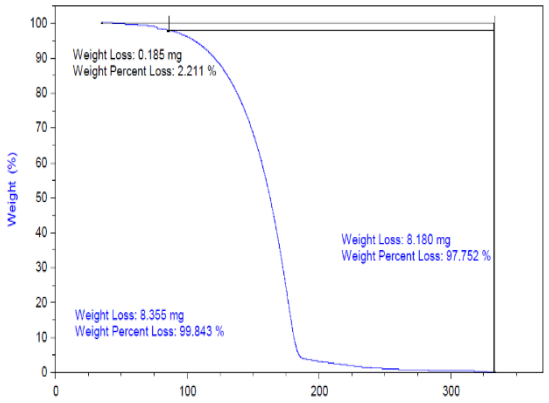


Fig. (9). TGA analysis of the prepared compound(B).

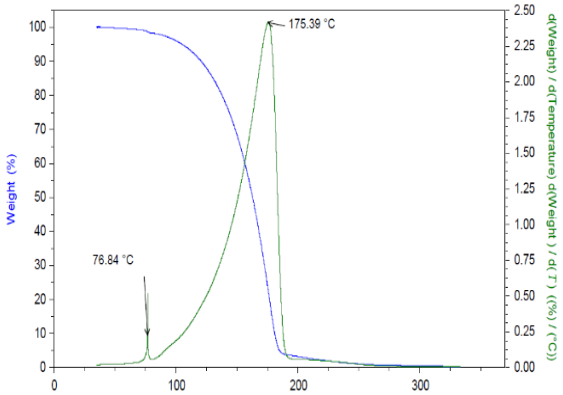


Fig. (10).DTG analysis of the prepared compound(B).

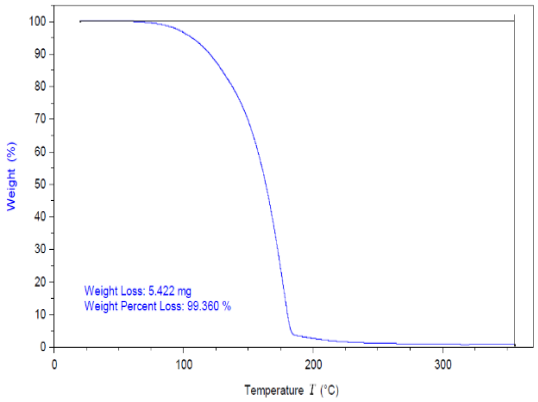


Fig. (11). TGA analysis of the prepared compound (C).

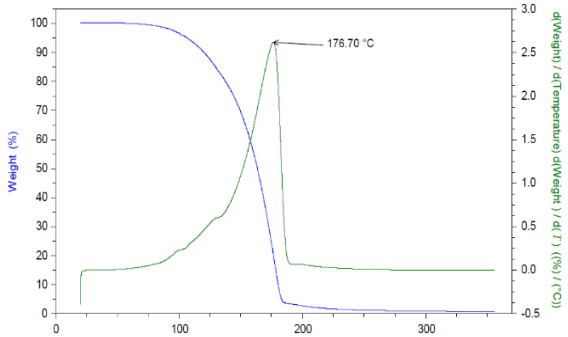


Fig. (12). DTG analysis of the prepared compound (C).

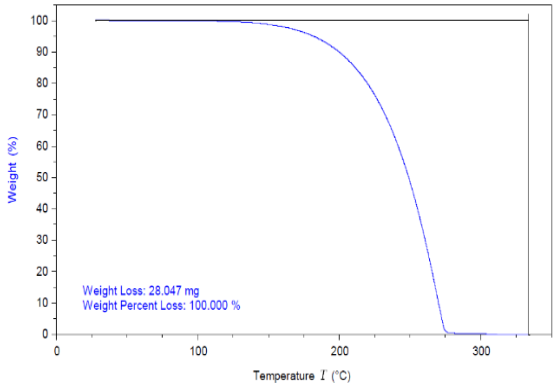


Fig. (13). TGA analysis of the prepared compound (D).

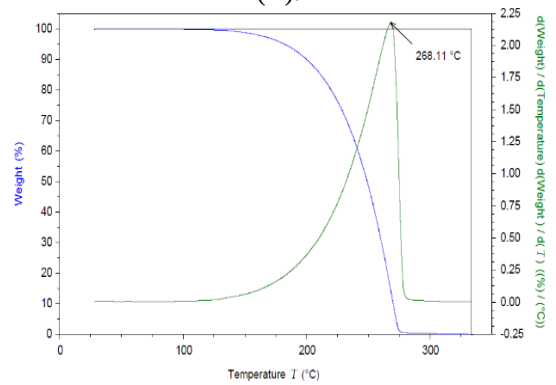


Fig. (14). TGA analysis of the prepared compound (D).

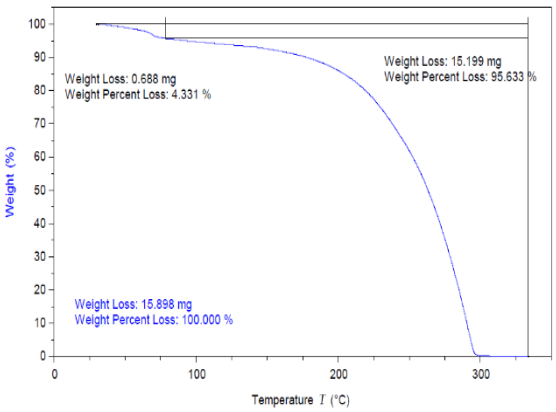


Fig. (15). TGA analysis of the prepared compound (E).

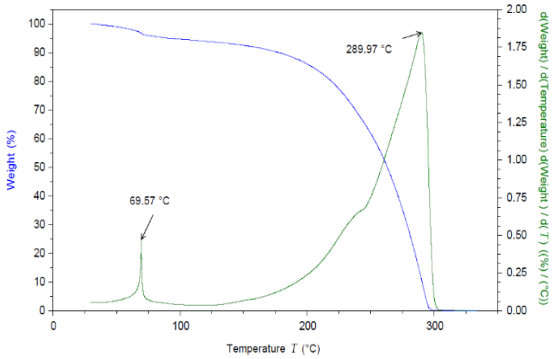


Fig. (16). DTG analysis of the prepared compound (E).

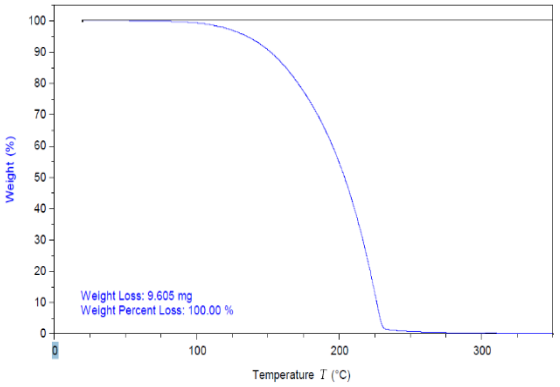


Fig. (17). TGA analysis of the prepared compound (F).

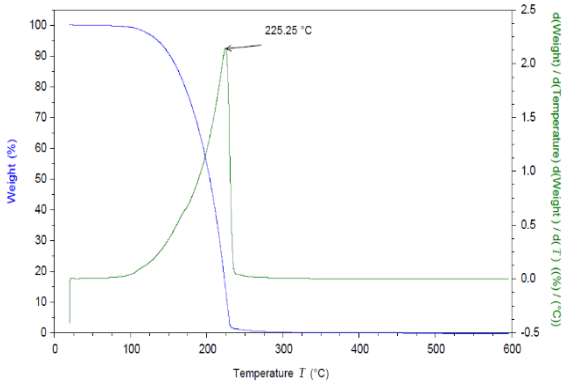


Fig. (18). DTG analysis of the prepared compound (F).

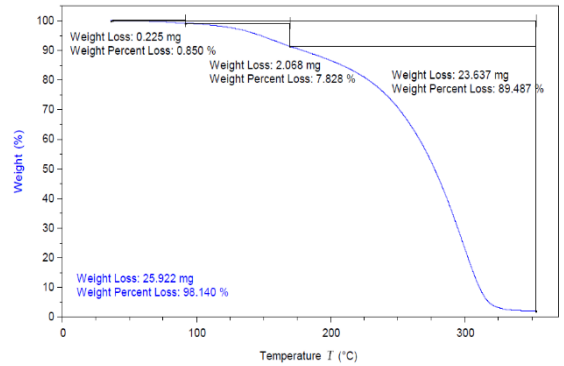


Fig. (19). TGA analysis of the prepared compound (G).

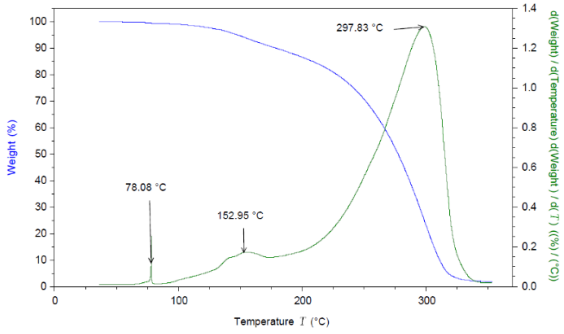


Fig. (20). DTG analysis of the prepared compound (G).

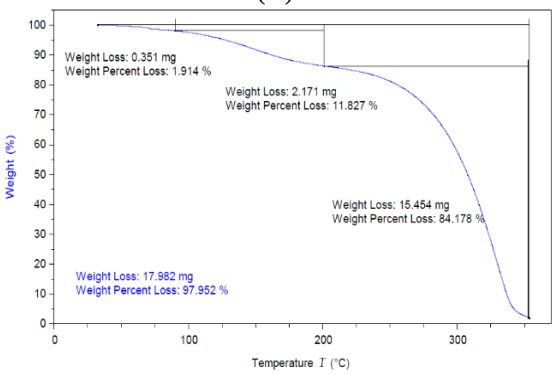


Fig. (21). TGA analysis of the prepared compound (H).

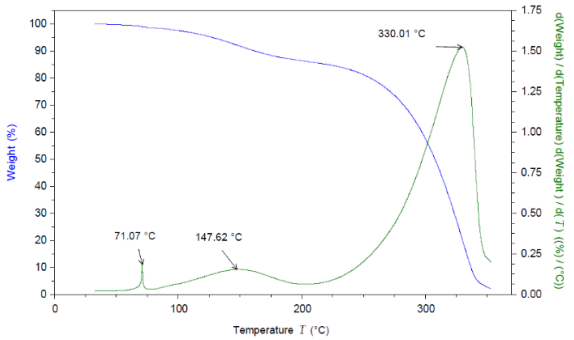


Fig. (22). DTG analysis of the prepared compound (H).

Total Acid Number in all prepared compound is very low even in compound (E) is nil and this indicate to the esterification is carried out successfully [9] as show in Table (2).

Table (2). The physico-chemical properties of prepared compounds

Properties	A	B	C	D	E	F	G	H
Total Acid Number (TAN) (mg KOH/g)	**0.03985**	**0.03725**	**0.03412**	**0.0452**	**nil**	**0.0747**	**0.02628**	**0.02659**
Density (g/ml) at 20 °C	**0.89657**	**0.87458**	**0.86357**	**0.8490**	**0.8458**	**0.9618**	**0.9616**	**0.9115**
Reflective Index at 28 °C	**1.4338**	**1.4398**	**1.4358**	**1.4438**	**1.4538**	**1.4428**	**1.4523**	**1.4538**
Specific Gravity at 15 °C	**0.89735**	**0.8753**	**0.8643**	**0.8497**	**0.8466**	**0.96260**	**0.9625**	**0.9123**
API gravity @ 60 °F	**26.19**	**30.16**	**32.21**	**35.02**	**35.65**	**15.49**	**15.51**	**23.60**
Flash point (COC) °C	**132**	**134**	**135**	**212**	**216**	**167**	**219**	**242**
The kinematic viscosity at 40°C	**2.46512**	**3.2984**	**3.5588**	**5.2948**	**5.97184**	**7.083132**	**18.5**	**21.9768**
The kinematic viscosity at 100°C	**1.009**	**1.2903161**	**1.383361**	**1.868076**	**2.113764**	**2.14977**	**4.00946**	**4.640026**
Viscosity Index	**76**	**111**	**138**	**151**	**185**	**104**	**115**	**131**
Pour Point	**>-45**	**>-42**	**-36**	**-33**	**-12**	**-36**	**-33**	**-30**

Density, Specific Gravity and API gravity show in Table (2). density show a regular variation its values diminishes as the length of the aliphatic alcohol increases, all the prepared compounds have density (0.8- <1) suitable with molecular weight and with viscosity index, also there is a relation between Specific Gravity and API gravity and also specific gravity is relative density (ratio between density of substance and density of water)

Reflective Index show in the Table (2) all the prepared compounds have reflective index between (1.43-1.45) which is suitable for synthetic oil.

Flash point for all the prepared compounds show in the Table (2) and there are relation between the molecular weight and the flash point, flash point of prepared compounds exceeds 200 ° C and shows a low tendency to evaporation which complies with one of the fundamental requirements of lubricants and can get the flash point from the thermal gravimetric analysis [10].

Viscosity Index for all prepared compound show in Table (2) by calculating the kinematic viscosity at 40 and 100°C and it was found that the value around the level of 76 to 185 the increase in molecular weight lead to increase in viscosity index for (A,B, C, D and E) due to increase in alkyl chain length and also the second group (F, G and H) it was found that the prepared compound from pentaerythritol has highest VI (131) due to increasing in the molecular weight.

The rheological behaviour for all the prepared compounds is Newtonian fluid which show in Figures (23-30) that is mean Newtonian fluids obey viscosity Newton's law. The viscosity is independent of the shear rate[11-13].

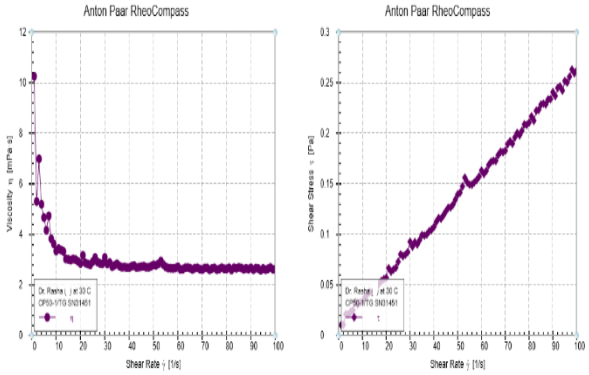


Fig. (23). The rheological behaviour of synthetic lubricating oil (A).

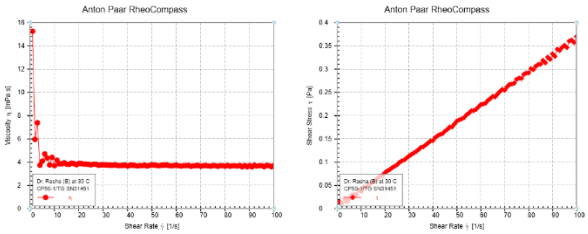


Fig. (24). The rheological behaviour of synthetic lubricating oil (B).

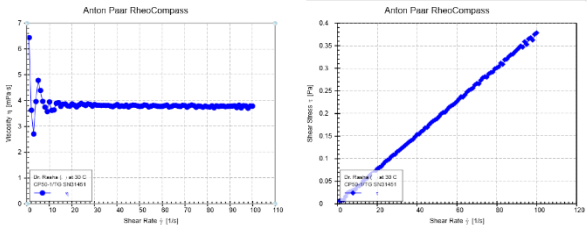


Fig. (25). The rheological behaviour of synthetic lubricating oil (C).

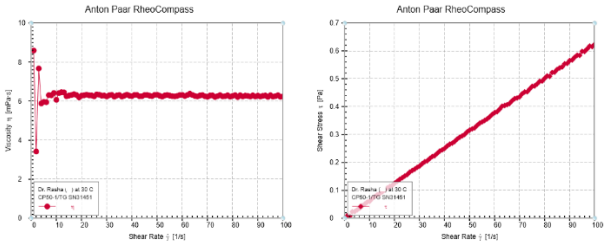


Fig. (26). The rheological behaviour of synthetic lubricating oil (D).

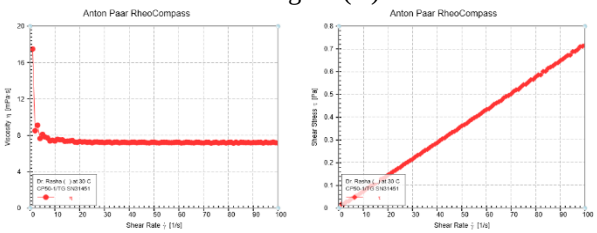


Fig. (27). The rheological behaviour of synthetic lubricating oil (E).

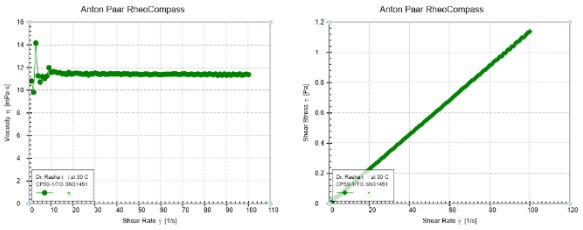


Fig. (28). The rheological behaviour of synthetic lubricating oil (F).

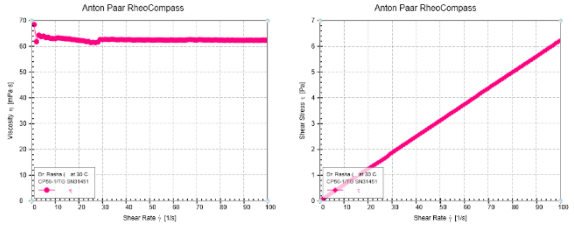


Fig. (29). The rheological behaviour of synthetic lubricating oil (G).

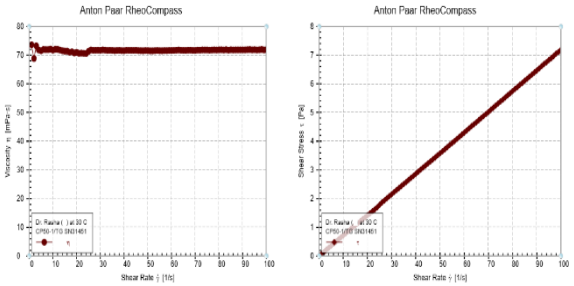


Fig. (30). The rheological behaviour of synthetic lubricating oil (H).

The Tribological behaviour as show in the Figures (31-24) friction factor increases with the sliding distance, the friction factor at the higher sliding velocity is larger than that at the lower sliding velocity. The impact on friction factor is complicated by velocity and sliding distance and their relations are not linear as evaluated [14,15].

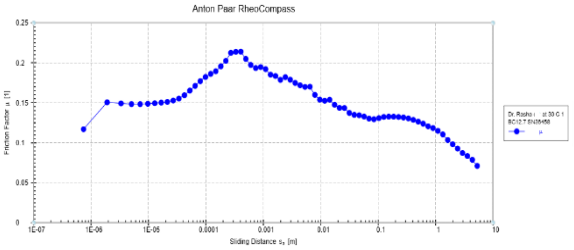


Fig. (31). Tribo curve Measured friction factor and its change sliding distance of synthetic lubricating oil (E).

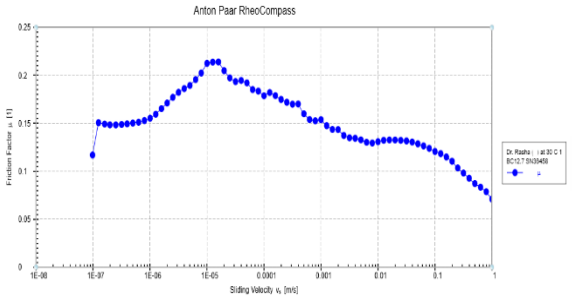


Fig. (32).stribeck curve Measured friction factor and its change with sliding velocity of synthetic lubricating oil (E).

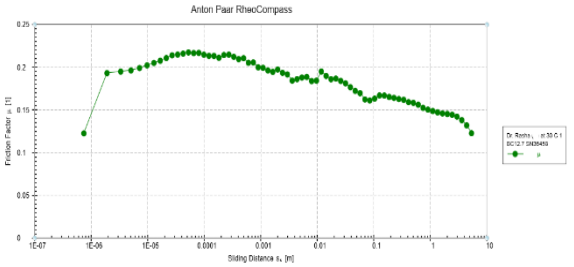


Fig. (33). Tribo curve Measured friction factor and its change sliding distance of synthetic lubricating oil (F).

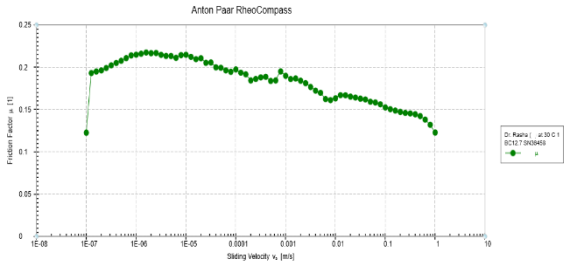


Fig. (34).stribeck curve Measured friction factor and its change with sliding velocity of synthetic lubricating oil (F).

Pour Point of the synthesizes compounds show in Table (2) that the pour point decrease due to decrease in the molecular weight of the prepared compounds and the best one is (A) >-45, the pour point of the synthetic oil is much lower than mineral one due to absence of wax crystal which is responsible for formation of interlocking growth limits pour of oil. Pour point of neopentyl glycol (-36) and trimethylol propane (-33), however the pour point of pentaerythritol is high, this suggesting that the molecular configuration of neopentyl glycol and trimethylol propane Esters are more effective at disrupting molecule packing compared to polyol esters [16].

CONCLUSION

The conclusions that can be known from the study findings are: -

1. All prepared synthetic ester based on reaction of different alcohols to get different esters divided into two groups polyol ester and mono esters
2. Study the physicochemical properties of all the prepared synthetic lubricants.
3. Thermal analysis showed good thermal stability for all prepared esters.
4. The best viscosity index results of the prepared esters (E) 185.
5. The best result for pour point is (A) >-45.
6. The rheological behavior for all the prepared esters is Newtonian fluid.
7. The Tribological behavior for prepared esters is friction factor increases with the sliding distance and the friction factor at the higher sliding velocity is larger than that at the lower sliding velocity.
8. According to all the result we suggest the prepared esters as synthetic lube oil.

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