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SYNTHESIS AND CHARACTERIZATION OF MIXED ESTERS AS SYNTHETIC LUBRICANTS

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Abstract

Esters have been used successfully in lubrication for more than 60 years and are the preferred stock in many severe applications where their benefits solve problems. In many ways esters are very similar to the more commonly known and used synthetic hydrocarbons. In the present work, the different mixed esters were prepared by reaction of pentaerythritol with different ratio of butyric acid and octanoic acid. Structure of the prepared compounds was confirmed by study the physico -chemical properties as (Infra-Red Spectroscopy, Nuclear Magnetic Resonance, Thermo Gravimetric Analysis TGA, Total Acid Number, density, reflective index, specific gravity, flash point and the Determination of the Molecular Weights) for all the prepared compounds. The efficiency of the prepared compounds were investigated as synthetic refrigeration lubricating oil. It was found that the prepared compounds have low temperature properties (pour point), high viscosity index (VI) and the rheological behavior is simple Newtonian fluid.

Keywords: *Synthetic lubricant; mixed ester; viscosity index; pour point and rheology.*

1. Introduction

Lubricants are necessary for the efficient use of machinery. Because of this, the variety of lubricating fluids has grown to satisfy the demands of new machines having more stringent requirements due to their operation under more severe conditions or in challenging environments [1]. Thus, while natural mineral oil-based fluids represent the majority of the market demand, many technological advances in equipment and machinery would not be possible without the benefits offered by the synthetic lubricants [2-3]. Organic esters represent one of the largest groups of synthetic lubricants in use today [4]. Synthetic esters have demonstrated during the last years to be a good ecological alternative to mineral based lubricants. This means that synthetic oils can combine a high biodegradability and low ecotoxicity with high technical features (although price can be four times higher) [5]. In addition to esters, mixtures of fatty alcohols with carboxylic acid esters have been proposed as lubricating additives [6]. Esters Just as categorizing a lubricant as synthetic is too broad, the same is true with categorizing a synthetic lubricant as an ester. Various types of esters are used as synthetic lubricants, including diesters, monoesters, phthalates, trimellitates/pyromellitates and polyol esters. While all contain a similar chemical structure, there are chemical variances in the entire molecule that provide differences in the performance. Ester-based synthetic lubricant may not be the same as another company's, and for that reason, it is a good idea to ask compatibility and performance questions of the lubricant marketer prior to just immediately making the lubricant change to or from an ester-based synthetic lubricant [7-9]. Synthetic ester lubricants, on the other hand are prepared from manmade base stocks having uniform molecular structures, and therefore well-defined properties that can be tailored to specific applications. Lubricants based on synthetic polyol esters are growing in popularity in cold rolling oil applications. Environmentally friendly synthetic polyol esters constitute alternatives to mineral and vegetable oil based cold rolling lubricants. Various types of synthetic-based oils used to formulate synthetic lubricants have certain advantages over conventional mineral-oil based products. These advantages are low pour point, low volatility, low toxicity, high viscosity index, high oxidation stability and high flash and fire points [10-14]. In the present work we prepared some synthetic lubricant based on mixed esters by esterification of pentaerythritol with butyric acid and octanoic acid, then study the physico-chemical properties and rheological properties of the prepared compounds.

2. Experimental

2.1. Preparation of mixed ester

Reaction of pentaerythritol with different ratio of butyric acid C_4 and octanoic acid C_8. The reactions were carried out in a resin kettle flask in presence of 1wt % a catalyst and xylene as a solvent. The esterification reactions were carried out under a slow stream of deoxygenated nitrogen; the reactions were agitated using mechanical stirrer at 500 rpm. The reactants which were mixed with an equal weight of xylene then heated gradually from room temperature to 170°C ± 0.5°C using a well controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give products A, B, C, D and E as given in Table (1)

Table 1. The designation of the prepared ester

Alcohol	Acids ratio (Butyric C_4+Octanoic C_8)	Prepared esters
1 mole of pentaerythritol	2 mole C_4 +2 mole C_8	A
1 mole of pentaerythritol	3 mole C_4 +1 mole C_8	B
1 mole of pentaerythritol	1 mole C_4 +3 mole C_8	C
1 mole of pentaerythritol	4 mole C_4	D
1 mole of pentaerythritol	4 mole C_8	E

2.2. Purification of prepared esters

The prepared esters were purified according to the following procedures:

- Filtrate it from the catalyst which washed with methanol and used it again
- Take the filtrate and washed it by 10% sodium carbonate solution in separating funnel and shaked well.
- The entire process was repeated several times to ensure complete removal of unreacted acid.
- The purified ester was then washed several times with distilled water to remove any traces of sodium carbonate then the ester was left overnight on calcium chloride anhydrous for drying.
- The anhydrous $CaCl_2$ was then removed by filtration and the xylene was removed by rotary.

2.3. IR spectroscopic analysis

IR spectra of the prepared compounds were determined by using FTIR spectrometer Model Type Mattson Infinity Series Top 961.

2.4. ^{1}HNMR spectroscopic analysis

The ^{1}HNMR spectra of prepared compounds were measured by Magnet: 400 Megahertz, console (Spectrometer): Varian model mercury plus, probe: Varian 5 millimeter.

2.5. Determination of the molecular weights

The molecular weights of the prepared ester were determined by using gas chromatography (GC- mass). Agilent technologies Model Type 5977A MSD, 7890B GC system, column DB- 5MS (0.25nm x 30cm, 0.1µm film) and flame ionization detector. Pure nitrogen was used as a carrier gas. The oven temperature program was varied from 40-320°C at a fixed rate of 20°C/min. The temperature of the injector detector was 300°C.

2.6. Thermal analyses

Thermogravimetric analyses (TGA) were performed to study the structural changes of the prepared samples with thermal treatment. A 10 mg of sample was heated up to 700°C, with a heating rate of 10°C min^{-1} in an (air or N_2) flow at a rate of 100 ml min^{-1} on SDTQ-600 (TA-USA) thermo balance instrument.

2.7. Total acid number (TAN)

The total acid number (TAN) of prepared compounds were determined according to ASTM D664 by using Model Type Mehrshom CLO-05.

2.8. Density

Density at 15 °C (g/ml) of the prepared compounds were determined by using Standard Test Method for Density according to ASTM D1298

2.9. Reflective Index

The reflective index of prepared compounds was determined according to ASTM D1747

2.10. Specific Gravity

Specific Gravity at 15 °C of the prepared compounds were determined by using Standard Test Method for Specific Gravity according to ASTM D4052 by using Model Type Metler Toledo DUO.

2.11. Flash Point

The flash point of prepared compounds was determined according to ASTM D 92 by using Cleveland open cup tester

2.12. Measure viscosity index

The kinematic viscosity of the prepared esters was determined at 40°C and 100°C. Then viscosity index was calculated according to ASTMD 22-70

2.13. Measure pour point

The pour point of the prepared compounds was determined according to the ASTM-97-93. The instrument used for measuring the pour point was the Cold Filter Plugging Point Automatic Tester (CFPPA-T), model 1st CPP97-2.

2.14. Study rheological properties

The rheological properties of prepared compounds were studied by using Model Type the Modular Compact Rheometer 502 (Anton Paar).

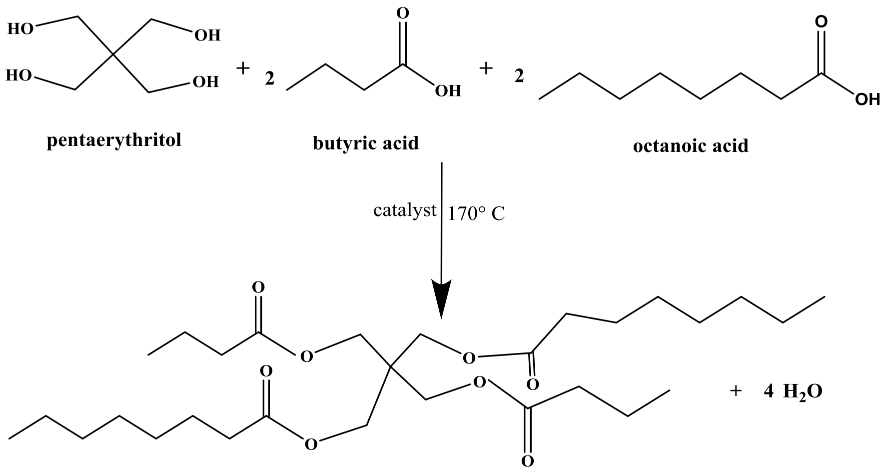
3. Results and discussions

3.1. Preparation of mixed ester

Reaction of 1 mole of pentaerythritol with 2 mole of butyric acid C_4 and 2 mole octanoic acid C_8. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product A, as showing in the reaction scheme A.

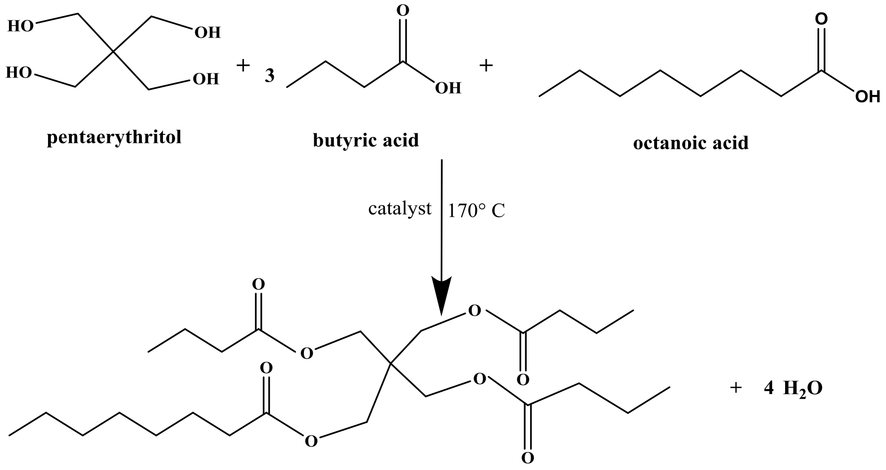
Reaction of 1 mole of pentaerythritol with 3 mole of butyric acid C4 and 1 mole octanoic acid C8. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product B, as showing in the reaction scheme B.

Reaction of 1 mole of pentaerythritol with 1 mole of butyric acid C_4 and 3 mole octanoic acid C_8. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product C, as showing in the reaction scheme C



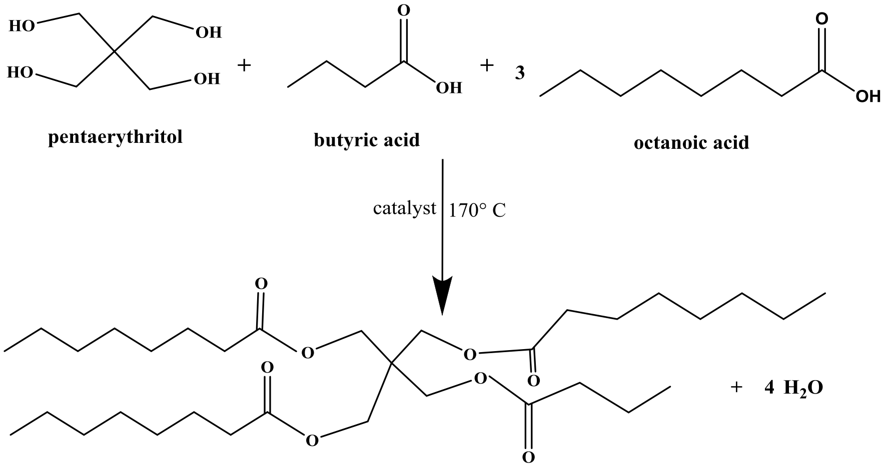
Prepared compound (A)

Reaction scheme A



Prepared compound (B)

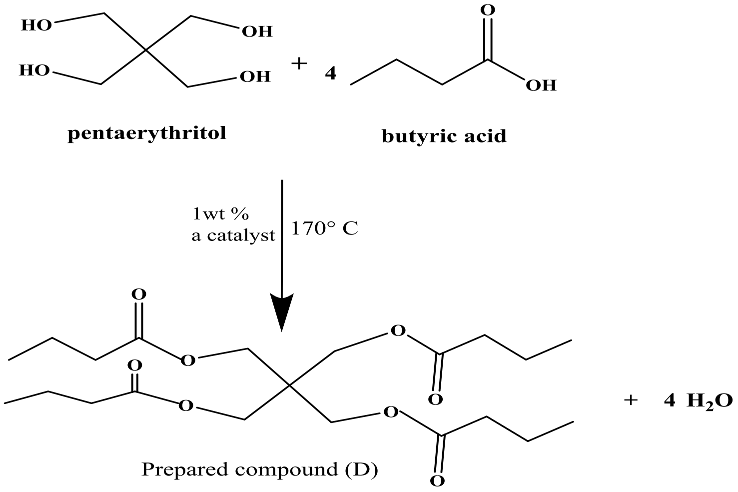
Reaction scheme B



Prepared compound (C)

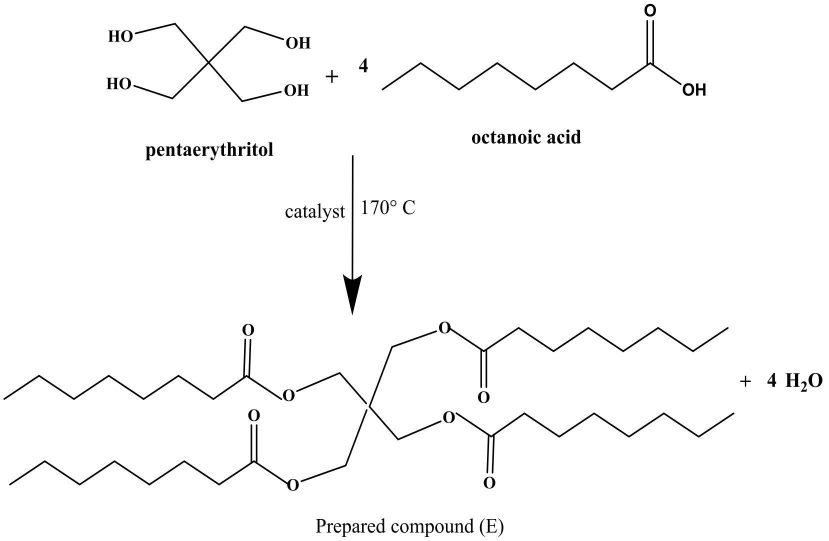
Reaction scheme C

Reaction of 1 mole of pentaerythritol with 4 mole of butyric acid C_4. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product D, as showing in the following reaction



Reaction scheme D

Reaction of 1 mole of pentaerythritol with 4 mole of octanoic acid C_8. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product E, as showing in the following reaction



Reaction scheme E

IR spectroscopy was used to elucidate the completion of the esterification reactions. All esters afford similar IR spectrum, IR spectrum given for example in Figure (1) which indicate the following: absence of strong absorption band at 3200cm^{-1} of aliphatic (–OH) group, the characteristic absorption bands of the carboxylic acids. These bands are broad peak extending from 3300 cm^{-1} to 2500cm^{-1} due to hydrogen bonded (– OH) and the (C-H) stretching vibrations. Appearance of the ester group bands at 1740 cm^{-1} ± 10 cm^{-1} and 1280 cm^{-1} ± 100 cm^{-1} due to (C=O) and (C-O-C) stretching respectively. The band for (C–H) aliphatic appear near 2850cm^{-1} & 2950cm^{-1}. This is indicates that the esterification process is carried out successfully.

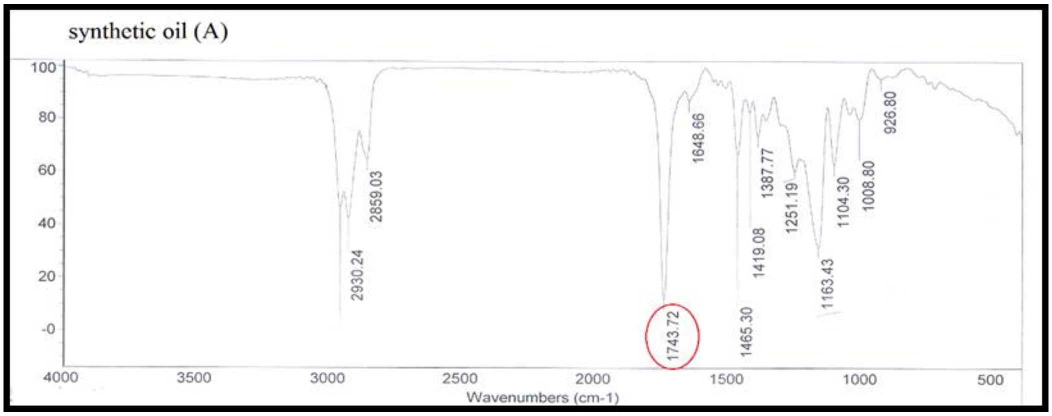


Figure 1. IR spectrum of the prepared compound (A)

The chemical structures of the prepared compounds can be proved from ^{1}HNMR analysis, which is represented for example in Figure (2). In this respect, the signal at 3.9 ppm (which is assigned to O-CH_2 groups), the signal at 2-2.5 ppm (which is assigned to O=C-CH_2 groups) and the signal at 1.5–2 ppm (which is assigned to aliphatic protons) were selected to determine the esterification of the prepared compounds.

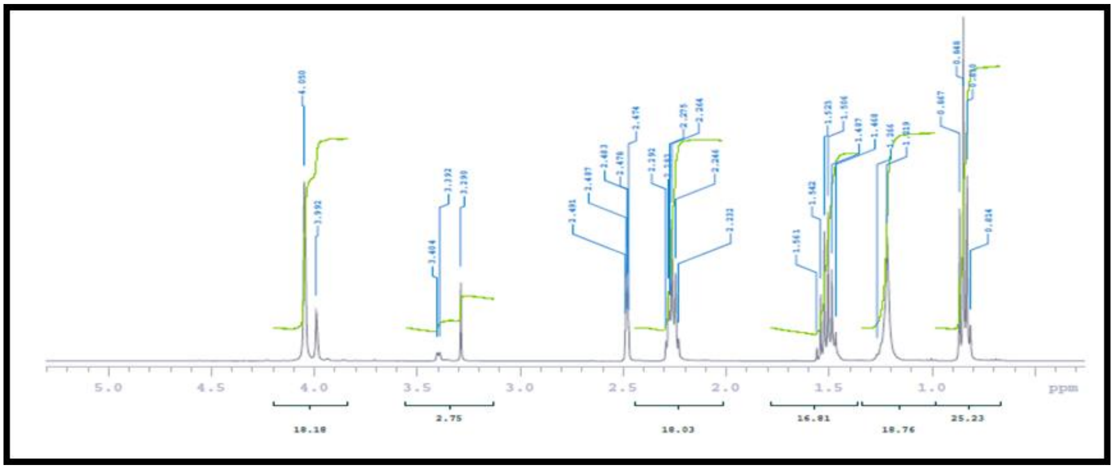


Figure 2. ^{1}HNMR spectrum of the prepared compound (B)

The mean molecular weights of prepared compounds by using gas chromatography are given in Table 2, as shown the theoretical and experimental mean molecular weight are equal for all prepared compounds. Finally compound E is the largest molecular weight while compound D is the smallest one.

Table 2. The mean molecular weights of prepared compounds

Designation of the prepared esters	Molecular formula	Mean molecular weight(gm/ mole)	
		Theoretical	Experimental
A	$C_{29}H_{52}O_8$	528.71838	528.1
B	$C_{25}H_{44}O_8$	472.61206	472.8
C	$C_{33}H_{60}O_8$	584.8247	584.8
D	$C_{21}H_{36}O_8$	416.50574	417.1
E	$C_{37}H_{68}O_8$	640.93102	640.8

Mass spectra for some prepared compound as example are given for example in Figures (3 and 4).

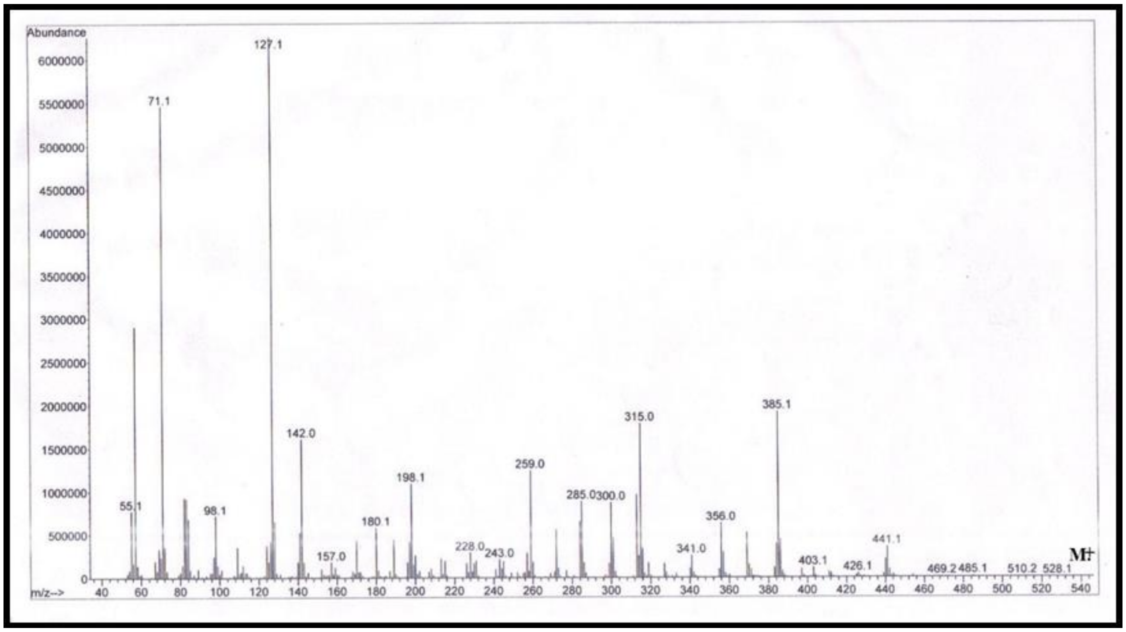


Figure 3. Mass spectra of the prepared compound (A)

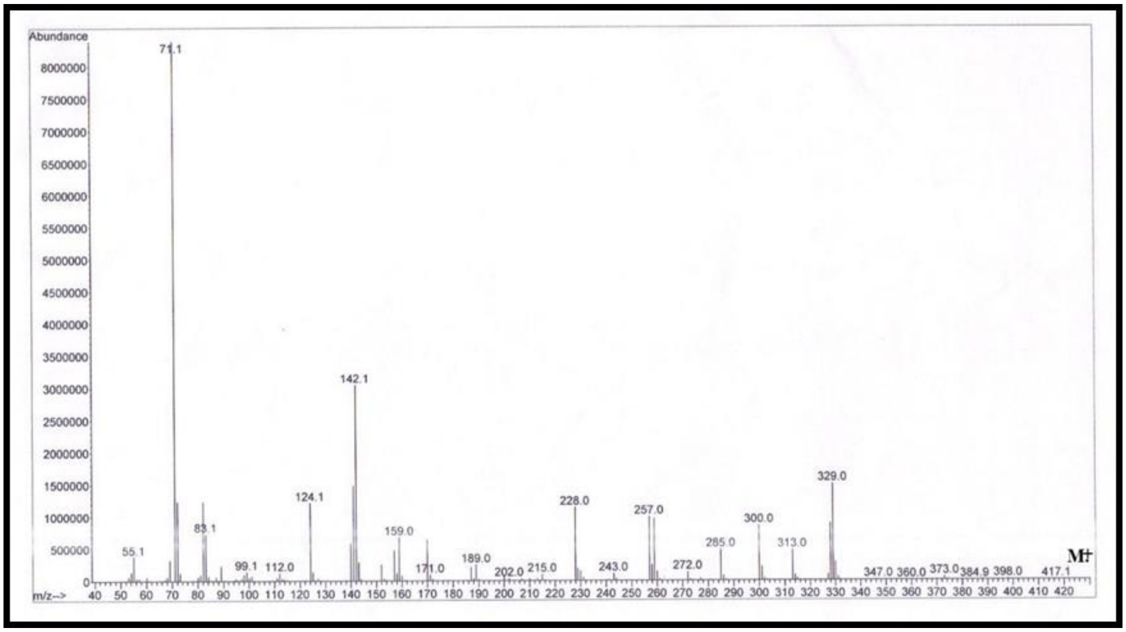


Figure 4. Mass spectra of the prepared compound (D)

Thermal analyses

Thermal stability of the prepared compounds was studied using thermal gravimetric analysis "TGA". TGA is a technique which the thermal properties of a material are determined as a function of temperature [19]. The thermal tests measure the change of weight and enthalpy as the sample is heated. TGA has been extensively used for measurement of degradation as we see in Table 3. (T_1) is the temperature when primary degradation step occurs with weight loss % (W_1) and (T_2) is the temperature when major degradation step occurs with weight loss % (W_2).

Table 3. The thermal stability of prepared compounds

Synthetic lube oil designation	T_1 (℃)	W_1 (%)	T_2 (℃)	W_2 (%)
A	292	7.88	374	97.757
B	260	13.99	335	97.799
C	311	13.6	379	99
D	247	13.9	303	99.04
E	341	14.71	399	98.3

TGA analysis, the thermo gravimetric study has shown a good thermal stability for the prepared compounds, and this confirms the suitability of using the prepared compounds as synthetic lubricating oil as it can be used at high temperature without degradation, which is represented for example in Figures (5 and 6).

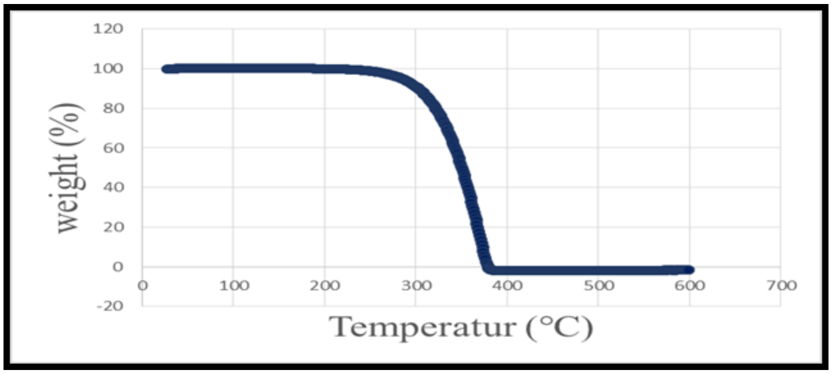


Figure 5. TGA analysis of the prepared compound (C)

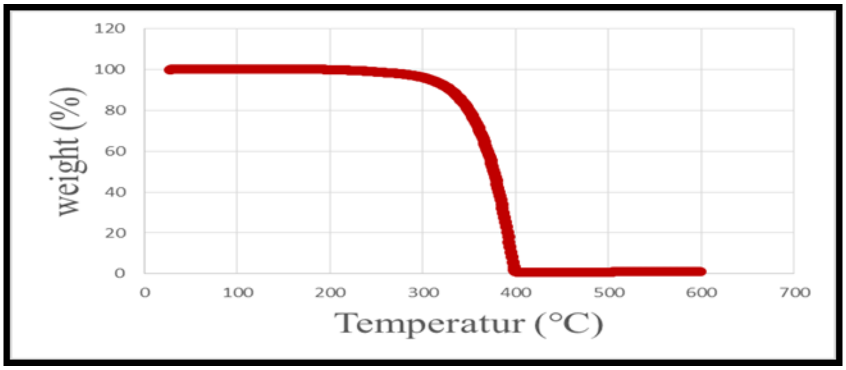


Figure 6. TGA analysis of the prepared compound (E)

Measuring the viscosity index

The VI increases with increasing the mean molecular weight of the prepared compounds compared with the mineral oil as shown in Table 4. [15].

Table 4. Measuring the viscosity at 40℃ and at 100℃and calculate the viscosity index

Designation of the prepared compounds	Viscosity at 40℃	Viscosity at 100℃	Viscosity index
A	23.49876	4.626468	116
B	21.65572	4.259288	101
C	25.3418	4.993648	125
D	14.51394	3.194466	72
E	27.6456	5.360828	131
Mineral Oil	86.16212	9.766988	90

Measuring the pour point

The pour point is defined as the lowest temperature at which the oil will pour or flow when it is chilled without disturbance under prescribed conditions [16]. A pour point in synthetic lubricating oil is lower than the mineral oil due to absence of crystal formed interlocking growth restricts the pour of oil, and pour point decrease according to decrease in the molecular weight of the prepared synthetic lubricating oil as shown in Figure 7.

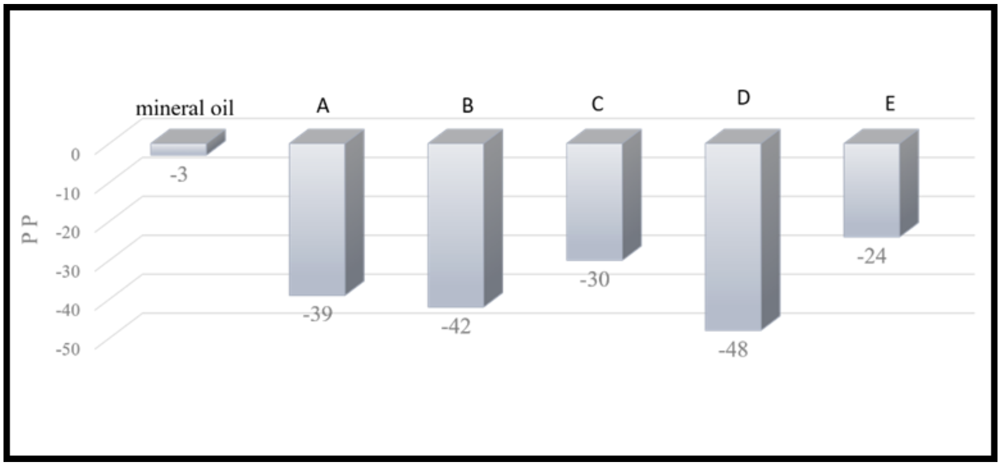


Figure 7. Dependence of PP on the mean molecular weight of synthetic lubricating oils (A, B, C, D and E)

Study rheological properties

The rheological behavior of oils and their products is generally simple Newtonian fluid (viscosity is independent of shear rate). Shear rate is a measure of the rate of shear deformation [17-8]. 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. All the prepared synthetic lubricating oil is Newtonian fluid behavior as shown for example in Figures (8 and 9).

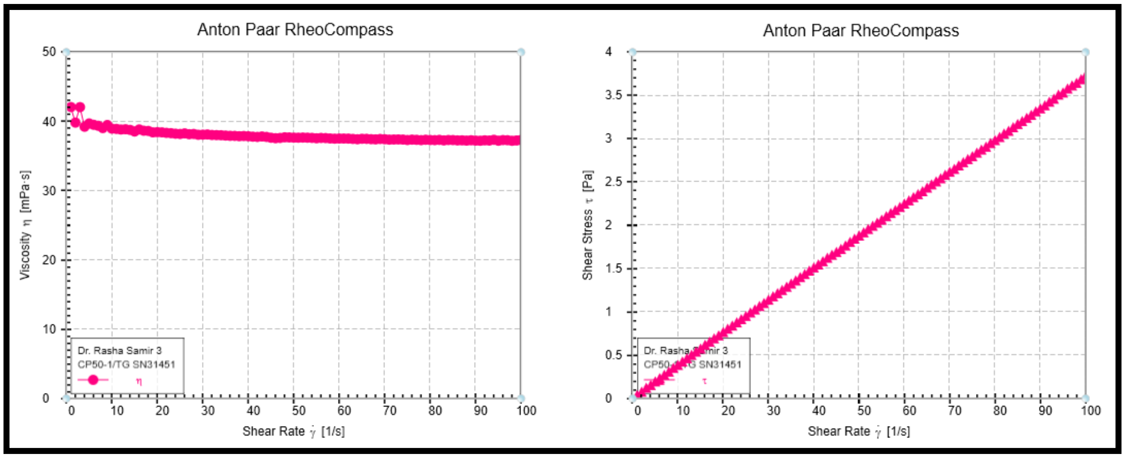


Figure 8. The rheological behavior of synthetic lubricating oil (C)

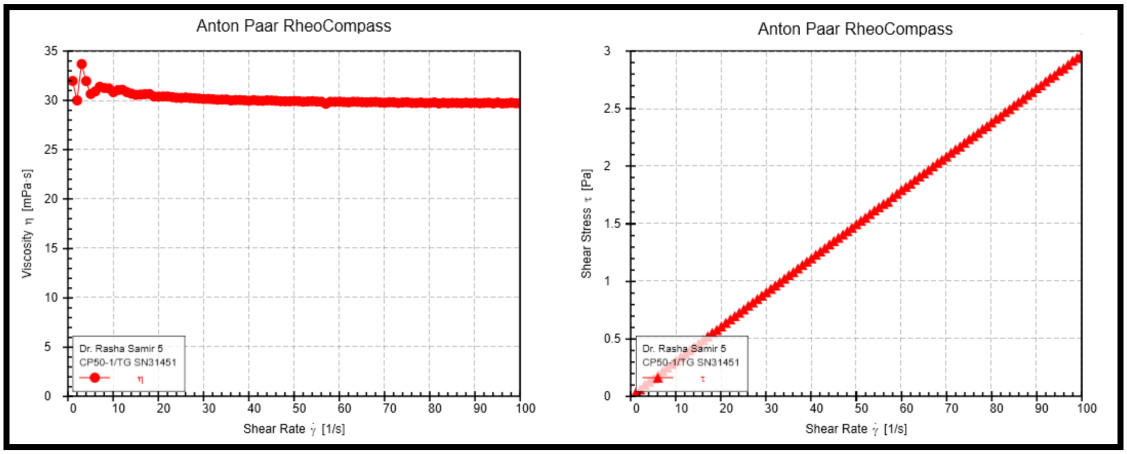


Figure 9. The rheological behavior of synthetic lubricating oil (E)

Comparison of the physical properties between the prepared esters and the comercial refrigeration oil specifications

The comparative study indicates that the prepared esters could be considered as synthetic refrigeration lubricating oil [20].

Table 5. The physico-chemical properties of prepared compounds

Properties	A	B	C	D	E
Total Acid Number (TAN) (mg KOH/g)	Nil	Nil	Nil	Nil	Nil
Density (g/ml) at 20°C	1.024	1.035	0.997	1.048	0.989
Reflective Index at 28°C	1.4565	1.4565	1.4566	1.4565	1.4566
Specific Gravity at 15°C	1.0516	1.0210	1.0580	1.0006	1.0616
Flash point (COC) °C	310	267	318	253	346

Table 6. Properties of the commercial refrigeration oil

Properties	Commercial refrigeration oil
Viscosity at 40°C	18.9
Viscosity at100°C	4.2
Viscosity index	120
Pour point	52-
Total Acid Number (TAN) (mg KOH/g)	0.01
Density (g/ml) at 20°C	0.995
Reflective Index at 28°C	1.4519

4. Conclusion

- The mixed ester obtained by reaction of pentaerythritol with different ratio of butyric acid and octanoic acid.
- Study the physicochemical properties (FTIR, ^{1}HNMR, determination of the molecular weights, TGA, total acid number TAN, density, reflective index, specific gravity and flash point) of the prepared compounds.
- Evaluation of the prepared esters as synthetic lubricating oil by measuring viscosity index, pour point and study rheological properties. It was found that the prepared compounds have low temperature properties (pour point), high viscosity index (VI) and the rheological behavior is simple Newtonian fluid.

- Comparative study between the commercial refrigeration oil and the prepared ester indicates that the prepared esters can be used as synthetic refrigeration lubricating oil

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