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STUDY THE EFFICIENCY OF SOME ESTERS AS SYNTHETIC LUBRICATING OIL

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Abstract

Polyolesters (POE) were the strongest candidates to replace the traditional mineral oil. It have good miscibility with the new alternative refrigerants and possess good electrical insulation that is important in hermetic compressors where the electrical motor is exposed to the lubricant. In the present work, the different mixed esters were prepared by reaction of trimethylol propane with different ratio of valeric, heptanoic and octanoic acids. Structure of the prepared compounds was confirmed by study the physico-chemical properties as (Infra-Red spectroscopy, Nuclear Magnetic Resonance, Thermo Gravimetric Analysis, Total Acid Number, the Molecular Weights Determination, Density, Reflective Index, Specific Gravity and Flash Point) for all the prepared compounds were determined. 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 a simple Newtonian fluid.

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

1. Introduction

Lubrication is the operation by which friction and wear are reduced between contact surfaces of solids moving in relation to each other by applying a substance with appropriate characteristics. Well-applied lubrication brings significant economic benefits in the form of energy-saving, conservation of materials, reduction in maintenance operations, and also positive effects on environmental impact [1].A lubricant is a substance introduced between two moving surfaces to reduce the friction between them, improving efficiency and reducing wear [2-3]. Synthetic lubricants do not originate from crude oil like conventional mineral oil. Instead, synthetic lubricants not only have high-performance base stock but usually also benefit from premium additive systems. In fact, many of the benefits that are commonly attributed to synthetic lubricants actually come from the additives with which they are formulated [4].

The lubricant industry generally treats synthetic esters as a monolithic class of Group V base oils with well-defined properties. It is not difficult to find a chart that lists esters as having "fair" hydrolytic stability, "good" biodegradability, "very good" lubricity, "excellent" oxidative stability and so on. Sometimes diesters and polyol esters are listed separately, but there is seldom further differentiation. However, the nature of esters defies such over simplification. There are endless varieties of esters that can be built from commonly available acids and alcohols, so almost anything is possible [5].Esters are another class of synthetic base, typically used for motor transport vehicles; these are polar compounds and for this reason are generally used in mixtures with PAOs. Depending on the type of acid and alcohol used in the synthesis, it is possible to give the base the desired rheological and performance characteristics. Thanks to their lubricating capacity and, when required, their pronounced biodegradability, esters are widely used in oils for two-stroke engines. Other classes of synthetic bases are used in particular lubricating sectors [1]. Esters are a broad and diverse family of synthetic lubricant base stocks which can be custom designed to meet specific physical and performance

properties. The inherent polarity of esters improves their performance in lubrication by reducing volatility, increasing lubricity, providing cleaner operation, and making the products biodegradable. A wide range of available raw materials allow an ester designer the ability to optimize a product over a wide range of variables in order to maximize the performance and value to the client. They may be used alone in very high temperature applications for optimum performance or blended with PAOs or other synthetic base stocks where their complementary properties improve the balance of the finished lubricant. Esters have been used in synthetic lubricants for more than 60 years and continue to grow as the drive for efficiency make operating environments more severe. Because of the complexity involved in the designing, selecting, and blending of an ester base stock, the choice of the optimum ester should be left to a qualified ester engineer who can better balance the desired properties [7-14].

In the present work we prepared some synthetic lubricant based on mixed esters by esterification of trimethylol propane with valeric acid, heptanoic 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 trimethylol propane with different ratio of valeric acid C_5, heptanoic acid C_7 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, E, F, G and H as given in the part 3.1.

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 calcium chloride was then removed by filtration and the xylene was removed by rotary evaporator.

2.3. I.R. spectroscopic analysis

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

2.4. ^{1}H NMR Spectroscopic analysis

The ^{1}H NMR 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 GC- MS 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

Thermo gravimetric 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. Refractive index

The refractive index of prepared compounds were 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 DEUO Density meter

2.11. Flash point

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

2.12. Measure viscosity index

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

2.13. Measure pour point

The pour point of the prepared compounds were 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 trimethylol propane with 1 mole of valeric acid C_5 , 1 mole of heptanoic acid C_7 and 1 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 A.

Reaction of 1 mole of trimethylol propane with 2 mole of valeric acid C_5 and 1 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 B

Reaction of 1 mole of trimethylol propane with 2 mole of valeric acid C_5 and 1 mole of heptanoic acid C_7. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product C.

Reaction of 1 mole of trimethylol propane with 2 mole of heptanoic acid C_7 and 1 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 D.

Prepared ester A

Prepared ester B

Prepared ester C

Prepared ester D
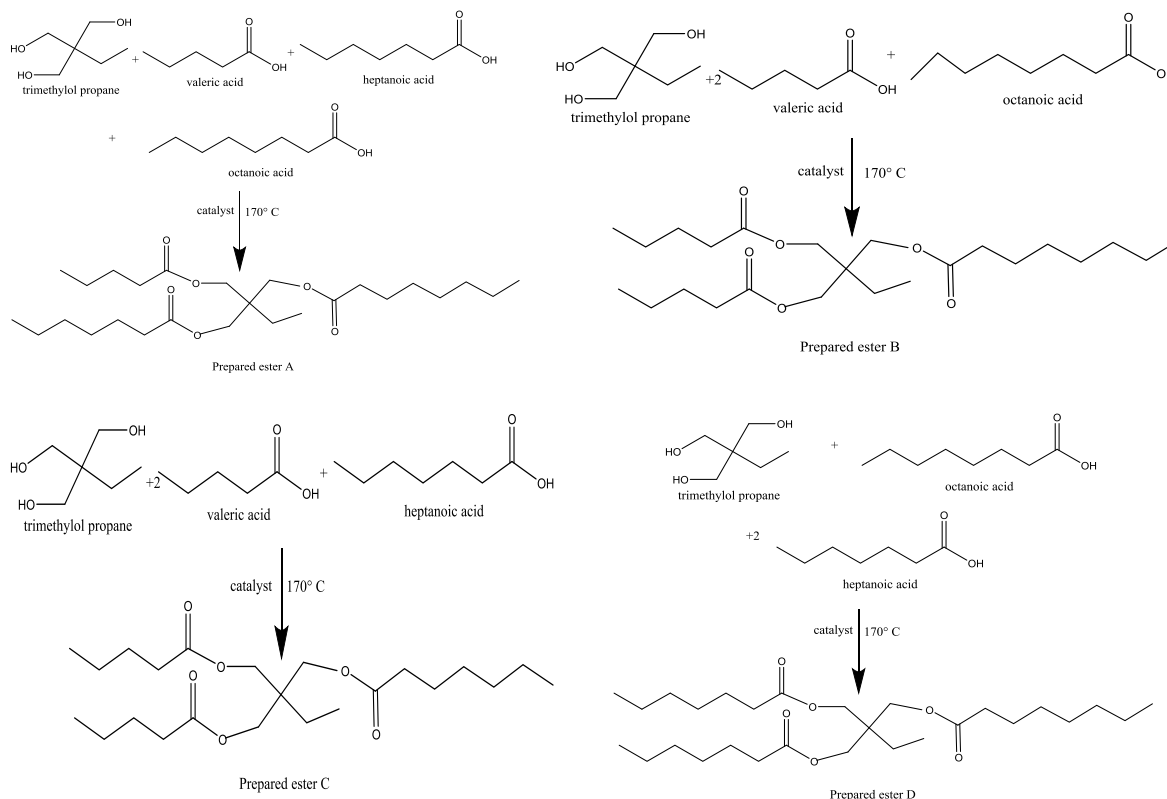
Reaction of 1 mole of trimethylol propane with 1 mole of heptanoic acid C_7 and 2 mole of octanoic acid C_8. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product E.

Reaction of 1 mole of trimethylol propane with 3 mole of valeric acid C_5. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product F.

Reaction of 1 mole of trimethylol propane with 3 mole of heptanoic acid C_7. The esterification reactions were carried out and the extent of reaction was followed by monitoring the amount of liberated water to give product G.

Reaction of 1 mole of trimethylol propane with 3 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 H.

Prepared ester E

Prepared ester F
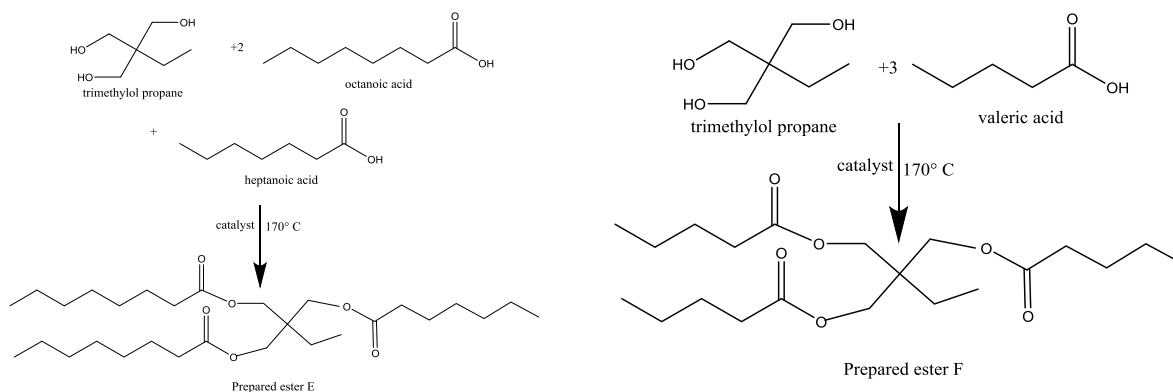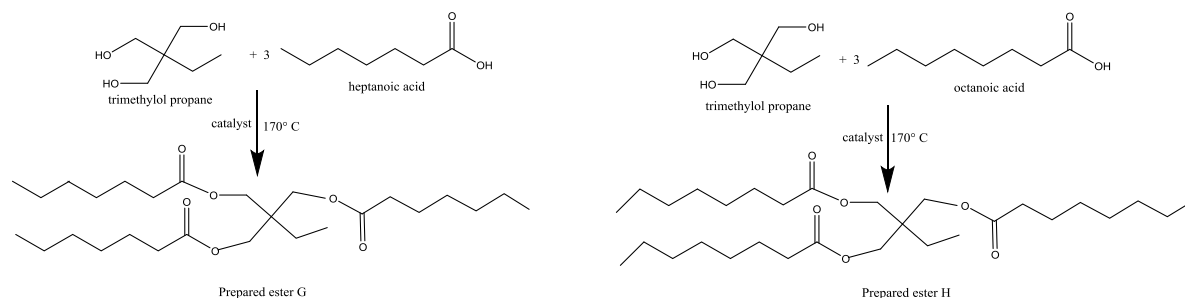
I.R. spectroscopy was used to elucidate the completion of the esterification reactions. All esters afford similar I.R spectrum, I.R spectrum of them are given in Figures (1-8) which indicate the following: absence of strong absorption band at 3200cm^{-1} of aliphatic (−OH) group, the characteristic absorption bands of the carboxylic acids. These bands are broad peak extending from 3300cm^{-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.

The chemical structures of the prepared compounds can be proved from ^{1}HNMR analysis, which is represented in Figures (9-16). 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 [15].

The mean molecular weights of prepared compounds by using gas chromatography are given in Table 1, as shown the theoretical and experimental mean molecular weight are equal for all prepared compounds. Finally compound H is the largest molecular weight while compound F is the smallest one. Mass spectra for prepared compound are given Figures (17 and 24).

Table 1. The mean molecular weight of prepared compounds

Designation of the prepared esters	Molecular formula	Mean molecular weight (g/mole)	
		Theoretical	Experimental
A	$C_{26}H_{48}O_6$	456.66112	455
B	$C_{24}H_{44}O_6$	428.60736	428
C	$C_{23}H_{42}O_6$	414.58048	414.2
D	$C_{28}H_{52}O_6$	484.71488	484.2
E	$C_{29}H_{54}O_6$	498.74176	495.5
F	$C_{21}H_{38}O_6$	398.622	396
G	$C_{27}H_{50}O_6$	470.688	469.5
H	$C_{30}H_{56}O_6$	512.6864	513.5

3.2. 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 [16]. 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 2. (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).

TGA analysis, the thermo gravimetric study has shown a good thermal stability for the prepared compounds, as in these compounds the temperature at when the primary degra-dation step occurs ranging from 243.68 to 308.86℃ and weight loss ranging from 12 to 19%, and the temperature when the major degradation step occurs ranging from 299 to 366°C and

the weight loss ranging from 98 to 99%, 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 in Figures (25-32).

Table 2. The thermal stability of prepared compounds

Synthetic lube oil designation	T_1 (°C)	W_1 (%)	T_2 (°C)	W_2 (%)
A	249.73	12.97	315.25	99.0726
B	252.59	19.74	309.28	98.922
C	245.65	15.44	305.58	99.0699
D	279.84	18.66	338.93	98.3359
E	288.25	16.25	352.53	98.143
F	234.68	17.32	299.69	99.7509
G	269.22	13.2	334.95	98.19
H	308.86	19.84	366.09	98.333

3.3. 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 3 & Figure (33) [17]. The increase in VI means that these oil can be used at a wide range of temperature.

Table 3. Kinematic viscosity and viscosity index of tested esters

Designation of the prepared esters	Kinematic viscosity at 40°C, mm²/s	Kinematic viscosity at 40°C, mm²/s	Viscosity index
A	16.81774	3.686596	104
B	6.22026	1.946054	94
C	8.75444	2.415356	93
D	10.3671	2.7649	109
E	11.97976	3.047594	112
F	11.74938	2.764947	62
G	8.0633	2.349952	108
H	17.50888	3.877282	115
Mineral oil	86.16212	9.766988	90

3.4. 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 [18]. 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 [19]. The pour point of all the prepared compounds A. B. C. D. E. F. G and H is lower than- 45°C. This means that these oil can be used at low temperature.

Table 4. The physico-chemical properties of prepared esters

Properties	A	B	C	D	E	F	G	H
TAN, (mg KOH/g)	0.0376	0.0202	0.0475	0.0101	0.0112	0.044	0.027	0.0196
Density at 20°C, (g/cm³)	0.9638	0.9672	0.9680	0.9516	0.9481	0.9692	0.9601	0.9372
Refractive index at 28°C	1.4669	1.4668	1.4569	1.4789	1.4879	1.4479	1.4787	1.4978
Flash point (COC), °C	255	248	248	276	289	234	276	303

3.5. 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 [20-21]. 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 in Figure (34- 42).

3.6. Comparison of the physical properties between the prepared esters and the commercial turbo engine oil (Turbo Nycoil 13B) specifications

The comparative study indicates that the prepared esters could be considered as synthetic base oil and may be used in formulations for turbo engine according to Air specification 3514 as illustrated from the comparison with commercial turbo engine oil (Turbo Nycoil 13B) [22].

Table 5. Properties of the commercial engine oil Turbo Nycoil 13B

Properties	Turbo Nycoil 13B
Kinematic viscosity at 40°C, mm^2/s	13.35
Kinematic viscosity at 100°C, mm^2/s	3.30
Viscosity index	124
Pour point, ^{o}C	-63
TAN, (mg KOH/g)	0.03
Density at 20oC, g/cm3	0.940
Refractive index at 28°C	1.4534
Flash point (COC), ^{o}C	218

4. Conclusion

- The mixed ester were prepared by reaction of trimethylol propane with different ratio of valeric acid. heptanoic acid and octanoic acid.
- Study the physicochemical properties (Fourier transform infrared spectroscopy FTIR. proton nuclear magnetic resonance ^{1}HNMR. determination of the molecular weights. Thermo gravimetric analysis TGA. total acid number TAN. density. reflective index. specific gravity and flash point) were determined for 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) (except F) and the rheological behavior is simple Newtonian fluid.
- Comparative study between the commercial turbo engine oil (Turbo Nycoil 13B) and the prepared ester indicates that the prepared esters could be considered as synthetic base oil

Figures
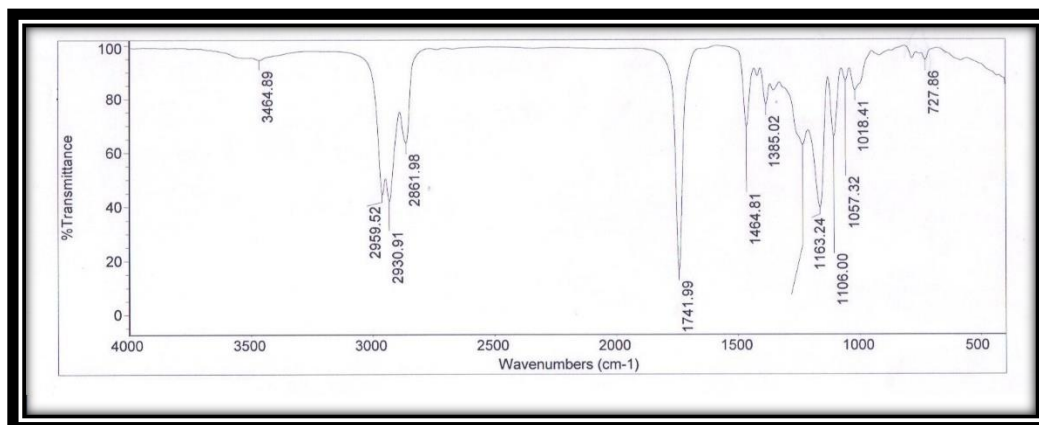
Figure 1. IR spectrum of the prepared compound (A)
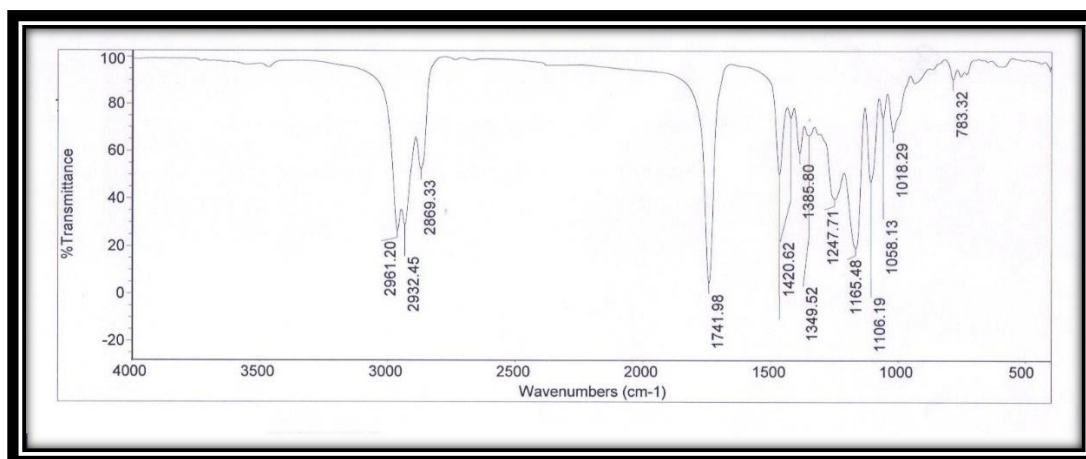
- Figure 2. IR spectrum of the prepared compound (B)
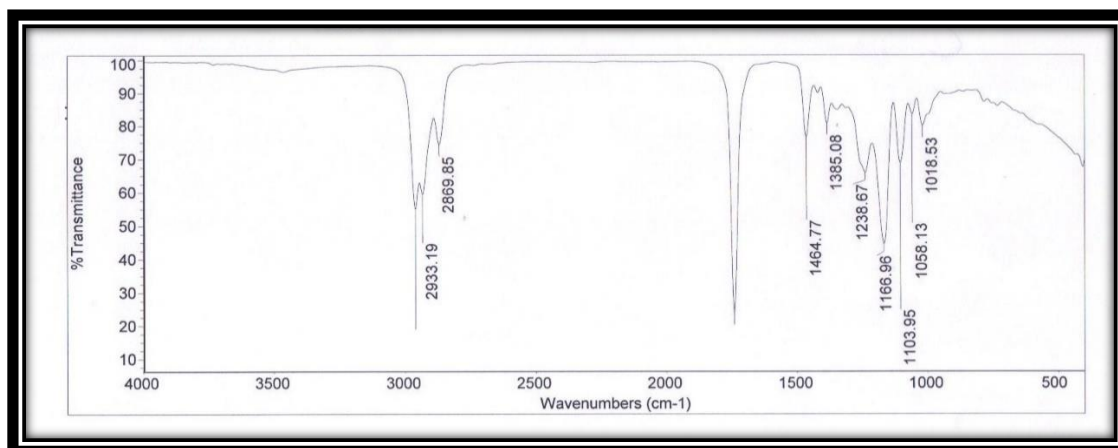
- Figure 3. IR spectrum of the prepared compound (C)
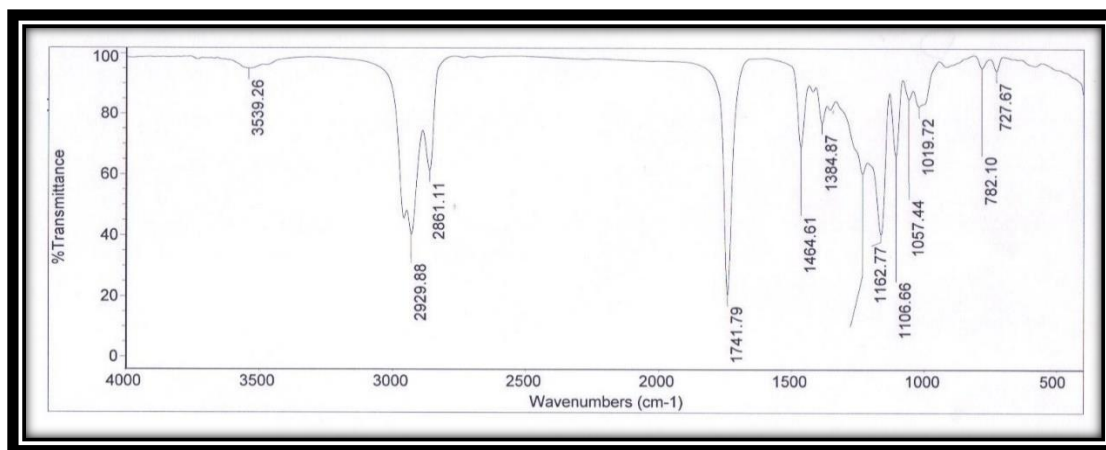
- Figure 4. IR spectrum of the prepared compound (D)
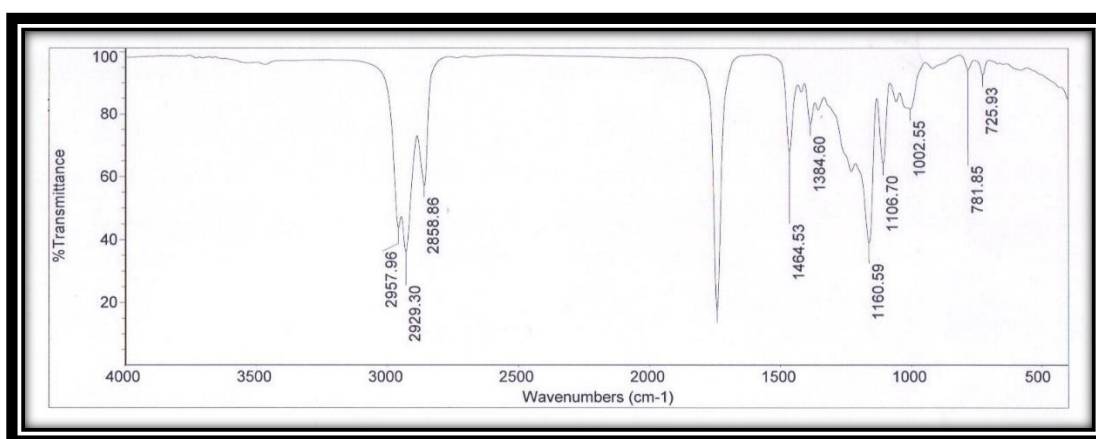
- Figure 5. IR spectrum of the prepared compound (E)
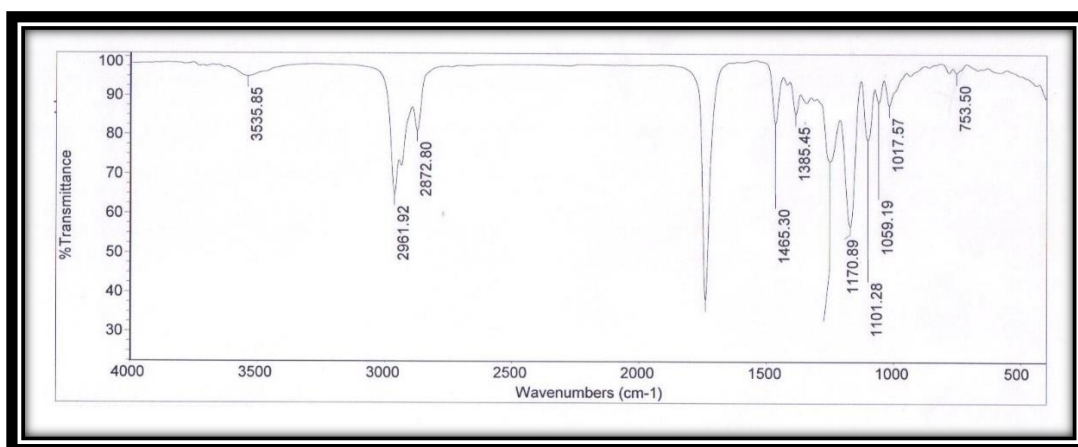
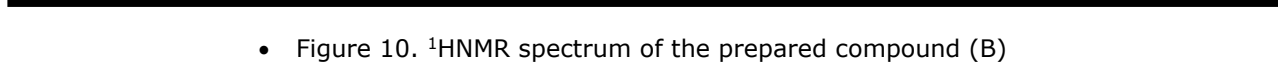

- Figure 6. IR spectrum of the prepared compound (F)
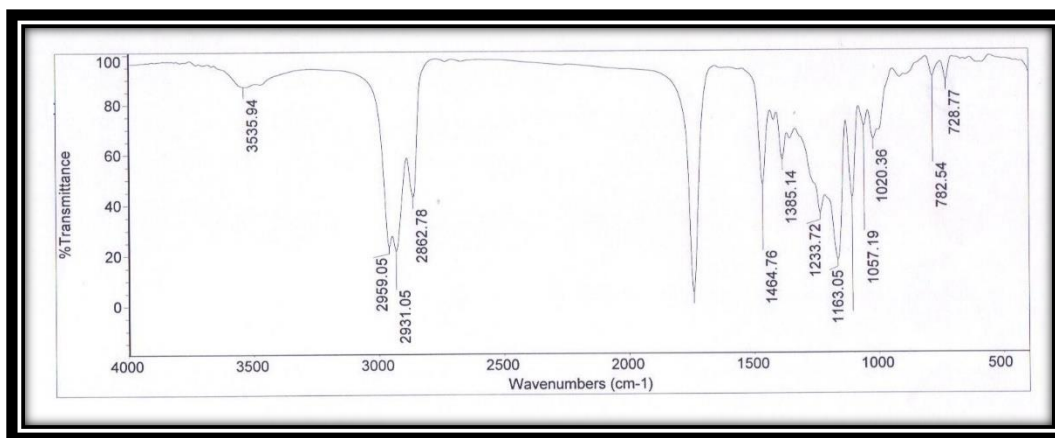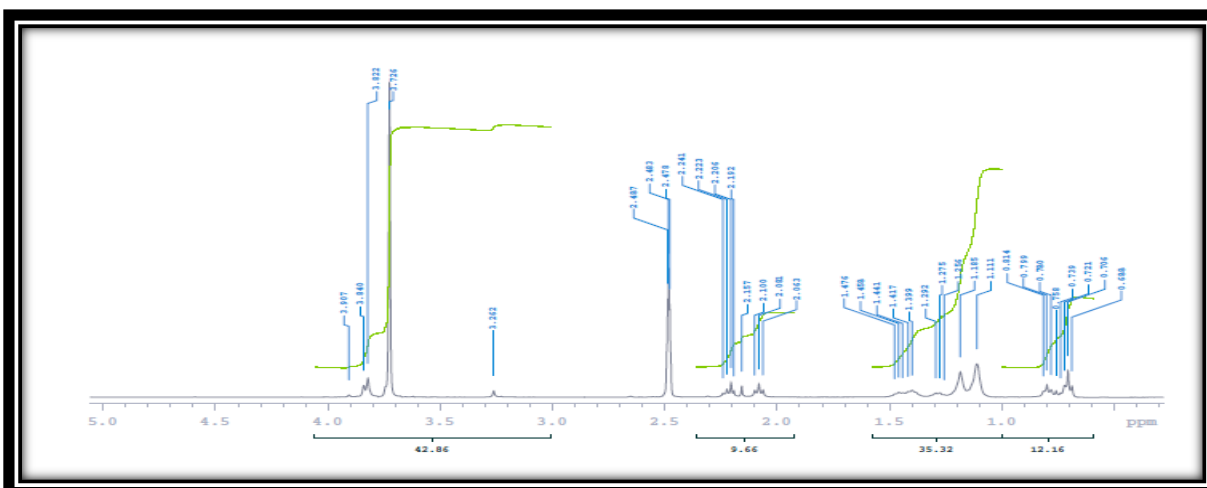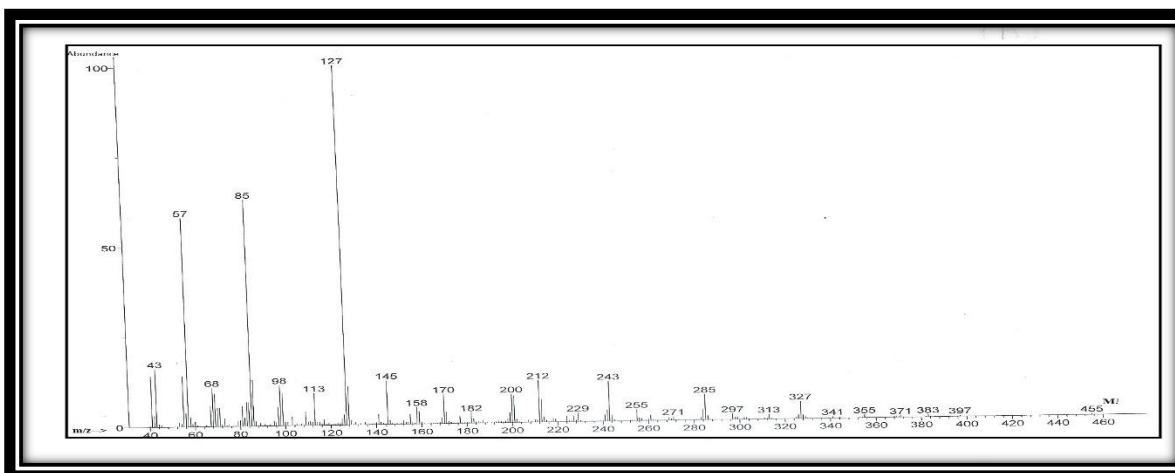
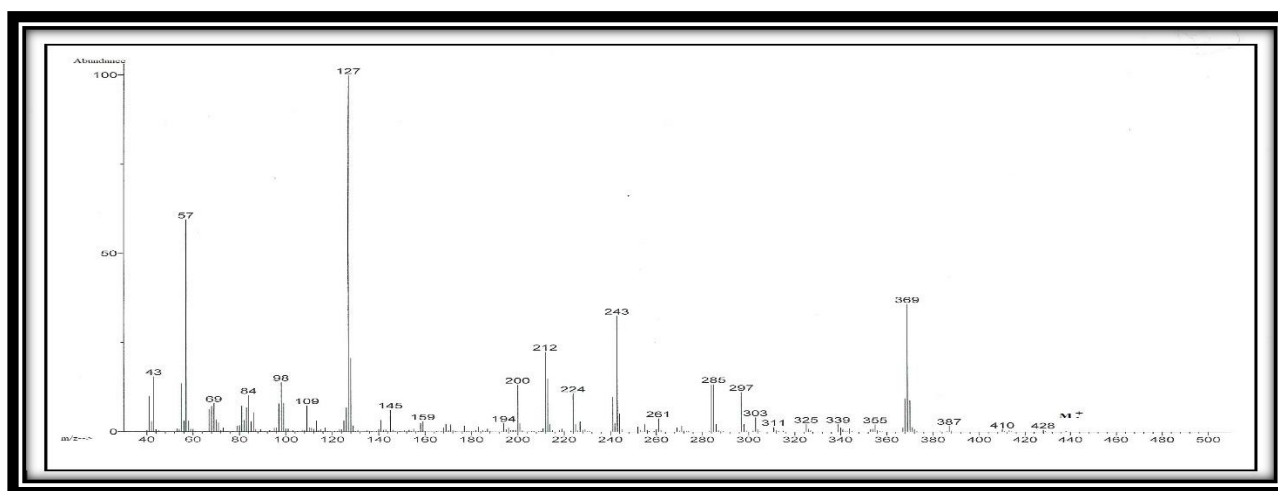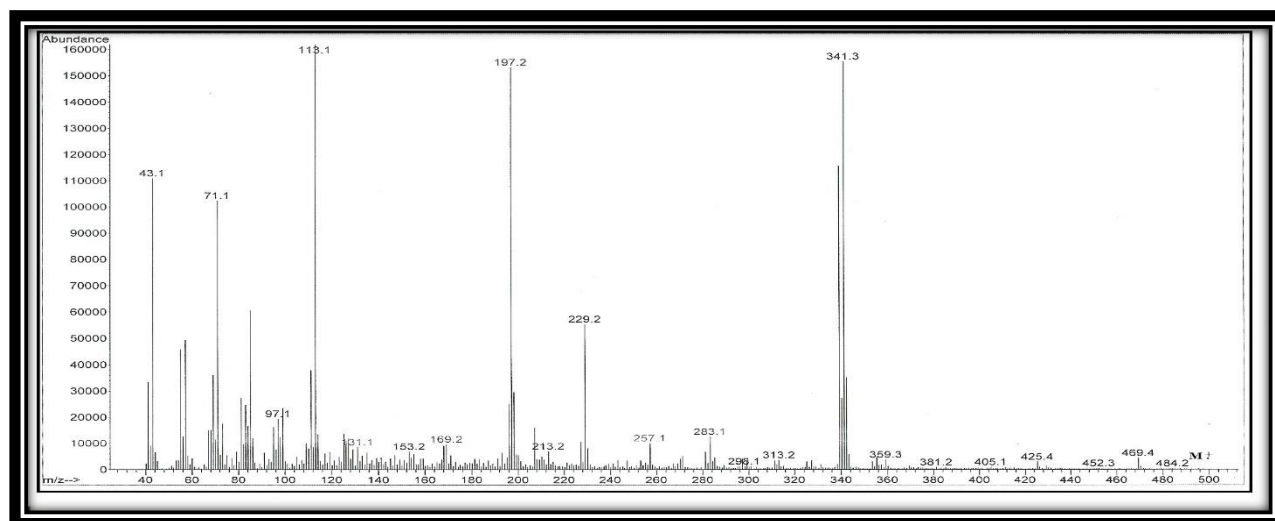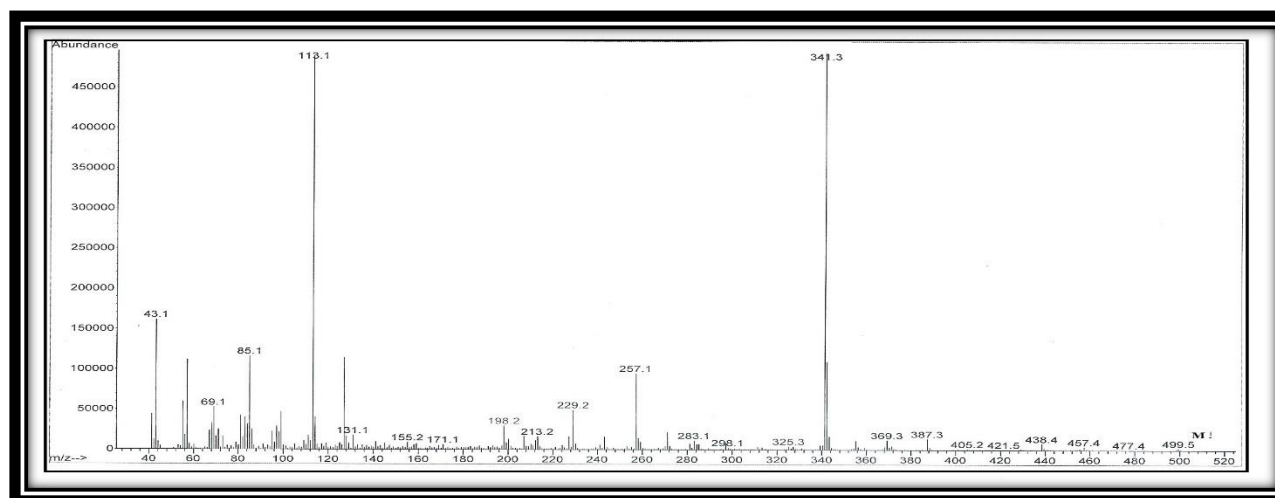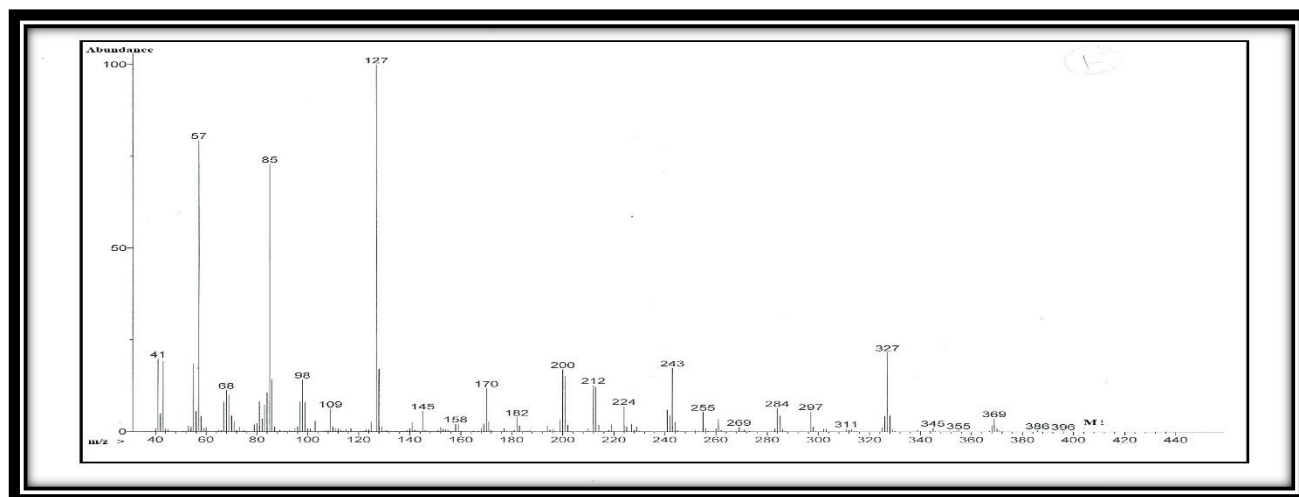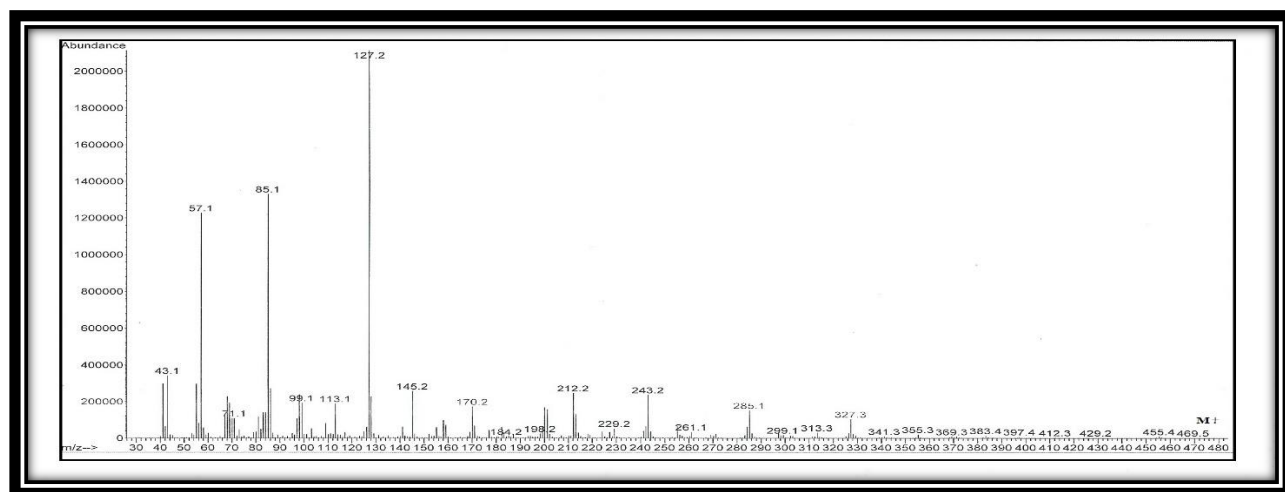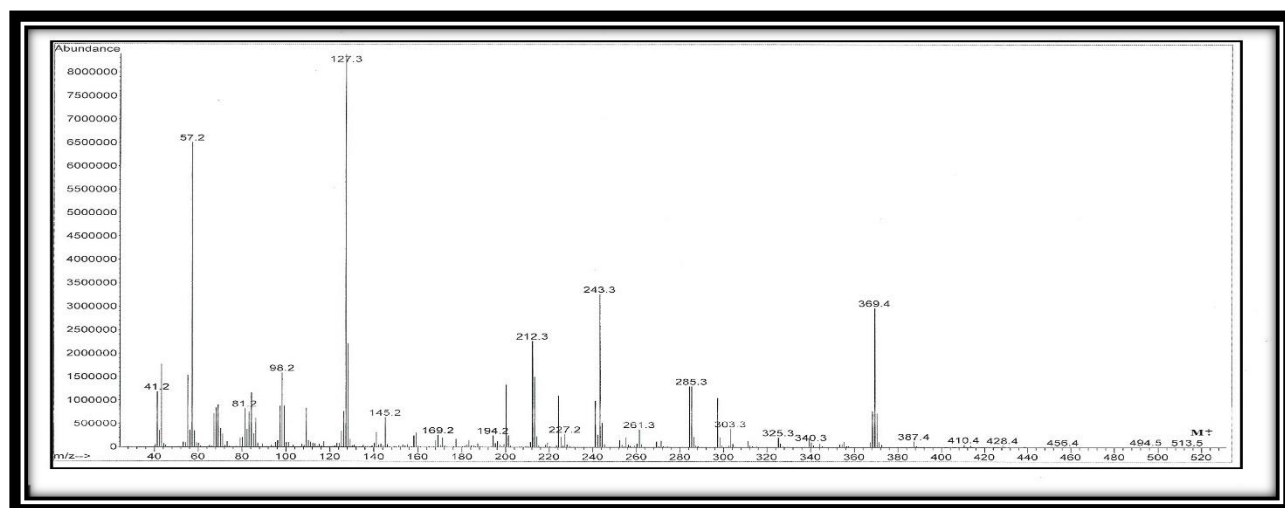- Figure 7. IR spectrum of the prepared compound (G)
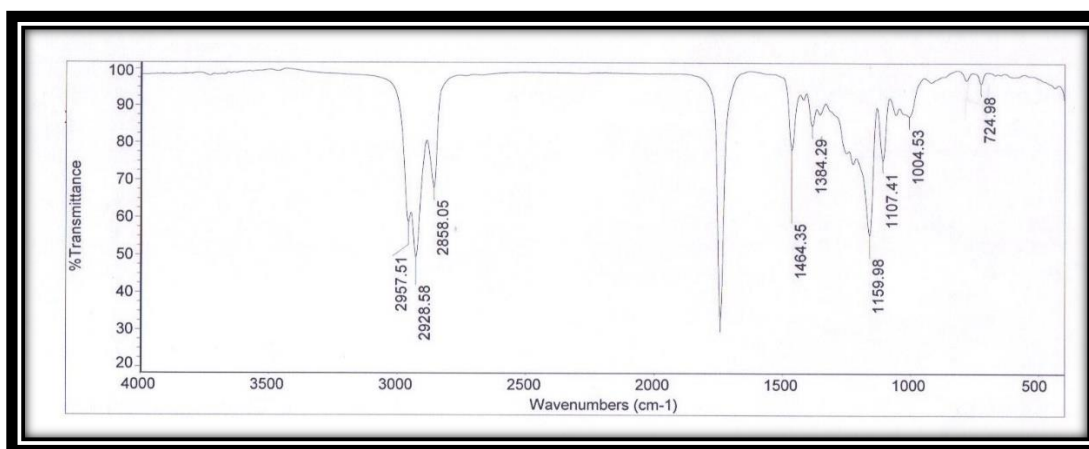
- Figure 8. IR spectrum of the prepared compound (H)
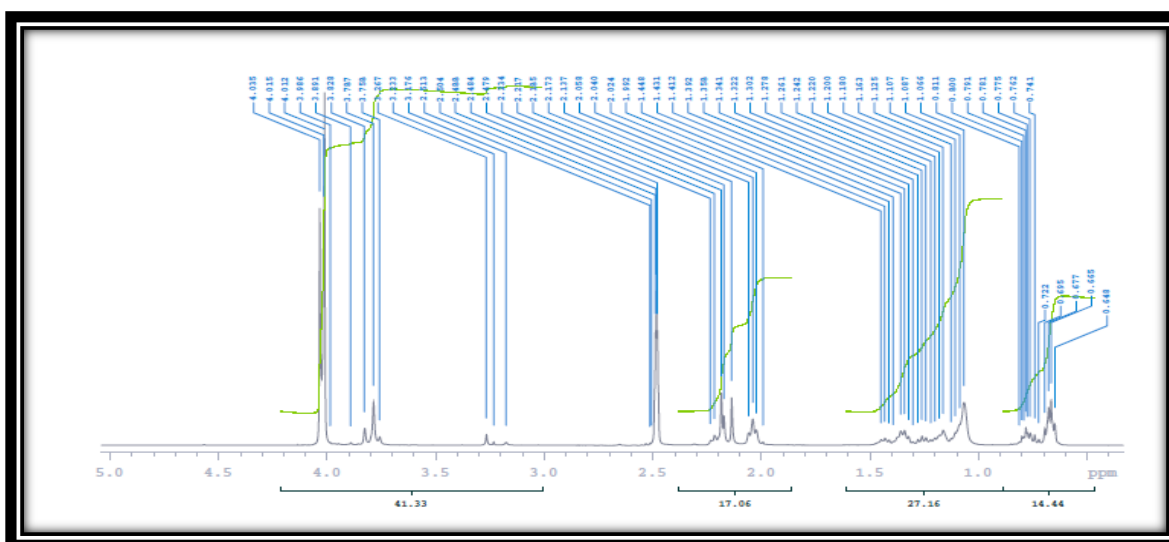
- Figure 9. ^{1}HNMR spectrum of the prepared compound (A)

- Figure 10. ¹HNMR spectrum of the prepared compound (B)

- Figure 11. ¹HNMR spectrum of the prepared compound (C)

- Figure 12. ¹HNMR spectrum of the prepared compound (D)
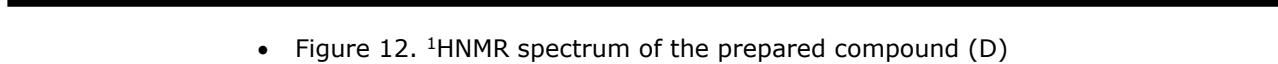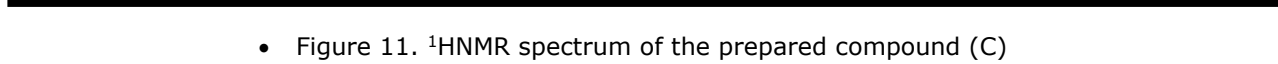
Figure 13. ¹HNMR spectrum of the prepared compound (E)

Figure 14. ¹HNMR spectrum of the prepared compound (F)

Figure 15. ¹HNMR spectrum of the prepared compound (G).

Figure 16. ^{1}HNMR spectrum of the prepared compound (H)

Figure 17. Mass spectra of the prepared compound (A)

Figure 18. Mass spectra of the prepared compound (B)
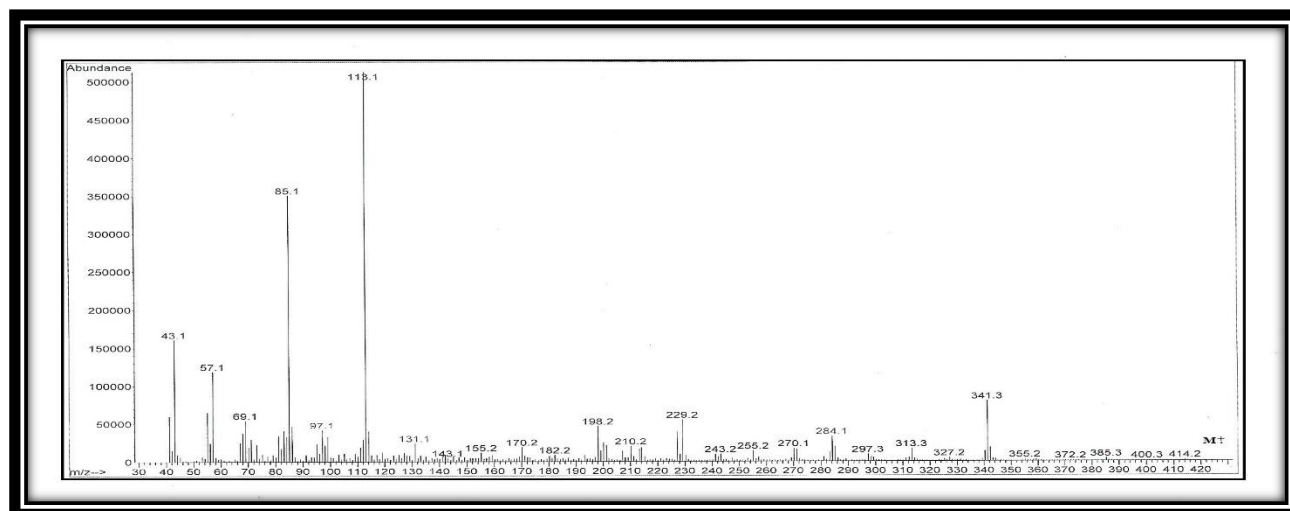
• Figure 19. Mass spectra of the prepared compound (C)

• Figure 20. Mass spectra of the prepared compound (D)

Figure 21. Mass spectra of the prepared compound (E)

Figure 22. Mass spectra of the prepared compound (F.

Figure 23. Mass spectra of the prepared compound (G)

Figure 24. Mass spectra of the prepared compound (H)
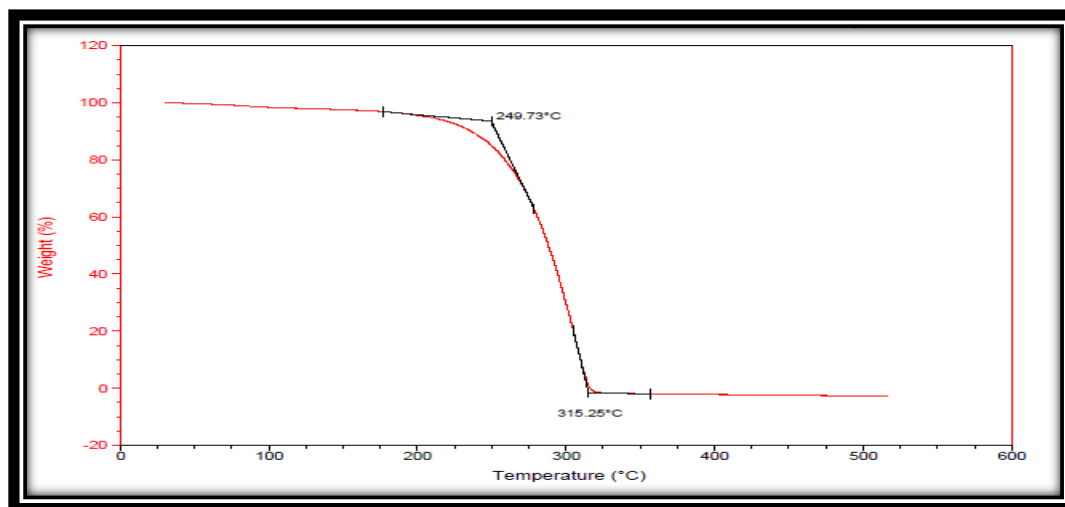
• Figure 25. TGA analysis of the prepared compound (A)
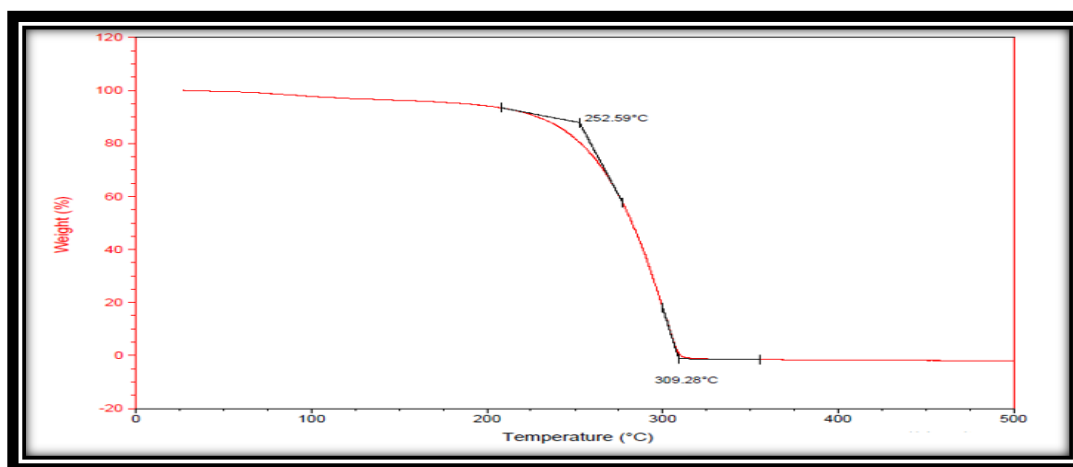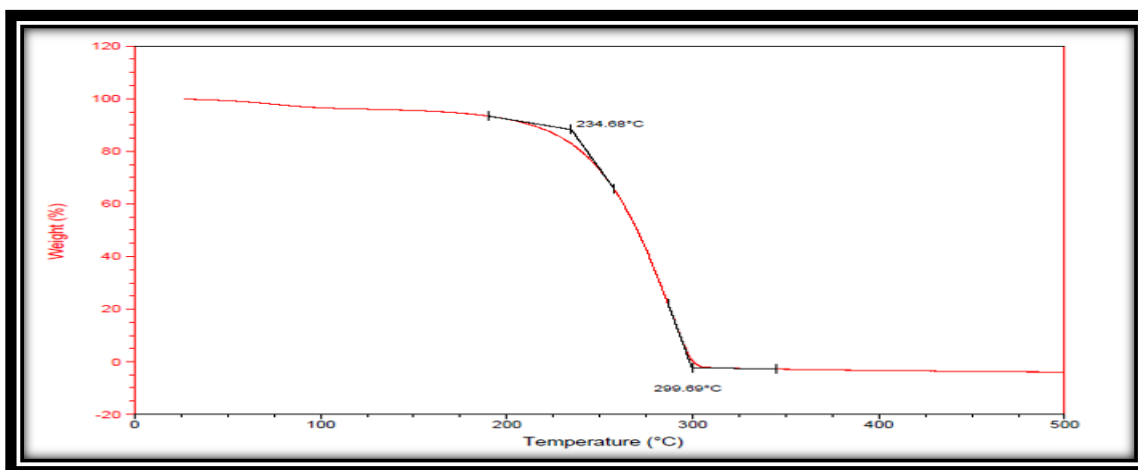

Figure 26. TGA analysis of the prepared compound (B)
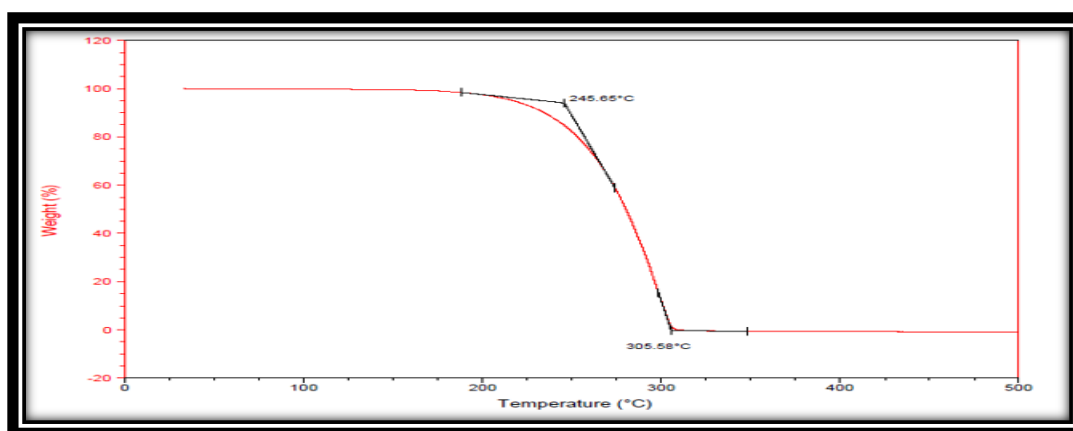
Figure 27. TGA analysis of the prepared compound (C)
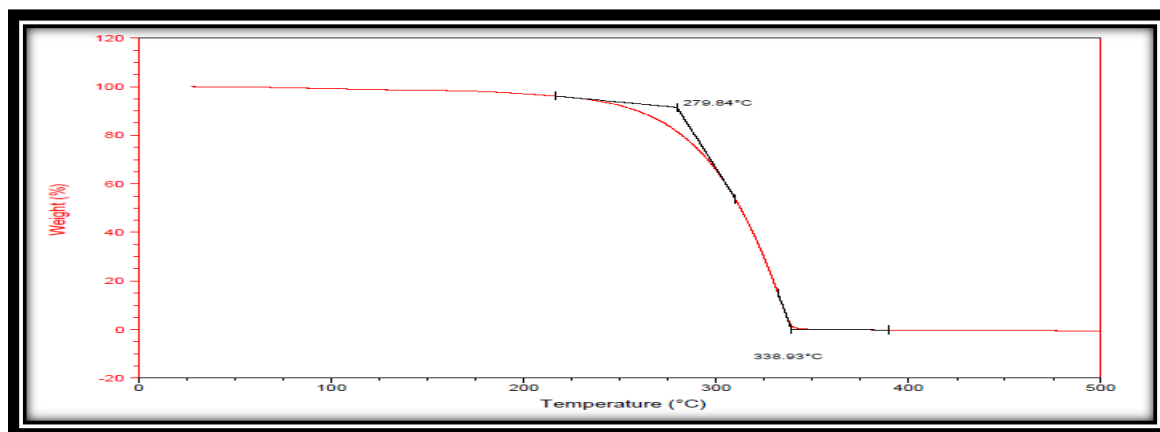
• Figure 28. TGA analysis of the prepared compound (D)
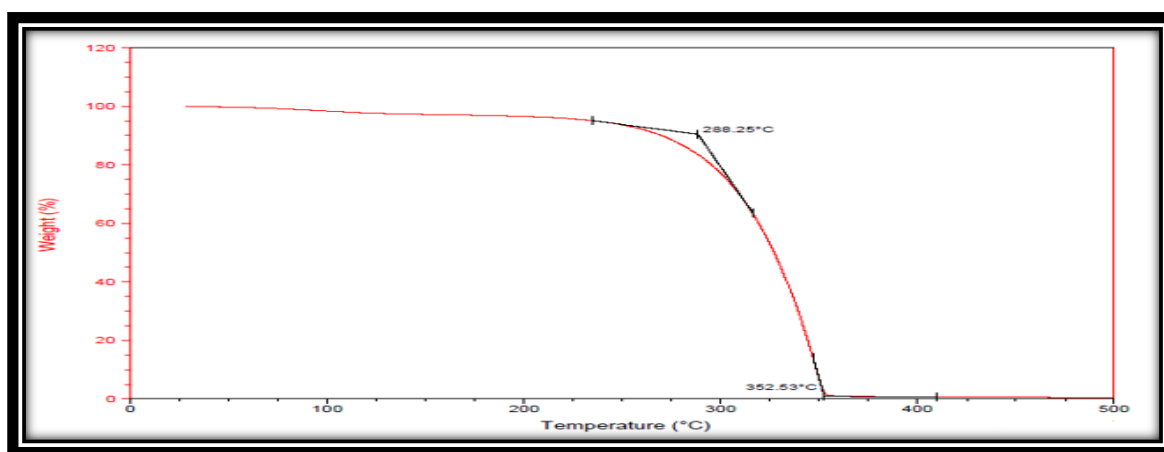
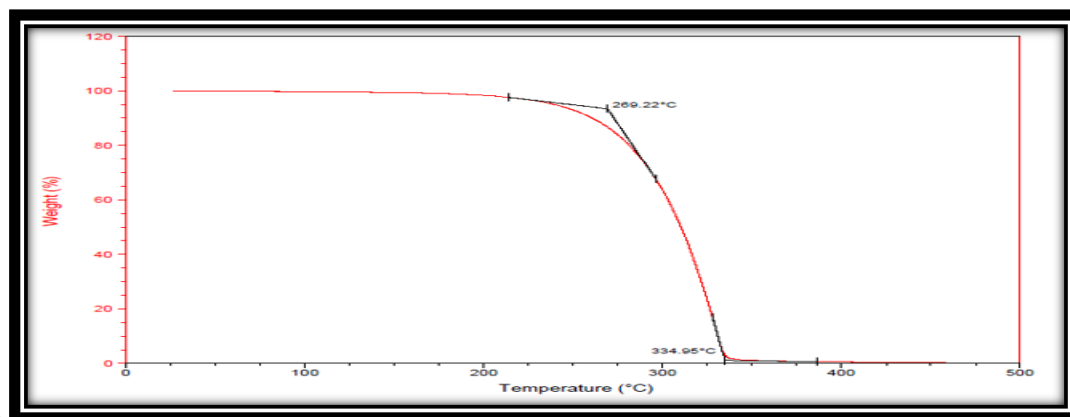
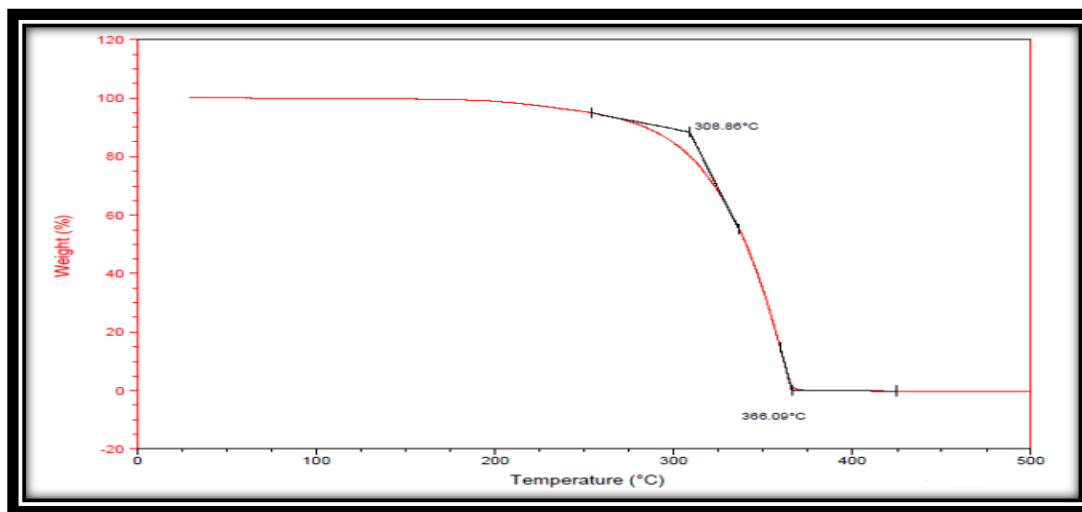Figure 29. TGA analysis of the prepared compound (E)

Figure 30. TGA analysis of the prepared compound (F)

• Figure 31. TGA analysis of the prepared compound (G)

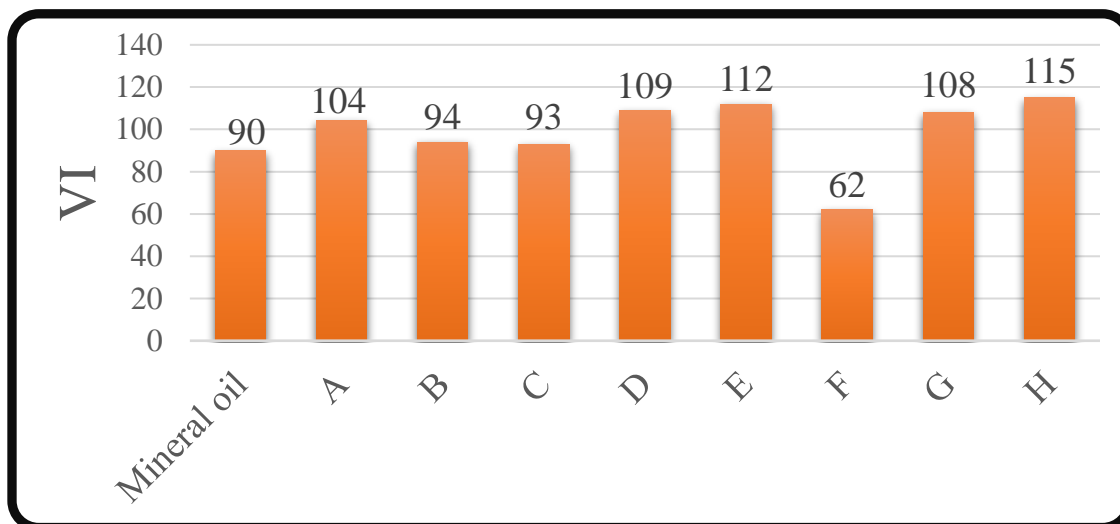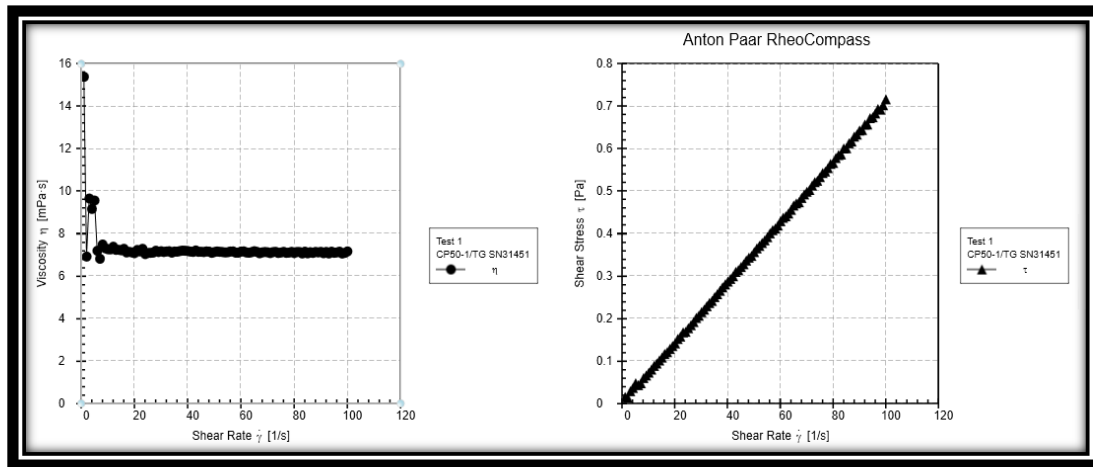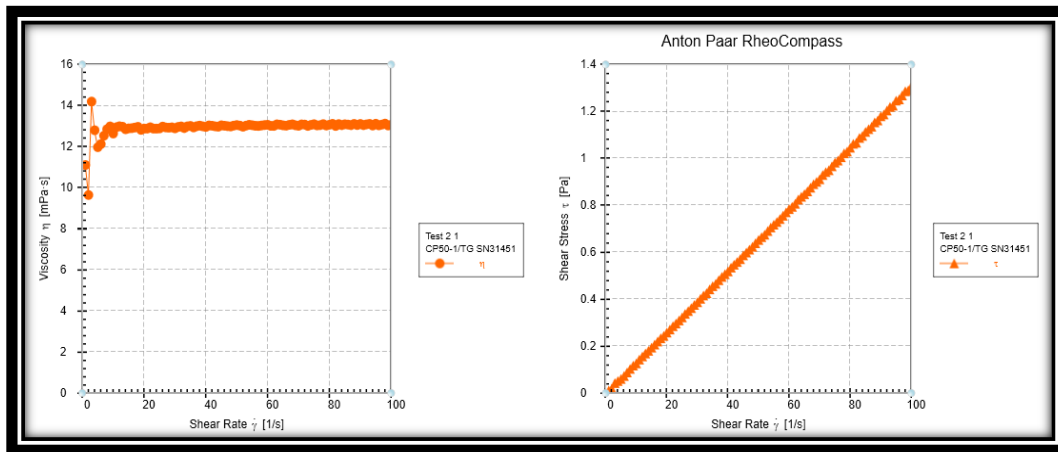• Figure 32. TGA analysis of the prepared compound (H)

Figure 33. Dependence of VI on the mean molecular weight of synthetic lubricating oils

(A. B. C. D. E. F. G and H).

• Figure 34. The rheological behavior of synthetic lubricating oil (A)

• Figure 35. The rheological behavior of synthetic lubricating oil (B)
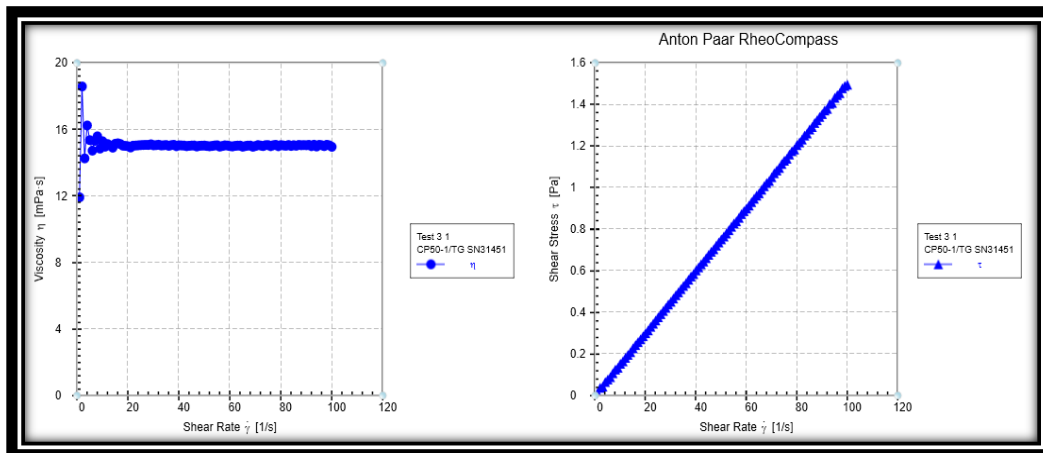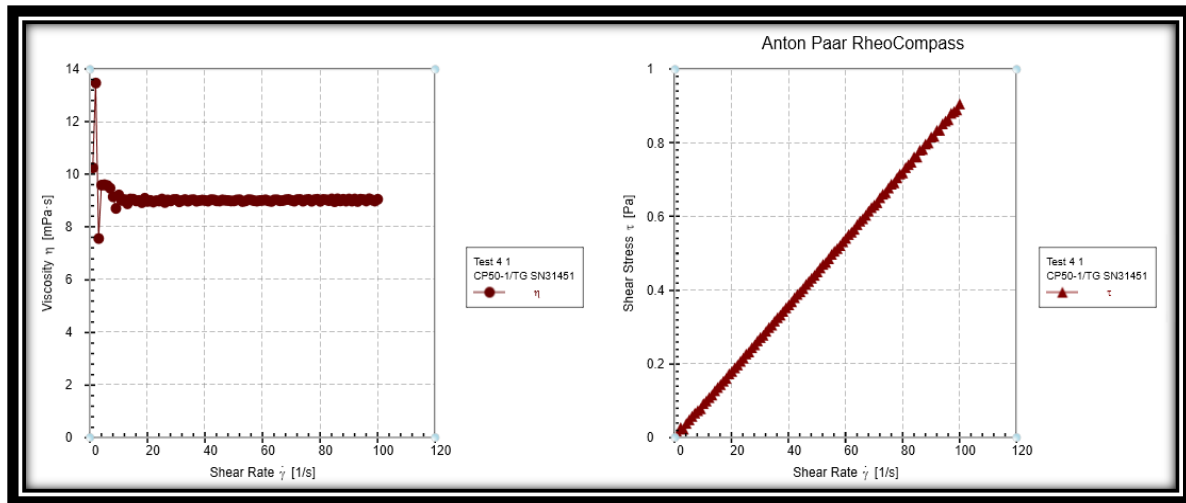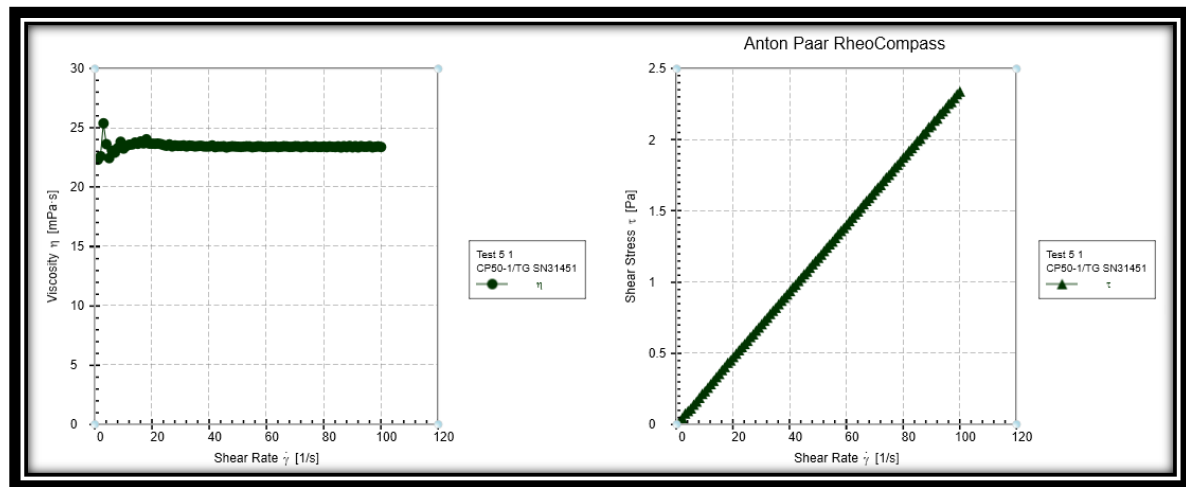

Figure 36. The rheological behavior of synthetic lubricating oil (C)

• Figure 37. The rheological behavior of synthetic lubricating oil (D)

• Figure 38. The rheological behavior of synthetic lubricating oil (E)
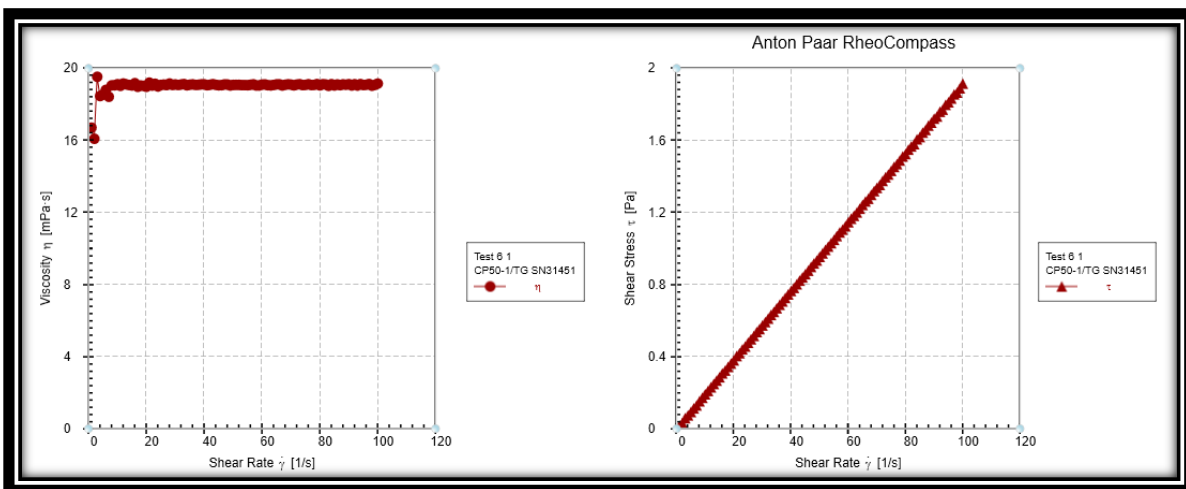

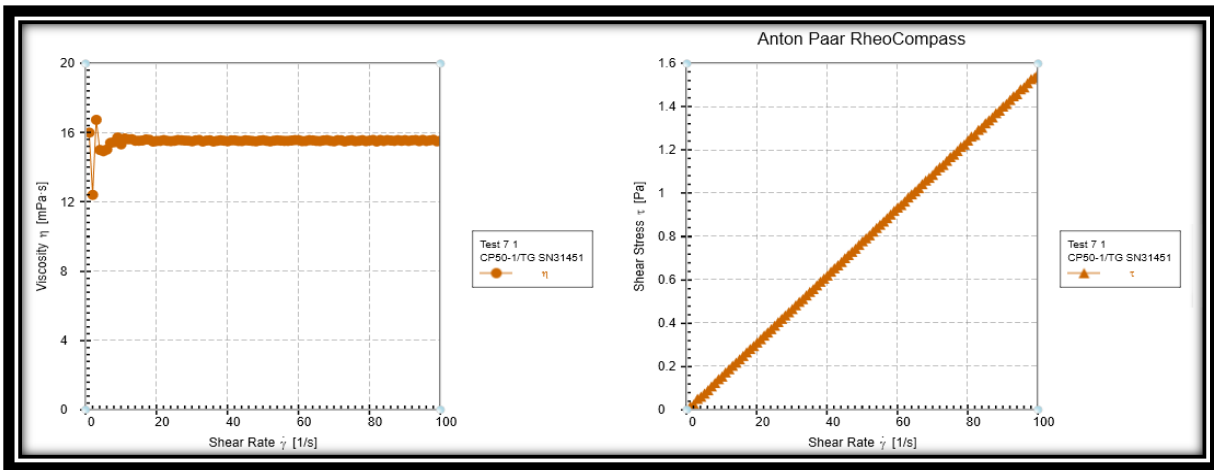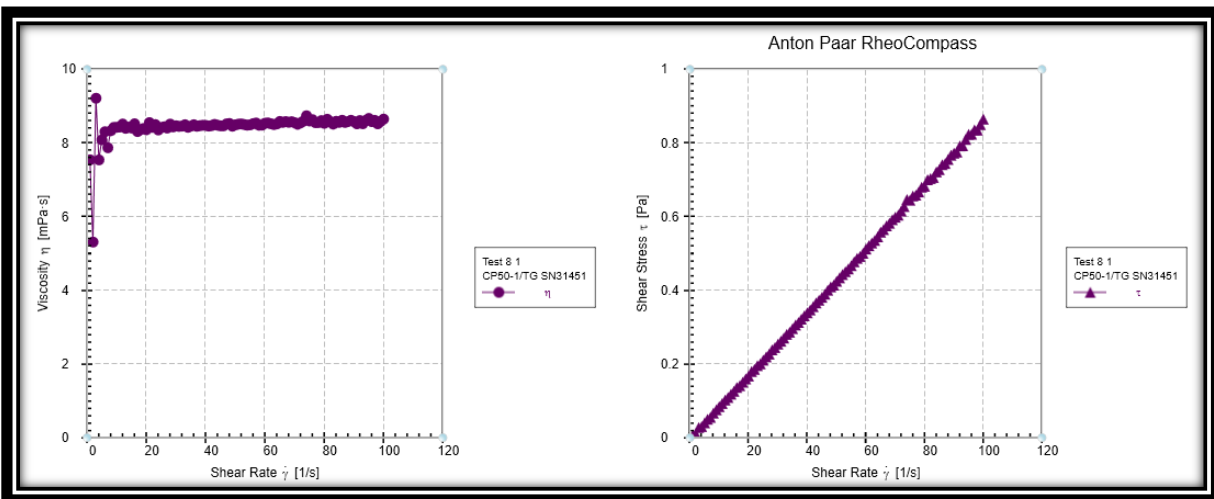Figure 39. The rheological behavior of synthetic lubricating oil (F)

Figure 40. The rheological behavior of synthetic lubricating oil (G)

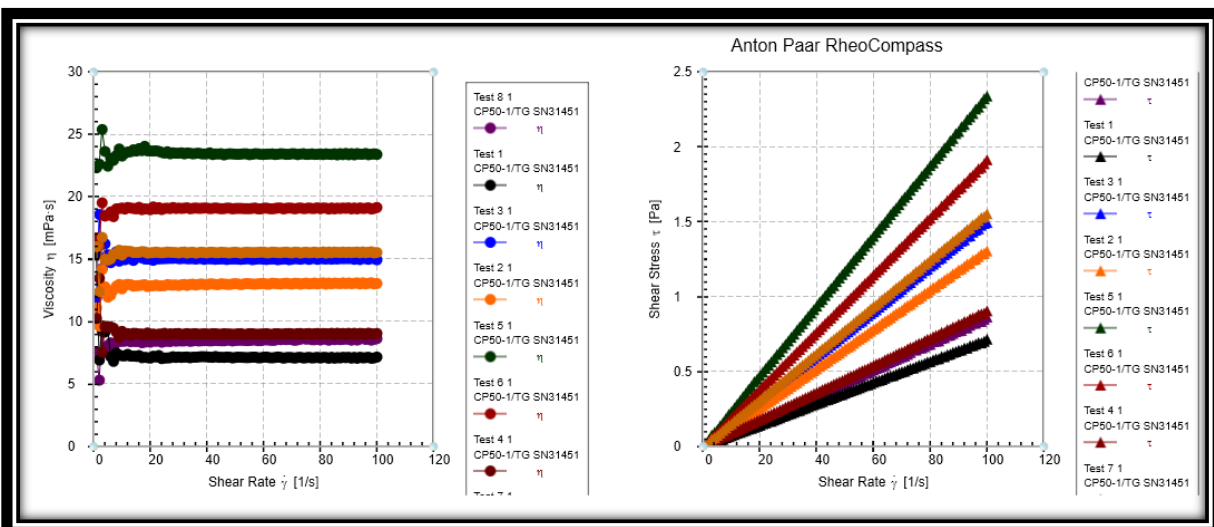• Figure 41. The rheological behavior of synthetic lubricating oil (H)

Figure 42. The comparative between rheological behavior of all synthetic lubricating oil (A. B. C. D. E. F. G and H)

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