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Synthesis of the Antioxidant Compounds from the Eugenol to the Lubricating Oils

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الخلاصة

في هذه الدراسة تم تحضير مضادات اكسدة جديدة باستخدام تفاعل (ثايول – اين) ، حيث ان هذه المركبات تم تحضيرها باستخدام نسب مولية (1:1) من (الثايول : الايجينول) بوجود بنزوايل بيروكسايد كبادى بدرجة حرارة (100) درجة مئوية لمدة تسع ساعات . تم تشخيص المركبات المحظرة بواسطة تقنية الاشعة تحت الحمراء، وتقنية الرنين النووي المغناطيسي وتقنية مطيافية الكتلة ومن ثم تقييمها كمضادات اكسدة بواسطة اضافة هذه المركبات المحضرة الى الزيت الاساس وزيوت التزييت، حيث اعطت فعالية كمضادات اكسدة ضد عمليات الاكسدة للزيوت.

Abstract

In this study new antioxidant compounds were prepared by (thiol-ene) click chemistry, where these compounds were prepared using (1:1) mole ratio of (thiol : eugenol) in the presence of benzoyl peroxide as initiator and the reaction is carried out at (100 ^{0}C) for (9) hrs.

(FT-IR), (1HNMR), and mass spectroscopy were used to characterize the synthesized compounds. They were evaluated as antioxidants by adding compounds to base oil and lubricant oil, where they showed high antioxidant activity against lubricant oil oxidation processes.

Keyword: Eugenol, Benzoyl peroxide, Lubricating oil, Base oil, Antioxidant.

1. Introduction

Oxidation is lead to the degeneracy of lubricating oils, which consist of many hydrocarbons (long chains) of carbon atoms, and leads to the production of degeneration products. The oxidation process can begin with the existence of an oxidizing factor like, oxygen that leads to formation of a large number of oxidation products that have molecular weights that may be high or low in comparison to the genuine lubricating oil according to the progression of the process. The occurrence of the oxidation processes in the lubricant oils can be known through the formation of sludge, varnish and a rise in the viscosity of the oils. Oxidation processes also cause corrosion, which is considered very significant for knowing the occurrence of the oxidation processes. There are some factors that cause an increase in the oxidation processes of lubricating oils such as, the presence of copper and iron, rising pressure and temperature,

friction increase and rising metal concentration. All these factors lead to a rise in the oxidation processes in lubricating oils. The generation of heat in the combustion machines, which is caused by the combustion processes that occur in the machines, is sufficient to lead to the occurrence of the oxidation processes in the lubricating oils unless the antioxidants are added to them sufficiently to perform the process of inhibiting and preventing the oxidation processes and the forming of degeneration products. Antioxidants are compounds that prevent the oxidation process of oils and also inhibit the process of cracking that occurs in lubricating oils[1,2]. Antioxidant compounds are considered very important in our lives because they are able to end chain reactions by striping free radicals.

Antioxidant compounds are used to prevent the oxidation of lubricating oils because the oxidation process reduce the activity of oils and causes deposits form, as well as increasing the viscosity and the acidity of oils, which leads to corrosion and reduces the efficiency of these lubricants [3-6].

Hundreds phenolic compounds and aromatic amines compounds are the most common antioxidant compounds found in lubricating oil [7-11]. Additives that give good activity as antioxidants, such as sulfur, nitrogen, and the compound phenolic, have been described as antioxidant compounds [12].

Antioxidant compounds also have functional importance in biological activities and in the pharmaceutical industries as radical scavengers [13,14]. In this study, antioxidant compounds were synthesized from the reaction of thiols with alkene compound such as, eugenol and then added them to industrial lubricating oils, and the oxidative stability of oils was observed.

2. Experimental:

2.1. Materials

The substances which are used in this search, were received from the company of (Sigma-Aldrich Merck) and the solvents were equipping from the (Fluka).

2.2. The properties of base oil

The specification of the base oil that was used is shown in the table (1).

Table (1) Show the specification of the base oil

Type of test	base oil	Methods. ASTM
Vis @40	62.0	D-445
Vis @100	8.4	D-445
VI	99	D-2270
Sp.Gr@60F^0	0.8830	D-4052

P.P	-5	D-97
F.P	249	D-92
Color	2.5	D-1500

The abbreviations which are used in the table (1) above are:
Vis = Viscosity, it is measured in units cSt (mm^2/s).
VI = Viscosity Index.
Sp.Gr = Specific Gravity.
P.P = Pour Point.
F.P = Flash Point.

2.3. Instruments

There are many instruments that are used in this research such as, melting point (BuCi510 Switzerland) for determining the melting points of the prepared compounds. (FT-IR) spectrophotometer (FTIR-84005, SHIMADZU-Japan), by using the disk from the (KBr) which is available in the college of education, chemistry department, the university of Basra. The cyclic voltammetry technique was developed by using the device vertex one/EIS, lvium technologies for electrochemical research, applied voltage (-1.5) to (1.5), made of Netherlands (Holland) in (Tehran university). The mass spectra for measuring the ratio of (m/z) were recorded on the type (SHIMADZU), (Tehran University).

In the technique of cyclic voltammetry, three electrodes are used to control on the voltage, and the supporting electrolyte that is used in the cell is (Bu_4NBF_6) to increase the conductivity of the solution. This technique is considered simple and easy to use. It consist of cycling potential of an electrode that is immersed in an unstirred solution and measuring the current that results.

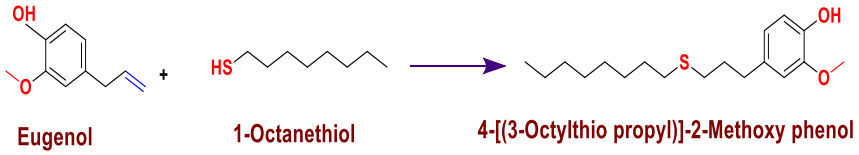
The cyclic voltammogram was gained through the measuring of the current to the (working electrode) during the scan of the potential. The (voltammogram) offers of the (current) in the vertical axis versus the (potential) in the horizontal axis because the potential differs (linearly) with the (time). The voltammogram of the cyclic voltammetry is drawn between the current and the potential.

Cyclic voltammetry includes applying an electric potential to the respective electrode immersed in a solution containing electrically active groups. With the measurement of the resulting current, the voltage of the working electrode is controlled relative to the reference electrode (saturated calomel electrode) or the electrode (Ag/AgCl). The controlled voltage applied across these two electrodes can be considered as an electrical excitation signal [40].

3. Synthesis of antioxidant compounds

3.1. Synthesis of 4-[(3-Octylthiopropyl)] -2- methoxy phenol (1)

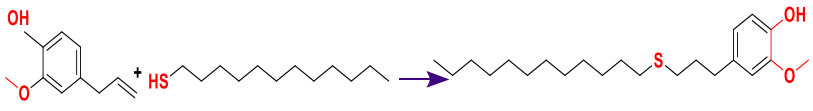
Eugenol (0.82 g, 5 mmol) was mixed with (0.73 g, 5 mmol) (1-Octanetiol) and (benzoyl peroxide) (0.06 g, 0. 25 mmol) as initiator. The mixture was refluxed in an oil bath (100 -110C^0) for (9) hrs. The product in yield (1.3 g, 83%) [37,41].



Eugenol 1-Octanethiol 4-[(3-Octylthio propyl)]-2-Methoxy phenol

3.2. Synthesis of 4-[(3-Dodecylthiopropyl)] -2-methoxy phenol (2)

Eugenol (0.82 g, 5 mmol) was mixed with (1.01 g, 5 mmol) (1-Dodecanethiol) and (benzoyl peroxide) (0.06 g, 0.25 mmol), as initiator. The mixture was refluxed in an oil bath at (100 -110C^0) for (9) hrs. The product at yield (1.5 g, 82%) [37,41].



Eugenol 1-Dodecanethiol 4[(3-Dodecylthio propyl)]-2-Methoxy phenol

Table (2) Show the molecular structures of the prepared antioxidants compounds

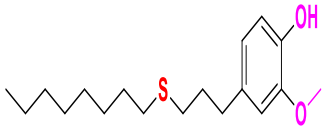
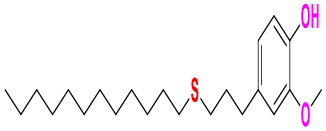
Com. No	Formula	Structure
1	$C_{18}H_{30}O_2S$	
2	$C_{22}H_{38}O_2S$	

Table (3) Show the physical properties of the prepare antioxidants compounds

Com. No	Molecular Weight g/mole	Color	M.P, C^0	Yield %
1	310.5	Light yellow	viscous	83
2	366.6	Light yellow	viscous	82

3.3. Synthesis a mixture of lubricating oils with prepared compounds

Mixed (0.02%) from each one of the prepared compounds (1) and (2) with (1:1) of (base oil: lubricant oil) at ($60C^0$) for (30 minutes) [38].

4. Results and discussion

4.1. Structure confirmation of the prepared antioxidant compounds

4.1.1. FT-IR spectroscopy of compounds (1,2)

The (FT-IR) spectra of the compound (1): **4-[(3-Octylthiopropyl)]-2-methoxy phenol**, as shown in the figure (1)[15-20]:

IR(cm^{-1}): 3523 (OH), 3003 (CH, Ar), 1269 (C-O,Ar), 648 (C-S,Al), 1514 (C=C, Ar) , 2935 (CH,CH_3, Al).

AL=Aliphatic.

Ar=Aromatic.

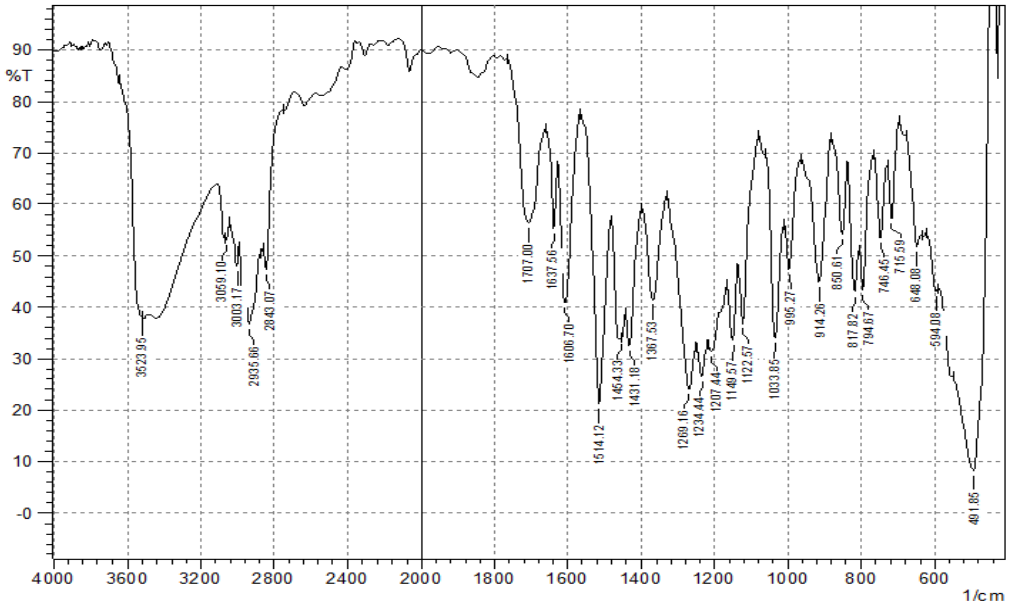


Figure (1) show the (FT-IR) of compound (1).

The (FT-IR) spectra of the compound (2): **4-[(3-Dodecylthiopropyl)]-2-methoxy phenol**, as shown in the figure (2)[15-20] :

IR(cm^{-1}): 1514 (C=C ,Ar), 3003 (CH, Ar), 2935 (CH,CH_3, Al), 3512 (OH, Ar), 1269 (C-O, Ar), 646 (C-S, Al).

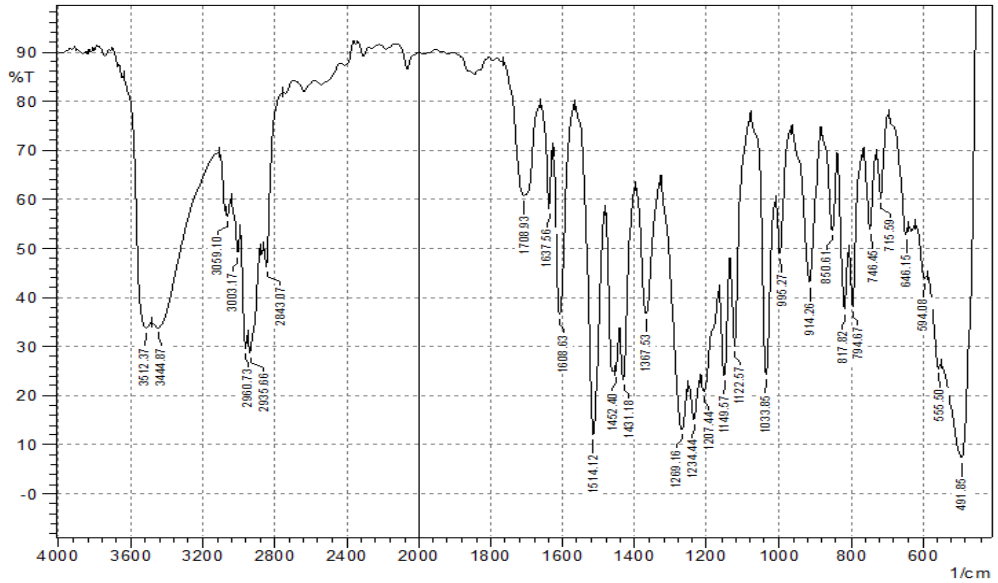


Figure (2) show the (FT-IR) of compound (2).

4.1.2. 1H-NMR spectroscopy of compounds (1,2)

The chemical shifts in (ppm) of the spectrum (1H- NMR) to the compound (1)[15-20]: as shown in the figure (3):

4-[(3-Octylthiopropyl)]-2-methoxy phenol, as shown in the figure (3):Multiple signals of the (Ar-H, 3H) at (6.56-7.99), singlet signal of the (Ar-OH, 1H) at (8.63), singlet signal of the (O-CH_3, 3H) at (3.76), triplet signals of the (CH_2-Ph, 2H) at (2.56), multiple signals of the (CH_2-S-CH_2) at (2.60-2.62), quartet signals of the (S-CH_2) at (2.59), multiple signals of the (CH_2) at (1.00-1.90), triplet signals of the (CH3) at (0.85).

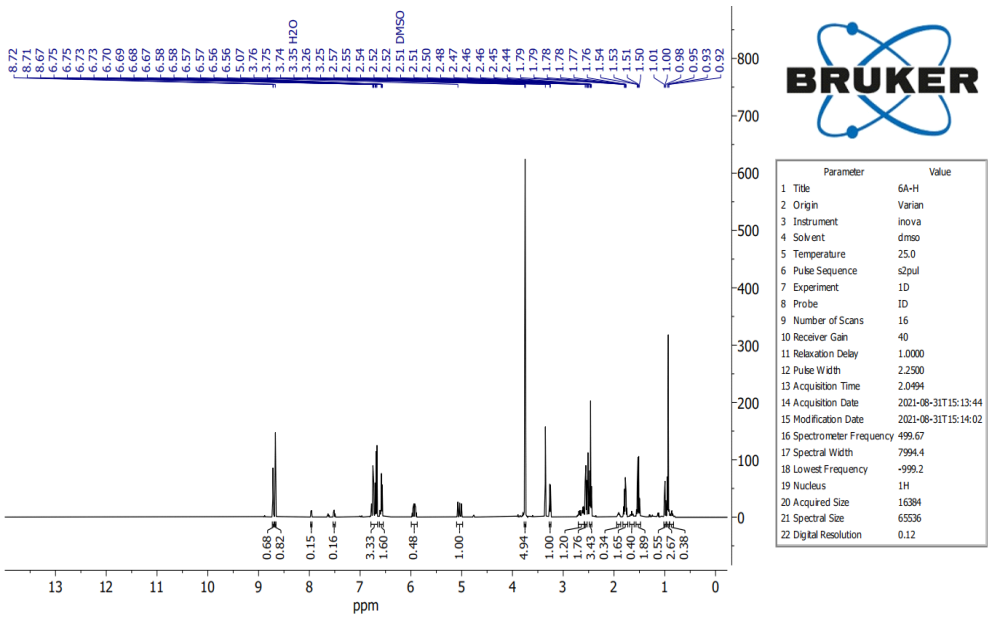


Figure (3) shows the (1H-NMR) of compound (1).

The chemical shifts in (ppm) of the spectrum (1H- NMR) to the compound (2)[15-20]:

4-[(3-Dodecylthiopropyl)]-2-methoxyphenol, shown in the figure (4):

Multiple signals of the (Ar-H, 3H) at (6.58-6.76), singlet signal of the (Ar-OH, 1H) at (8.73), singlet signal of the (O-CH_3, 3H) at (3.75), triplet signal of the (CH_2-ph) at (2.56), multiple signals of the (CH_2-S-CH_2) at (2.66-2.69), quartet signals of the (S-CH_2) at (2.44), multiple signals of the (CH_2) at (1.02-1.81), triplet signals of the (CH_3) at (0.88).

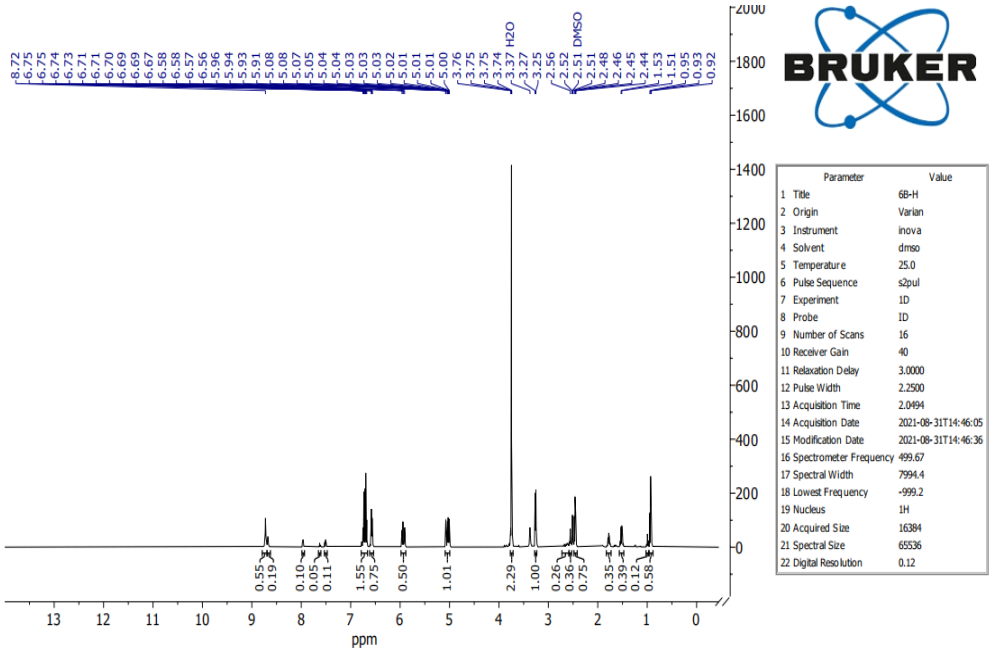


Figure (4) shows the (1H-NMR) of compound (2).

4.1.3 MASS spectroscopy of compounds (1,2)

The mass spectrum of the compound (1)[21-25]: **4-[(3-Octylthiopropyl)]-2-methoxy phenol**, indicate the molecular ion peak [M^+] at (310.5) of the prepared antioxidant compound, as shown in the figure (5). This technique is an analytical tool used for determining the ratio of mass to charge m/z to one or more of molecules which exist in the sample. These techniques are commonly used to determine the exact molecular weight of sample components. The ion signal is plotted as a function of the mass to charge. A sample, which might be solid, liquid, or gaseous, is ionized in a typical (MS) operation by bombarding it with a beam of electrons, for example.

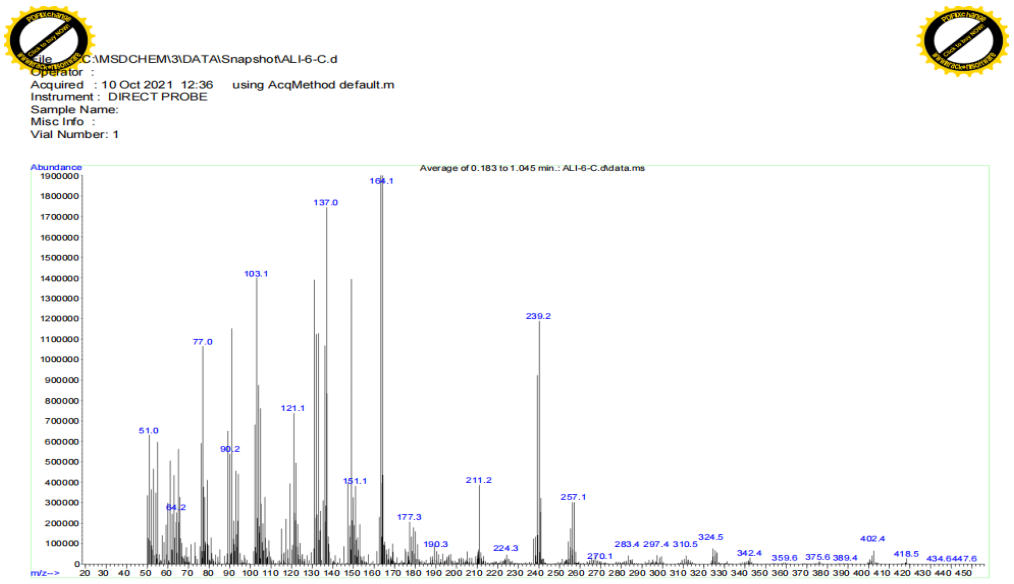


Figure (5) show the mass spectrum of compound (1).

The mass spectrum of the compound (2): **4-[(3-Dodecylthiopropyl)]-2-methoxyphenol**, indicate the molecular ion peak [M^+] at (366.6) of the prepared antioxidant compound, as shown in the figure (6) [21-25].

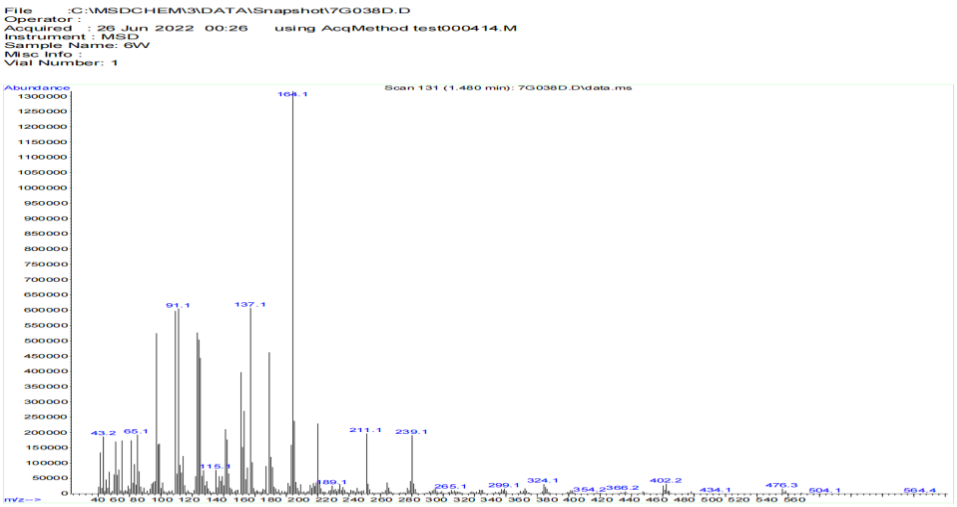


Figure (6) show the mass spectrum of compound (2).

5. Discussion

The (FT-IR) was measured on the lubricating oils when it was exposed to the oxidation process (heat) at (60 ^{0}C). It was observed that a band at (1731) cm^{-1} appeared as a result of the degradation process (oxidation) which obtained to the lubricating oils, as shown in the figure (7). The band of carbonyl at (1731) cm^{-1} was appeared when the lubricant oils were subjected to the process of oxidation, the groups of [(CH_2)n] in lubricant oils are transformed to ($CH^{\cdot}$) through the heat, and by atmospheric oxygen transformed to carbonyl group, which lead to appear this band at carbonyl in the region (1731) cm^{-1}.

When added the antioxidant compounds, the band in the region (1731) cm^{-1} will disappear, this indicates that the lubricating oil is resistant to the degradation process and that there has not happen any oxidation [26-29], as shown in the figure (8):

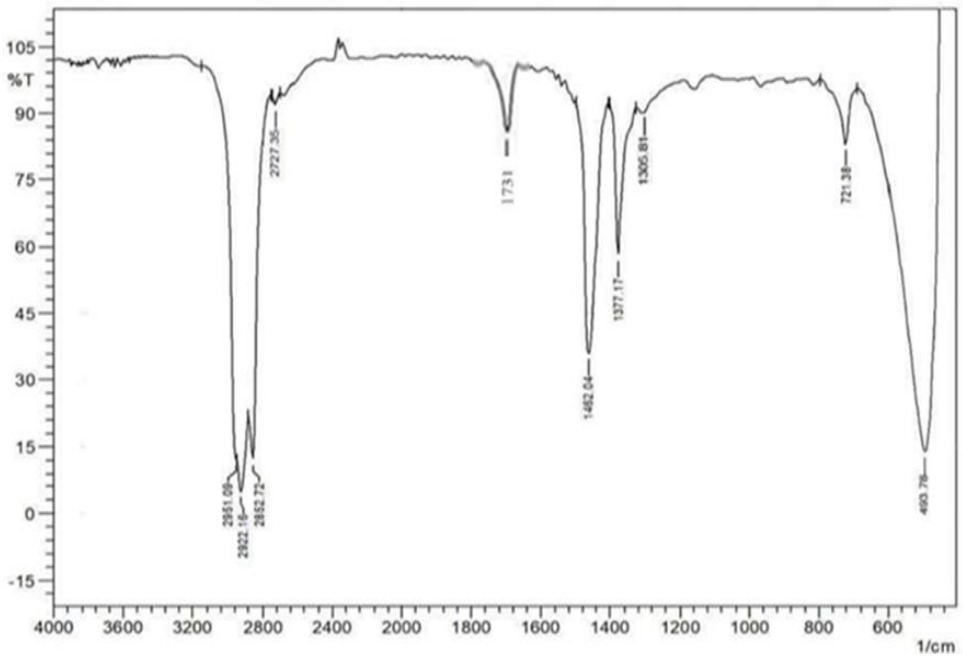


Figure (7) show the degradation process of the lubricant oil.

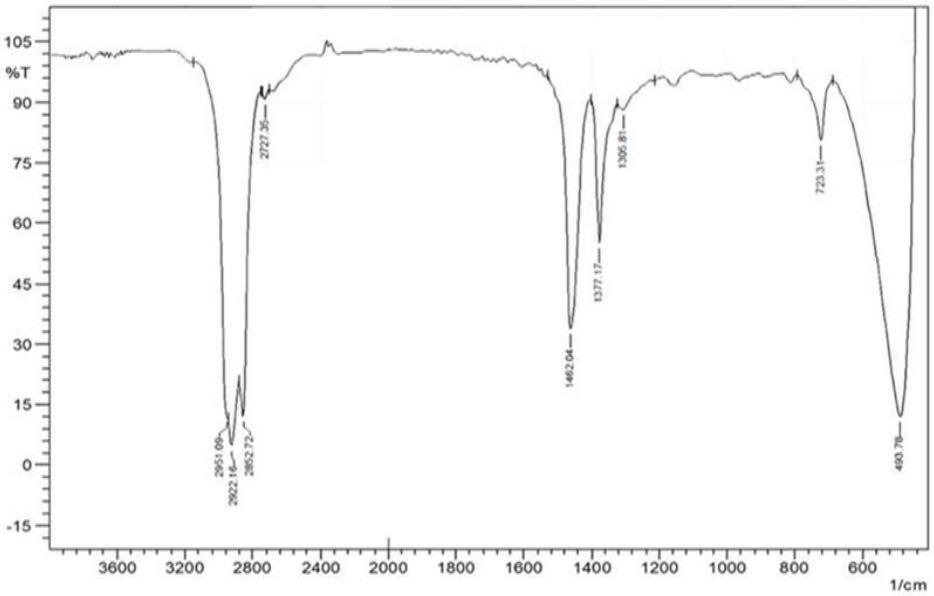


Figure (8) show the effect of the antioxidant compounds (A1, A2).

The efficiency of the synthesized antioxidant compounds from (eugenol) and thiols, they were compared with one of the most important commercial antioxidants Butylated Hydroxy Toluene (BHT)[35,38]. It was observed that when the synthesized antioxidant compounds were added to lubricating oils, the

band of the carbonyl directly disappears, as shown in the figure (8). This is due to the ability of the synthesized antioxidant compounds to scavenge free radicals were generated as a result of oxidation process that occur in lubricating oils and the ability of hydrogen donating of these synthesized antioxidants and reduce the rate of propagation reaction and thus inhibits the oxidation process.

Eugenol compound with alkyl thiols appears high antioxidant activity. These antioxidant compounds decreases the capability of generate radicals by abstract a hydrogen atom from the substrate and thus decreases the forming of an alkyl radical able to initiation oxidation [38]. This indicate that these antioxidant compounds act as a good antioxidants, which helps to save and store lubricating oils for a longer period until they are used in the lubrication processes of machinery and equipment industrial. But when adding the (BHT) compound, it was observed less effective in preventing oxidation process to lubricating oils, as this can be seen through the band of carbonyl that didn't disappear when added the compound (BHT), as shown in the figure (9) [34,36,38].

The intense absorption band at (1731) cm^{-1} is noticed by the carbonyl stretching whose increased of the force constant by the nature of electron attracting (the inductive affect) of the neighboring oxygen atom of the bond to the (C-O) [38]. The measurement of the concentration to the carbonyl compounds by carboxylates, this connected of the concentration to the products of oxidation in the lubricating oils [38]. In general, the band in the (1731) cm^{-1} of carbonyl is clear through existence of different carbonyl groups which contains the products of degradation of the lubricant oils such as, lactones, esters, aldehydes, ketones and carboxylic acids [38].

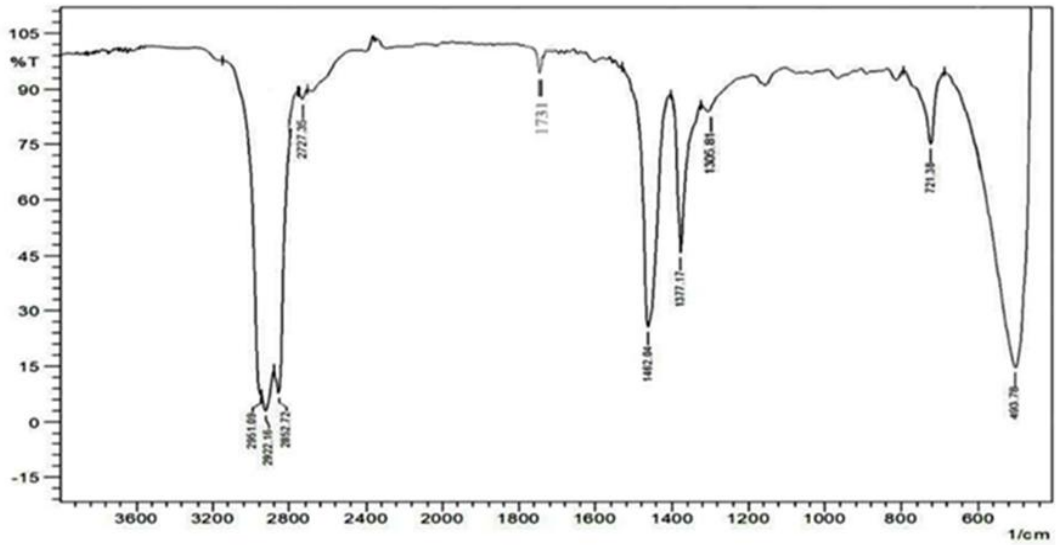


Figure (9) show the efficiency of the commercial antioxidant (BHT).

The efficiency of the synthesized antioxidant compounds can also be determined when they are added to the lubricating oil by the technique of cyclic

voltammetry (cv), and measuring the oxidation potential. It was noticed that these antioxidant compounds possess high oxidation potential, E_p^a. As a result, these antioxidants are considered good antioxidant compounds [30-33], as shown in the figures (10) and (11), table (4). The relation between the cyclic voltammetry oxidation potential (E_p^a) and the activity of the antioxidant compounds has been registered through a number of laboratories. Two types of antioxidant compounds were synthesized and the chemistry of redox reaction was estimated utilizing (cv) [31,34].

The comparison between the oxidation potential (E_p^a) of the synthesized antioxidant compounds and the commercial antioxidant (BHT) as shown in the table (4), a high value of oxidation potential refere to high efficiency of the antioxidant. Because of the antioxidant with lowest oxidation potential has the ability to produce of free radicals [31,35].

Strength of the antioxidant compounds can be measured by the position of the peaks in the cyclic voltammetry. A peak which has a lower potential indicates a stronger reducing agent. Lubricating oils with mineral base oil or synthetic base oil able to degrade and polymerized because of the oxidation processes. The lubricating oils contain many of hydrocarbons and this lead to prone to the oxidation process [31,36].

The secondary antioxidant such as the synthesized antioxidant compounds, sulphurised compounds, considered as a good inhibitors for preventing the oxidation process as a result of possess them high value of (Ep^a) which are found in a modern motor vehicles and diesel machines for preventing the oxidation processes and to raise their stability of thermal- oxidative, these secondary oxidation inhibitors have the ability to decompose the compounds of the hydroperoxides to grant minimum hurtful forms. The values of the oxidation peak potential (E_p^a) and the areas of the total peak are utilized for comparative of the new and consumed machine oils [31,34].

It was existed that a connection found between the depletion of the antioxidant and the kind of the engine as well as service time. The technique of cyclic voltammetry doesn't require rise temperature and this gives a fast screening of antioxidants on the basis of their oxidation potential values [31,35].

The oxidation and reduction peak potentials (E_p^a) and (E_c^p) respectively as well as the deference (ΔE_p) represented as the absolute value of the variation between (E_p^c) and (E_p^a) were tested for a better analysis [42]. As it was observed that (BHT) compound has less (E_p^a) than the synthesized antioxidant compounds and this indicate that (BHT) less efficiency as antioxidant than the synthesized antioxidants, as shown from the (E_p^a) values in the table (4).

The values of (ΔEp) were acquired in different experiments for each substance, using a glassy carbon working electrode in a three-electrode conventional electrochemical cell [42]. In addition, cyclic voltammetry tests were used to assess the electrochemical behavior. These studies produced anodic and cathodic peak potentials (E_p^a) and (E_p^c) respectively, as well as the value of (ΔEp). (BHT) has less (E_p^a) value (0.05V) and less (ΔE_p) (0.1, 0.8V) while the

synthesized antioxidant compounds have large (E_p^a) values (0.41, 0.45V) and large (ΔEp) values (0.46, 1.26V) and (0.48, 1.35V).

There is a relationship between the structure and the efficiency of the antioxidants. There is a relationship between structure and antioxidant capacity.

The results indicate that the conjugation and high molecular weight of the compounds are important in the antioxidant activity and electrochemical characteristics of the substances evaluated [30,36].

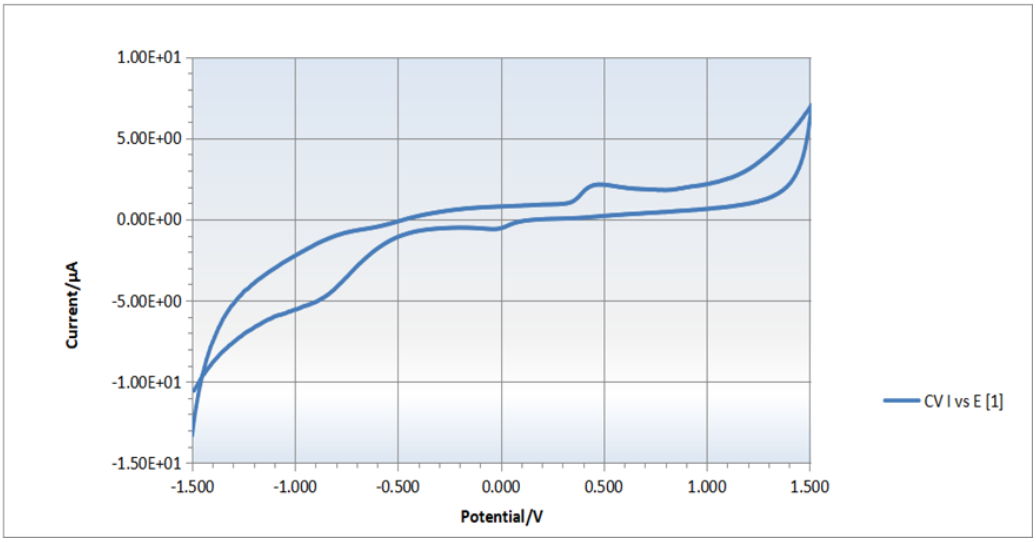


Figure (10) show the cyclic voltammetry graph of the compound (A1).

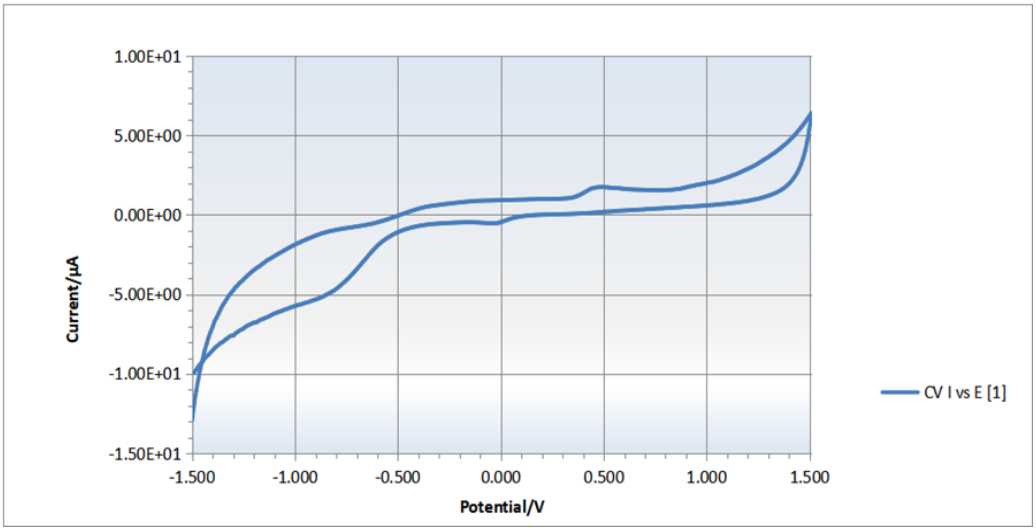


Figure (11) show the cyclic voltammetry graph of the compound (A2).

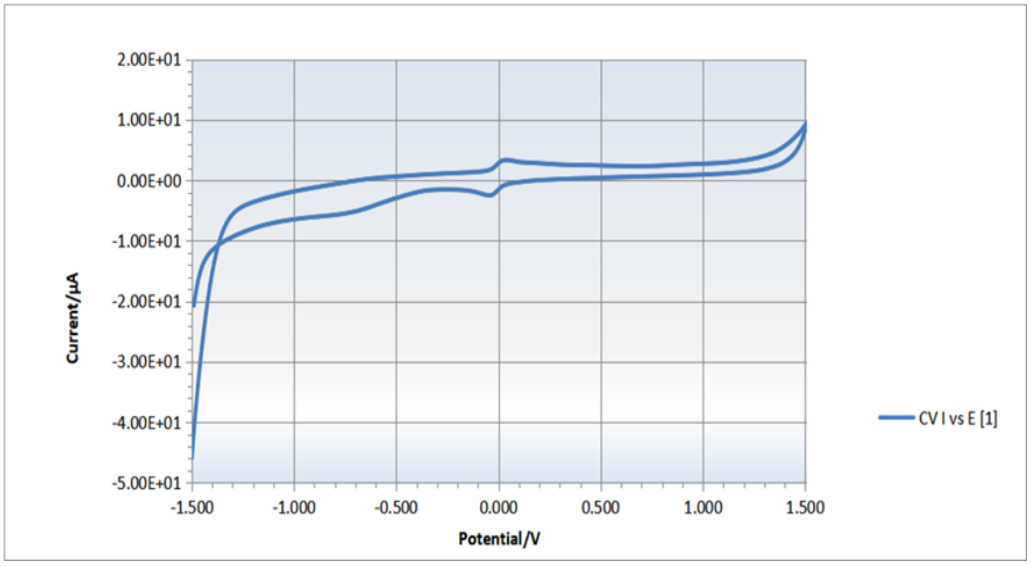


Figure (12) indicate the efficiency of the antioxidant compound (BHT), for reducing the degradation process (oxidation)

Table (4) below, indicates the values of the oxidation potential and the reduction potential of the prepared antioxidant compounds.

Table (4) show the (E_p^a, $E_p^c{}_{(1,2)}$, $\Delta E_{p\ (1,2)}$ to the antioxidants compounds (A1, A2).

Comp. NO	E_p^a (v)	$E_P^C{}_{(1,2)}$(v)	$\Delta E_{P(1,2)}(v)=\lvert E_P^C - E_P^a \rvert$
1	0.41	-0.05 -0.85	0.46 1.26
2	0.45	-0.03 -0.9	0.48 1.35
BHT	0.05	-0.05 -0.75	0.1 0.8

6. Conclusions

The important points that have been concluded are:

1. The techniques of (FT-IR) and (cyclic voltammetry) gave good results in the estimation of the prepared compounds as antioxidants.
2. The high values of the oxidation potential (E_p^a) of the prepared antioxidant compounds show that they are good antioxidants, compared to (BHT) have low value (E_p^a).

3. The high relation between (E_p^a) and antioxidant efficiency, as well as the common use of (cv) in the evaluation of antioxidants, suggests that (cv) is a quick and easy way to screen antioxidants.
4. There is a relationship between the structures of the antioxidants and there efficiency against the oxidation processes that occur to the lubricating oils.
5. Sulphurised antioxidant compounds, considered as a good inhibitors for preventing the oxidation process.
6. Eugenol compound with alkyl thiols appears high antioxidant activity, because of the ability to decrease from generate the radicals by abstract a hydrogen atom from the substrate and thus decreases the forming of an alkyl radical able to initiation oxidation.
7. The calculation of the oxidation potential (E_p^a) by (cv) technique can be used on the evaluation effectiveness of antioxidants against oxidative processes to lubricating oils.

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