

# Comparative Study in Evaluating the Antioxidation Efficiency for Native Types Antioxidants Extracted from Crude Oil with the Synthesized Class

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**Abstract**—The natural native antioxidants N,N-P-methyl phenyl acetone and N,N-phenyl acetone were isolated from the Iraqi crude oil region of Kirkuk by ion exchange and their structure was characterized by spectral and chemical analysis methods. Tetraline was used as a liquid hydrocarbon to detect the efficiency of isolated molecules at elevated temperature (393 K) that it has physicochemical specifications and structure closed to hydrocarbons fractionated from crude oil. The synthesized universal antioxidant 2,6-ditertiaryisobutyl-p-methyl phenol (Unol) with known stoichiometric coefficient of inhibition equal to (2) was used as a model for comparative evaluation at the same conditions. Modified chemiluminescence method was used to find the amount of absorbed oxygen and the induction periods in and without the existence of isolated antioxidants molecules. The results of induction periods and quantity of absorbed oxygen during the oxidation process were measured by manometric installation. It was seen that at specific equal concentrations of N,N-phenyl acetone and N, N-P-methyl phenyl acetone in comparison with Unol at 393 K were with (2) and (2.5) times efficient than do Unol. It means that they had the ability to inhibit the formation of new free radicals and prevent the chain reaction to pass from the propagation to the termination step rather than decomposition of formed hydroperoxides.

**Keywords**—Antioxidants, chemiluminescence, inhibition, unol.

## I. INTRODUCTION

SINCE all liquid fuels fractionated from crude oil are hydrocarbons, they tend to oxidize, thermally decompose, and polymerize relatively quickly [1], [2]. Lubricating oils, fuel get, greases and diesel are usually used in presence of air, whereby oxidative chemical reactions can take place. The rate of these oxidative processes varies greatly with the nature of the fuel, the extent of processing in refining, the temperature, and the presence of metallic catalyst [3]. Such oxidations have a drawback on the fuel, thus leading to failures its function that accompanied by damage of equipments at which it is used. Large degree of damage is due to the formation of viscous, solid bodies, or jelly-like emulsions which interfere with the regular distribution of the fuel. Antioxidant additives are seriously required to decrease fuel oxidation and reducing corrosion of certain types of sensitive bearing materials [4].

Antioxidants play an important role in protecting the petroleum fuels against injurious chemical transformations during the life of its operation. The suitability of antioxidants

depends on its complete solubility [2]. They are working by two mechanisms, either by radical scavenging or by decomposition of hydroperoxides. In the first case they react with peroxy radicals to prevent the further propagation step of the free radical chain [5]. In this case they are considered as primary antioxidants because they break the propagation chain [6]. In the second case, decomposition reaction proceeds with the hydroperoxides molecule to prevent the formation of peroxy radicals. Antioxidants may vary in their chemical structures. Hindered phenols, amines, sulfur and phosphorus compounds are important classes of these compounds [3]. Hindered phenol and aromatic amines are examples of primary antioxidants. They functionalized by donating hydrogen atom to a peroxy radical. 2, 6-di-tert-butyl-4-methylphenol is an examples of hindered phenols in which the hydroxyl group is strictly blocked or hindered. On the other side aromatic amines are considered as peroxide radical traps, they can interrupt the oxidation chain reaction. N-phenyl-naphthylamine, alkylated diphenyl amine and dialkyldithiophosphate are examples of aromatic amines. All these types are chemically synthesized prior use [3].

Generally, the strength of an antioxidant is evaluated from its stoichiometric coefficient of inhibition ( $f$ ) which is equal to the number of radicals successively reacted with one molecule of inhibitor and conversion products from the inhibitor molecule [7].

Many methods are published in the literatures concerning the calculation of stoichiometric coefficient of inhibition of antioxidants, some of them depend on kinetics of radical acceptor consumption in which when the initial rate acceptor is measured, only  $K_i$  can be determined. If the experiment is conducted in this manner that all the initiator has decomposed during the time, then the kinetic curve for combustion of free radical acceptor can be determine both  $K$  (equilibrium constant) and  $e$  (the probability of escape of radicals into the bulk volume from a cage of solvent, if  $K$  is the rate constant for decomposition of initiator into two radicals, then  $K_i = 2eK$ ) [8].

Another method depends on the rate of chain reaction in presence of initiator, in this case if the chain is not very long (less than 20) then the measured rate of chain reaction must be equal to the rate of chain reaction plus the rate of initiation [9]. Chemiluminescence method is the recommended method in calculating the rate constant of decomposition, a method in which the conditions are selected so that the oxidation products (peroxides) give particularly no chain initiation in

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comparison with that of the added initiator. In this method, the rate constant of decomposition can be determined from the change in chemiluminescence intensity. The light intensity ( $I$ ) is recorded. From the plot of  $\log(I_0/I)$  vs.  $tK$  can be found [10].

In this research, we evaluate the efficiency of inhibition for native N-P-methyl phenyl acetone and N,N- phenyl acetone in a comparison with the synthesized universal inhibitor (Unol) at elevated temperature (393 K) by modified chemiluminescence method so that molecular oxygen was used as free radical initiator instead of peroxides.

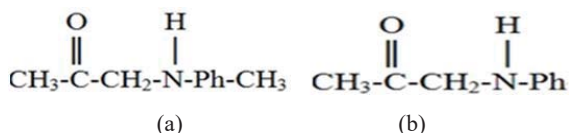


Fig. 1 The chemical structures of extracted anilines: (a) N, N-P-methyl phenyl acetone, and (b) N, N- phenyl acetone

## II. MATERIALS AND METHODS

1. N, N-P-methyl phenyl acetone and N, N- phenyl acetone were extracted from Iraqi Crude Oil region of Kirkuk by ion exchange method. A column of dimensions (25 cm. x3 cm.id) filled with Amberlyte (15) cationic resin was used to extract the molecules from a mixture of crude oil dissolved in xylene (1:3). The resin was activated by 0.1 N hydrochloric acid for 24 hrs then dried before use. The mixture (100 ml. crude oil: 300 ml. xylene) was circulated continuously through the column in a rate of 150 ml./min. for 3 hrs then eluted with absolute ethanol. Ethanol was distilled. The obtained product was ( $6.22 \times 10^{-2}$  gm.); it was characterized by spectral methods: IR, UV, and Gas chromatography [11].
2. Tetraline and Unol are purchased from Fluka GmbH Company highly pure and used without any purification.
3. Oxygen gas was pure and passed through drying agent containing (calcium oxide: aluminum oxide: calcium chloride) in a ratio of (1:1:1) pre oxidation process.
4. Manometric installation equipped with weak chemiluminescence intensity and oxygen gas characterized with simplicity, easily controlled, and high accuracy was used to measure the quantity of absorbed oxygen by tetraline in presence and without presence of the isolated antioxidants [12].
5. Thermostatic oil bath type HDKU-2 supplied from Hyde Science and Technology Limited to control the sample temperature at 393 K.
6. 5 ml. of tetraline was used as a hydrocarbon has chemical and physical properties closed to those fractionated from crude oil to examine the oxidation process in presence and without presence of the isolated antioxidants at elevated temperature.
7. The maximum rate of oxidation was calculated according to the numerical equation [7]:

$$W_{O2} = \frac{\Delta V_{O2} \times 1000}{\Delta t \times 60 \times 22400 \times V} \quad (1)$$

where,  $\Delta V_{O_2}$  is the difference in oxygen volume (in milliliter),  $\Delta t$  is the difference in time (in minutes),  $V$  is the volume of used tetraline (in milliliters).

8. The rate of initiation for Unol was calculated according to:

$$W_i = \frac{f[\text{InH}]}{T_{\text{min}}} \quad (2)$$

where:  $f$  is the stoichiometric factor of inhibition,  $[\text{InH}]$  is the concentration of inhibitor, and  $T_{\text{min}}$  is the induction period after the end of oxidation process in minutes.

## III. RESULTS & DISCUSSION

### A. Oxidation Stability Measurements

In this research the oxidation stability measurements were carried out according to the standard method ASTM- D7545 developed by subcommittee D02.14 which is recommended to be used for middle petroleum distillates like diesel, lubricant oil and based on the induction period values. This method uses a small sample and gives a result in a short time period under accelerated oxidation conditions [13].

### B. Oxidation of Pure Tetraline

Pure tetraline (5 ml.) was subjected to oxidation with oxygen by manometric installation under 393 K and normal pressure. Fig. 2 shows the kinetic curve of oxidation behavior for tetraline, it is seen that after 48 sec, the slope of the curve is not changed which means that tetraline after this point was reached its maximum rate of oxidation with induction period of 48 sec.

By applying Relation (1) the maximum rate of oxidation of tetraline can be calculated and it was equal to  $2.3 \times 10^{-4}$  mol/l.sec.

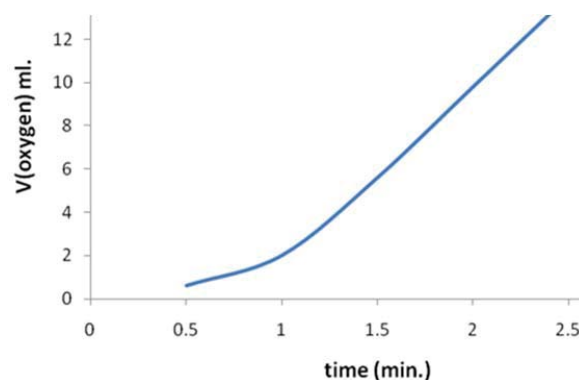


Fig. 2 The kinetic curve of oxidation for tetraline at 393 K

### C. Oxidation of Tetraline in Presence of Unol

A measure of 5 ml. of tetraline was subjected to oxidation process in presence of  $7.2 \times 10^{-2}$  mol/l. of Unol by manometric installation at 393 K. Fig. 3 shows the kinetic curve of oxidation of tetraline in the presence of added concentration of Unol.

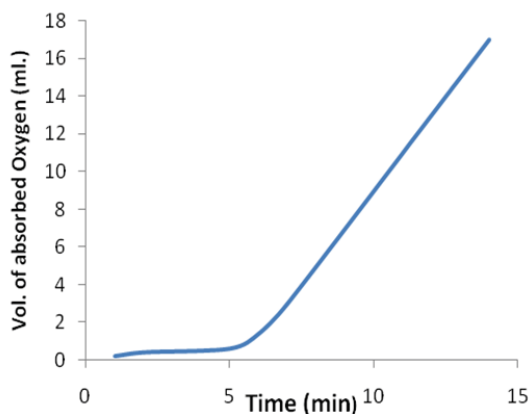


Fig. 3 The kinetic curve of oxidation for tetraline in presence of  $7.2 \times 10^{-2}$  mol/lit. of Unol at 393 K

It is seen that after 330 seconds, the slope of the curve is not changed which indicates that the system was arrived to maximum rate of oxidation of tetraline, so the induction period of oxidation for Unol is:  $330 - 48 = 282$  sec.

By applying (1) the maximum rate of oxidation of tetraline in presence of Unol can be calculated and it was equal to  $2.3 \times 10^{-4}$  mol/l.sec.

In the literatures, it is mentioned that the rate of initiation ( $W_i$ ) for tetraline in existence of Unol has a value of  $1.9 \times 10^{-6}$  mol./lit.sec. [7], [8].

#### D. Oxidation of Tetraline in Presence of N,N-Phenyl Acetone

The same concentration ( $7.2 \times 10^{-2}$  mol/l.) of extracted antioxidant N, N-phenyl acetone in 5 ml of tetraline was subjected to oxidation process. Fig. 4 shows the kinetic curve of oxidation process.

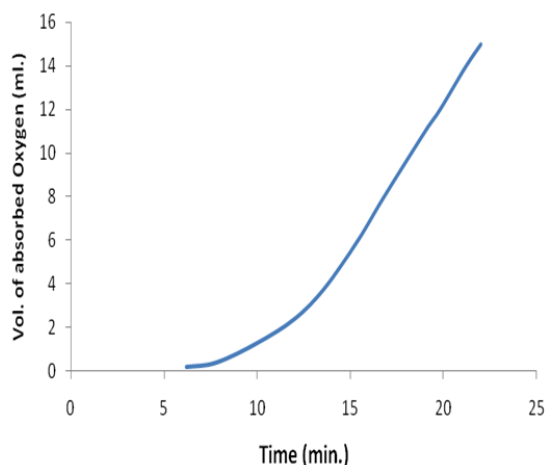


Fig. 4 The kinetic curve of oxidation for tetraline in presence of  $7.2 \times 10^{-2}$  mol/lit of N, N-phenyl acetone at 393 K

It seen that the after 660 seconds the system was arrived to the maximum rate of oxidation of tetraline  $2.3 \times 10^{-4}$  mol/l.sec. i.e. no change in the slope of the curve and the calculated induction period for N, N-phenyl acetone at 393 K is  $660 - 48 = 612$  seconds (10.2 min).

N, N-phenyl acetone was two times efficient than do Unol in preventing the formed hydroperoxides from decomposition to form new free radical and preventing the chain reaction to approach from the propagation to termination step.

#### E. Oxidation of Tetraline in Presence of N,N-P-Methyl Phenyl Acetone

The same sequence was carried out for oxidation of tetraline in presence of  $7.2 \times 10^{-2}$  mol/lit. of N,N-P-methyl phenyl acetone.

Fig. 5 shows the kinetic behavior of the oxidation process. It is seen that the system was arrived to the maximum rate of oxidation for tetraline after 900 seconds, then the induction period of N,N-P-methyl phenyl acetone is:  $720 - 48 = 672$  sec. Then, N,N-P-methyl phenyl acetone was efficient 2.5 times than do Unol to inhibit the chain reaction from passing to the termination step and prevent the decomposition of formed hydroperoxides.

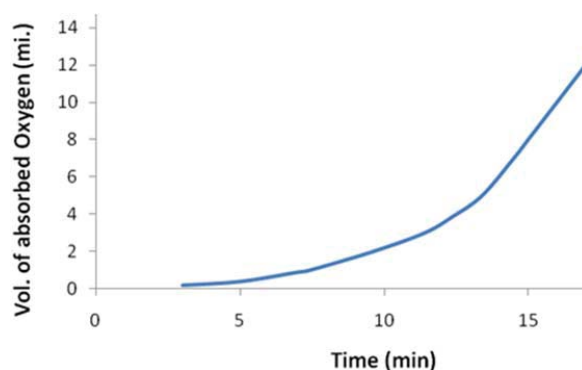


Fig. 5 The kinetic curve of oxidation for tetraline in presence of  $7.2 \times 10^{-2}$  mol/lit of N,N-P-methyl phenyl acetone at 393 K

#### IV. CONCLUSIONS

From the facts obtained from this research it can be concluded that:

1. Evaluation of antioxidant ability by manometric installation is an efficient method characterized with short time and simplicity in control.
2. The isolated natural antioxidant molecules from Iraqi crude oil proved higher efficiency of antioxidation for petroleum fractions from the universal antioxidant, Unol. This phenomenon is caused by the existence of versatile hydrogen bonded on the nitrogen in their structure which is easily donated to the formed free radicals and then creating an effective antioxidant free radical during the oxidation process.
3. The isolated natural antioxidant molecule N,N-P-methyl phenyl acetone was more efficient than N, N- phenyl acetone; the methyl group in N,N-P-methyl phenyl acetone is an electron donating group gives the molecule higher basicity [14].

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