Journal homepage www.jzs.univsul.edu.iq
Journal of Zankoy Sulaimani
Part-A- (Pure and Applied Sciences)

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

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Article info

Original:18 January 2016
Revised: 20March 2016
15January 2016
Accepted:
21 April 2016
Published online:
20 September 2016

Key Words: Inhibition, Antioxidants, Unol, Tetraline, Chemiluminescence

Abstract

The natural native antioxidants N,N-P-methyl phenyl acetone and N,N- phenyl acetone were isolated from 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 stochiometric 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 the quantity of absorbed oxygen during the time of oxidation process measured by manometric installation showed that at specific equal concentrations of N,N- phenyl acetone and N, N-P-methyl phenyl acetone in comparison with Unol at 393˚ K are with (2) and (2.5) times efficient than do Unol 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.

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 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. Consequently, antioxidant additives became highly required to decrease fuel oxidation, with a secondary effect of 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 act in two different ways: (1) by radical scavenging and (2) By decomposition of hydroperoxides.

Radical scavengers react with peroxy radicals generated from peroxidation of the fuel, preventing further propagation of the free radical chain [6] and are referred to as primary antioxidants, as they operate by breaking the propagation chain [5]. Peroxide decomposers react with the hydroperoxides molecule, preventing the formation of peroxy radicals Antioxidants can generally be considered as free radical inhibitors of peroxide decomposition, and may vary in their chemical structures.

The important classes of antioxidants used in engine oils include hindered phenols, amines, and sulfur and phosphorus compounds [3]. The two types of primary antioxidants are hindered phenol and aromatic amines. Both function by donating a hydrogen atom to a peroxy radical. Examples of hindered phenols include 2, 6-di-tert-butyl-4-methylphenol phenols, in which the hydroxyl group is strictly blocked or hindered. Aromatic amines act as peroxide radical traps to interrupt the oxidation chain reaction. Examples of aromatic amines include N-phenyl– naphthylamine and alkylated diphenyl amine. All these types are chemically synthesized prior use.

Generally the strength of an antioxidant is evaluated from its stochiometric 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 stochiometric 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 Ki 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 Ki= 2eK) [8].

Another method is depend 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 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 (Io/I) vs. t K 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.

$$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{H}{|}}{N}\text{-}Ph\text{-}CH_3$$

N, N-P-methyl phenyl acetone

$$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{H}{|}}{N}\text{-}Ph$$

N, N- phenyl acetone

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. The crude oil was dissolved in xylene (1:3) and extracted through a column (25 cm. x3 cm.id) containing Wafatit KPS-200 cationic resin 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 ($6.22x10^{-2}$ 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 based on a chemical reaction where the product has an excited intermediate. This intermediate emits light when falling into the ground state [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 numerical equation: [7]

$$Wo_2 = \frac{\Delta Vo_2 \text{ x } 1000}{\Delta t \text{ x } 60 \text{ x } 22400 \text{ x } V} \quad \text{--------------------------} (1)$$

Where:

ΔVo_2 is the difference in oxygen volume (in milliliter)
Δt 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 the relation:

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

Where:

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

Results & Discussion

1. 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. Compared to some other oxidation and storage stability test method, this method uses a small sample and gives a result in a short time period under accelerated oxidation conditions [13].

2. Oxidation of pure tetraline

Pure tetraline (5 ml.) was subjected to oxidation with oxygen by manometric installation under 393 K and normal pressure. Fig. 1 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 x 10^{-4} mol/l.sec.

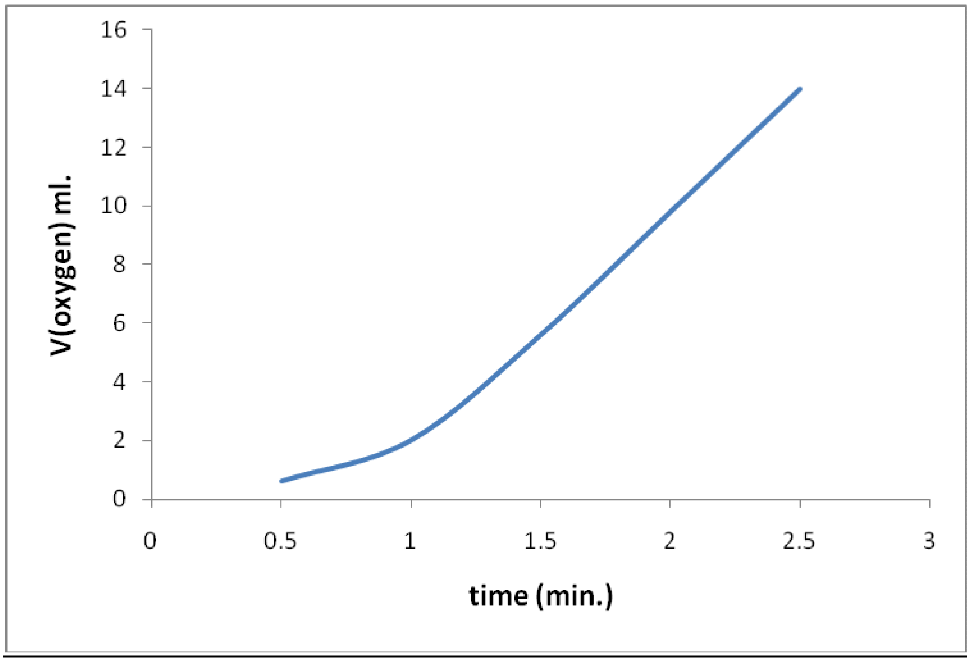

Figure (1): The kinetic curve of oxidation for tetraline at 393˚ K

3. Oxidation of tetraline in presence of Unol

5 ml. of tetraline was subjected to oxidation process in presence of 7.2 x 10^{-2} mol/l. of Unol by manometric installation at 393 K. Figure (2) shows the kinetic curve of oxidation of tetraline in presence of added concentration of Unol.

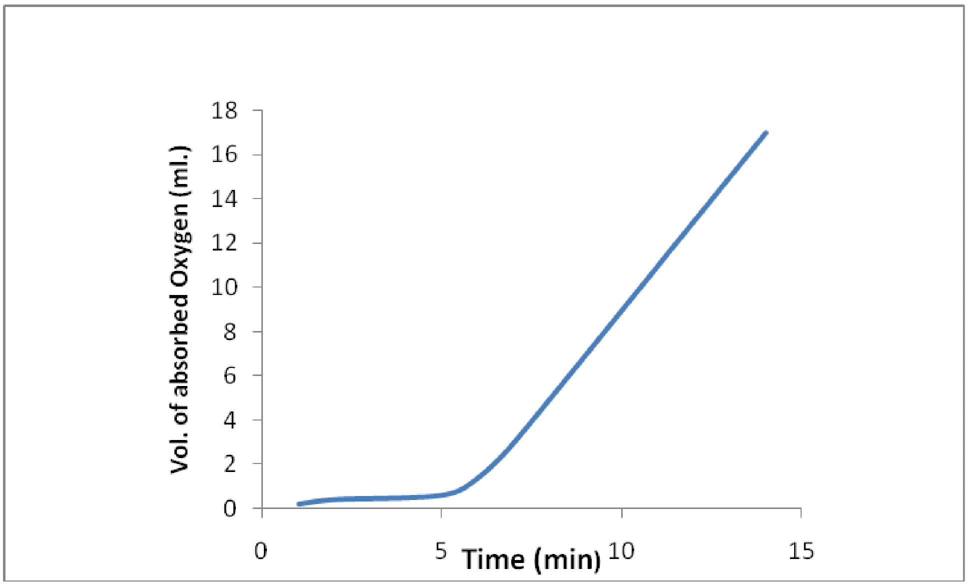

Figure (2): The kinetic curve of oxidation for tetraline in presence of 7.2x10^{-2} mol/lit. of Unol at 393˚ K

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

In the literatures it mentioned that the rate of initiation (W_i) for tetraline in existence of Unol has a value of 1.9 x 10^{-6} mol./lit.sec.

4. Oxidation of tetraline in presence of N,N- phenyl acetone

The same concentration (7.2 x 10^{-2} mol/l.) of extracted antioxidant N, N-_phenyl acetone in 5 ml. of tetraline was subjected to oxidation process. Figure (3) shows the kinetic curve of oxidation process.

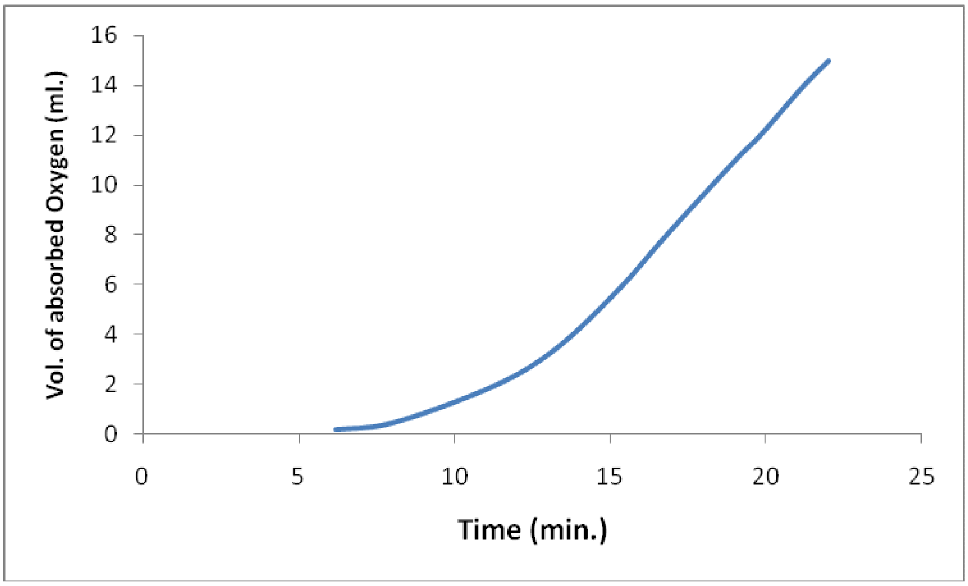

Figure (3): The kinetic curve of oxidation for tetraline in presence of 7.2x10^{-2} mol/lit. of N, N-_phenyl acetone at 393˚ K

It seen that the after 660 seconds the system was arrived to the maximum rate of oxidation of tetraline 2.3 x 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 (2) 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.

5. 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 7.2x10^{-2} mol/lit. of N,N-P-methyl phenyl acetone.

Figure (4) 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.

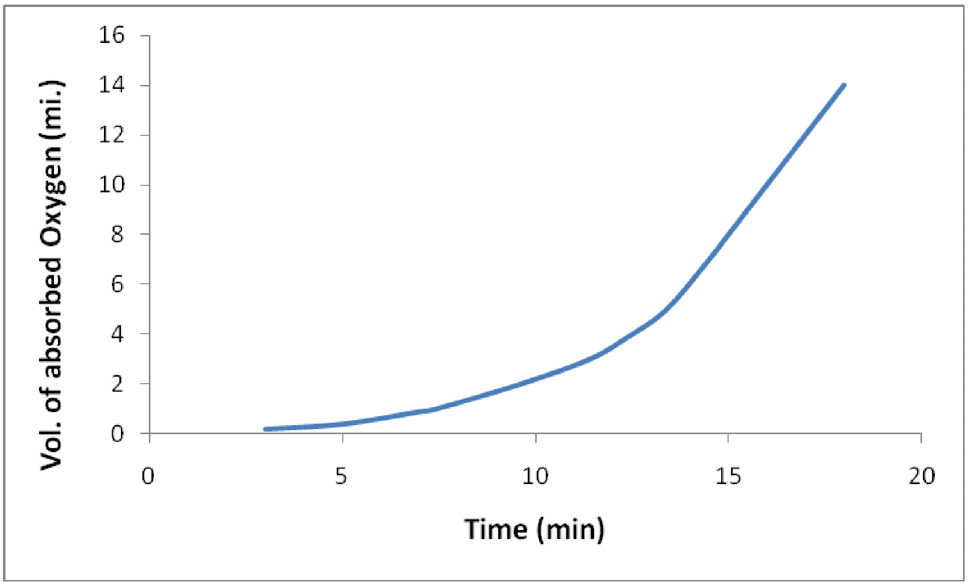

Figure (4):The kinetic curve of oxidation for tetraline in presence of 7.2x10^{-2} mol/lit. of N,N-P-methyl phenyl acetone at 393˚ K

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.

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 do the universal antioxidant Unol. This phenomena 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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