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ALKYL IMIDAZOLINES AND THEIR ETHOXYLATED DERIVATIVES AS ANTIOXIDANTS FOR HYDROCARBON PRODUCTS

Dariush Farkhani*, Habibolah Rezaei, Nader Gholami, Mitra Sina, Ali Asghar Khalili, and Ali Mehdizadeh

Chemical Science and technology Research Division, Research Institute of Petroleum Industry, West Blvd., Azadi Sports Complex, Tehran, 1485733111, Iran

ABSTRACT

Alkyl imidazolines have been reportedly used in a wide range of industrial formulations with different applications. Ethoxylated alkyl imidazolines with appropriate ethoxylation degrees can be used as antioxidants and retarders in the formation of peroxides resulting from oxidation in hydrocarbon media. In this work, ethoxylated imidazolines were shown to be more effective in hydrocarbon media in comparison with reference antioxidants. According to the experimental results, ethoxylated alkyl imidazolines (12 moles EO), as an antioxidant, were twice as efficient as zinc dialkyldithiophosphoric acid (ZDDP).

Keywords: Antioxidants, Corrosion Inhibitors, Ethoxylated Alkyl Imidazolines, Peroxides

INTRODUCTION

Alkyl imidazolines are prepared by reacting a polyethylenepolyamine structure (ethylenediamine, diethylenetriamine, triethylenetetraamine, and tetraethylenheptentamine) and a carboxylic acid such as tall oil fatty acid or acid cuts [1-7].

In general, in addition to their applications in pharmaceutical industry as anti-bacterial agents, bitumen and asphalt as emulsifiers, detergents, and demulsifiers, alkyl imidazolines have also been reported to function as additives in oil products with different applications.

Some of these functions include dispersing agents [8-10], metal inactivators [11], corrosion inhibitors [12-18], antirust agents [19], detergents [20-21], anti-gum formation agents [22], and antiabrasive agents [20]. Ethoxylated and propoxylated imidazolines have been used as multipurpose fuel additives [23]. These compounds prevent the decomposition of organic compounds accelerated in the presence of a metal. Antioxidants are one of fuel additives. An antioxidant is an organic compound used in rubbers, natural fats, food products, and fuels such as gasoline and diesel [24-25] to prevent and retard the oxidation and decomposition of molecules as well as gum formation. For example, an alkyl imidazoline has been used to prevent explosion. Furthermore, alkyl imidazolines have been applied in lubricants for corrosion and oxidation inhibition [26].

The most pronounced outcome of not using an appropriate additive in petroleum products such as lubricants and different organic-based fuels is their conversion into peroxides and hydroperoxides, which is also known as auto-oxidation.

***Corresponding author**
Dariush Farkhani
Email: farkhanid@ripi.ir
Tel: +98 21 4825 5031
Fax: +98 21 4473 9752

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The acidification of the medium and corrosion and knocking in engines are some of the adverse effects of hydrocarbon degradation and conversion to peroxide, the mechanism of which is shown in Figure 1.

The oxidation of hydrocarbon substrates initiated by AIBN occurs according to a free radical mechanism shown in Figure 1.

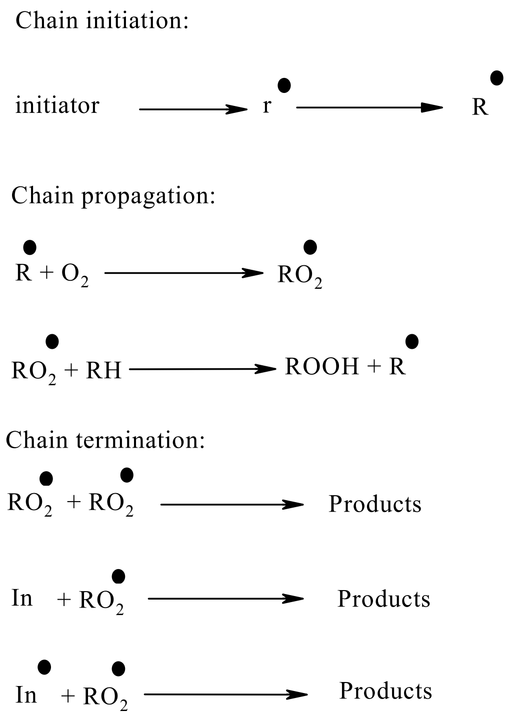


Figure 1: Hydrocarbon degradation

where, $r^{\bullet}$ is a radical formed from the initiator; RH is a hydrocarbon; $R^{\bullet}$ and $RO_2^{\bullet}$ are free alkyl and peroxide radicals respectively; In stands for an inhibitor and $In^{\bullet}$ represents a radical resulted from the inhibitor [27].

A small amount of an antioxidant is added to prevent or retard the oxidation and formation of explosive peroxide intermediates. Depending on the effectiveness of the antioxidant, the amount of absorbed oxygen increases. Thus, antioxidants, which are soluble in hydrocarbon media are favorable.

Ethoxylated alkyl imidazolines have been synthesized and used as fuel antioxidants and their performance is evaluated in this work.

EXPERIMENTAL

Instrumentation and Chemical

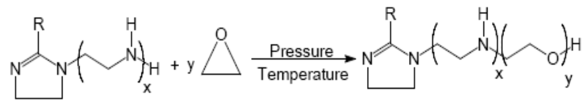
Cumene was distilled over Na in a nitrogen atmosphere for 2 hours to obtain a fraction with a boiling point of 152 °C. Azobisisobutyronitrile (AIBN) was purchased from Fluka. Zinc dialkydithiophosphoric acid (ZDDP) was prepared from Lubrizol Company. The imidazoline used herein was supplied by a local chemical factory.

Oxidation Rate Measurement

The apparatus used was previously described elsewhere [28]. In order to evaluate the oxidation rate, the following general method was applied (the proper amount of the chemicals needed for each experiment will be described later in each case). 25 ml of the testing sample was dissolved in purified cumene and 0.35 g of AIBN was added to a double-wall borosilicate reactor. Then the reactor was immediately purged with pure oxygen gas under 1 atmospheric pressure to empty out the any gases in the reactor. In this case, the oxidation reaction starts as soon as the temperature of the flask reaches 60 °C and since then the internal pressure of the reactor is measured as the indication of the amount of consumed oxygen in the reaction. The initial reactor pressure made as a result of the released heat of the reaction should be reduced by adjusting the mercuric manometer; another manometer filled with a chemical having a lower density such as dibutyl phthalate is applied. The measured pressures are corrected by the application of a conversion factor against the relative densities of dibutyl phthalate to mercury.

Synthesis

Ethoxylated alkyl imidazolines are prepared by reacting alkyl imidazolines and ethylene oxide using a base catalyst at a known temperature and pressure (Figure 2).



R=C_{12}-C_{18}
x=1-3
y=4, 8, 12, 18

Figure 2: Ethoxylated alkyl imidazolines

Evaluation

To evaluate the antioxidant performance, the amount of oxygen consumption and oxidation retardation time in isopropyl benzene (cumene) media in the presence of Azobisisobutyronitrile (AIBN) as a radical initiator are measured. Cumene is converted into cumene hydroperoxide in this process (Figure 3). The influence of ZDDP and ethoxylated imidazolines on the oxidation retardation and peroxide formation is subsequently studied.

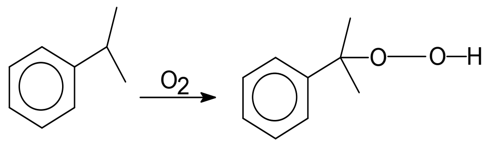


Figure 3: Isopropyl benzene(cumene) oxidizied to cumen hydroperoxide

A typical experiment of evaluation procedure is described as follows. The antioxidant agent and AIBN (0.35 g) were dissolved in pure cumene in a two-wall borosilicate reactor [28]. After purging the reactor with oxygen, the oxygen consumption rate was measured at atmospheric pressure at 60 °C by the difference of initial and final pressures of O_2. The effectiveness of ethoxylated imidazoline as antioxidant was expressed in terms of oxygen consumption as shown in Table 1 and Figures 4-9.

Table 1: Effectiveness of ethoxylated imidazoline as antioxidants in terms of oxygen consumption

Antioxidant type	Retardation time (min)
Lubrizol ZDDP	28
Alkyl imidazoline	30
Alkyl imidazoline 4 EO	25
Alkyl imidazoline 8 EO	38
Alkyl imidazoline 12 EO	52
Alkyl imidazoline 18 EO	24

As observed in Figures 4-9, oxygen is completely used at a retardation time of zero in the absence of any antioxidant and its consumption rate varies depending on antioxidant structure. For example, Lubrizol ZDDP, as a standard antioxidant, gives the same retardation time as alkyl imidazoline, while ethoxylated alkyl imidazolines of up to 12 EO increases this to 52 minutes, which is an appreciable enhancement.

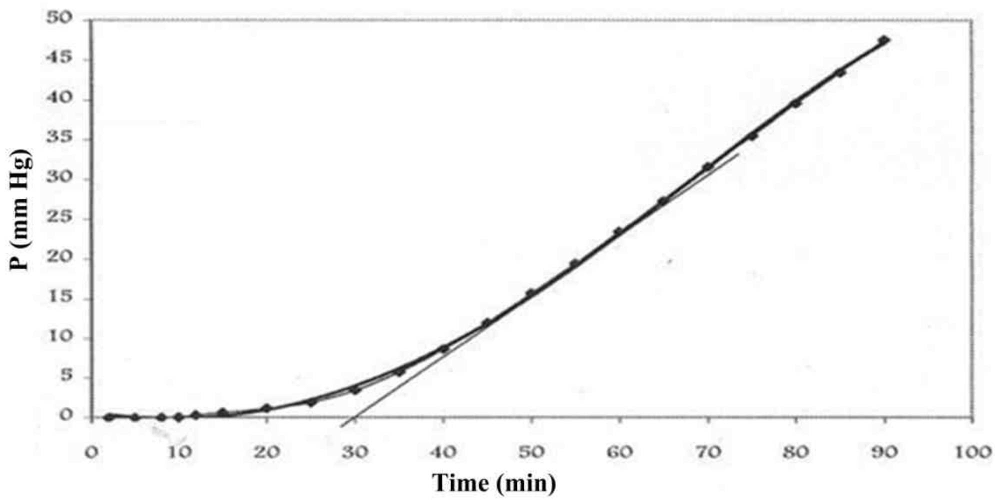


Figure 4: Oxygen consumption as a function of time using 0.001 moles alkyl imidazoline in cumene oxidation (25 ml) in the presence of 0.35 g of AIBN at 60 °C

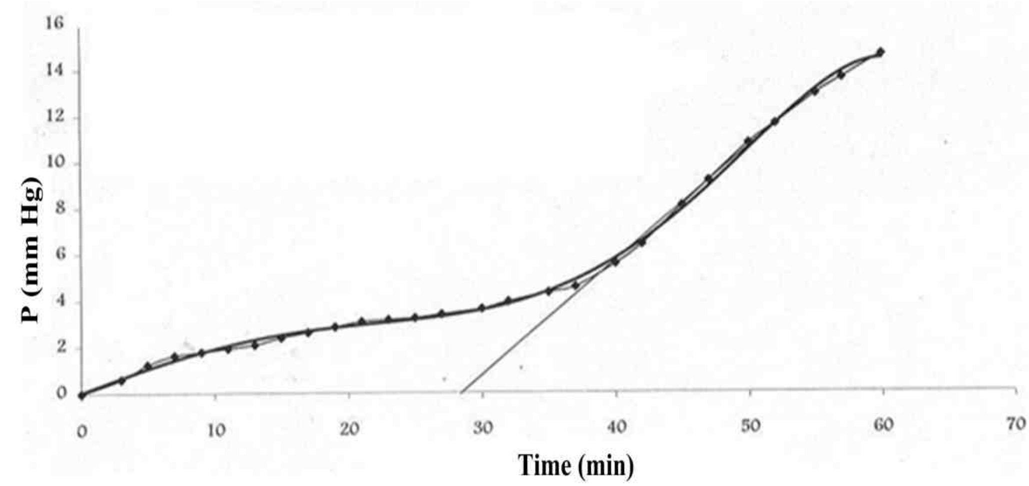


Figure 5: Oxygen consumption as a function of time using 0.001 moles Lubrizole ZDDP in cumene oxidation (25 ml) in the presence of 0.35 g of AIBN at 60 °C

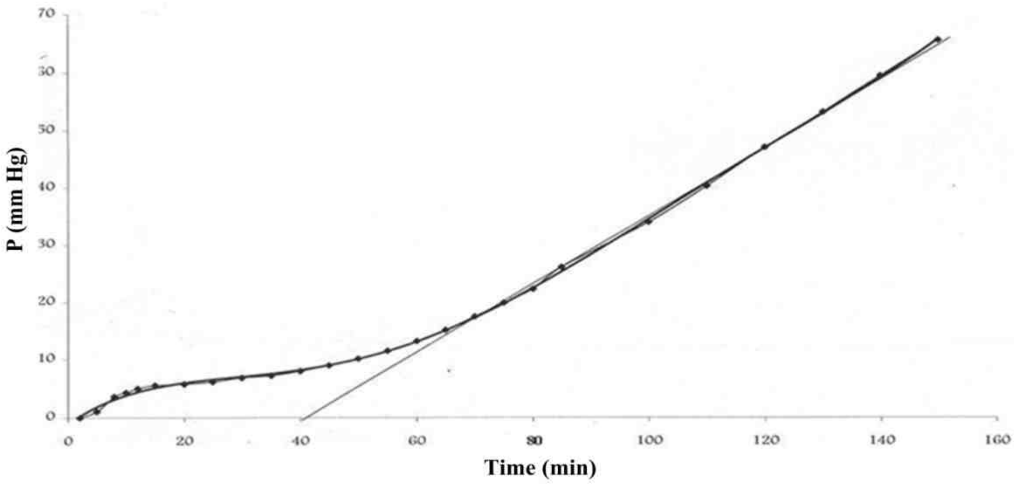


Figure 6: Oxygen consumption as a function of time using 0.001 moles ethoxylated (4 ethylene oxide units) alkyl imidazoline in cumene oxidation (25 ml) in the presence of 0.35 g of AIBN at 60 °C

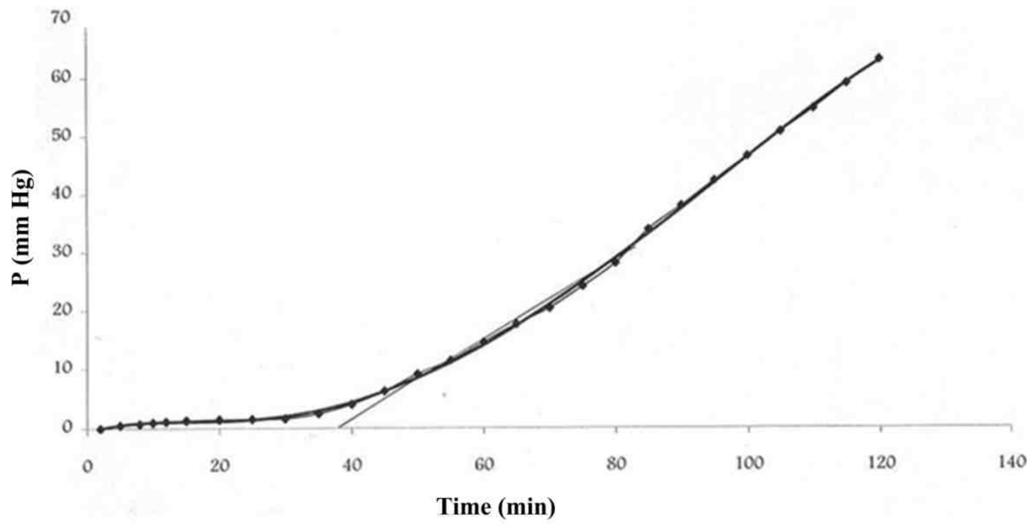


Figure 7: Oxygen consumption as a function of time using 0.001 moles ethoxylated (8 ethylene oxide units) alkyl imidazoline in cumene oxidation (25 ml) in the presence of 0.35 g of AIBN at 60 °C

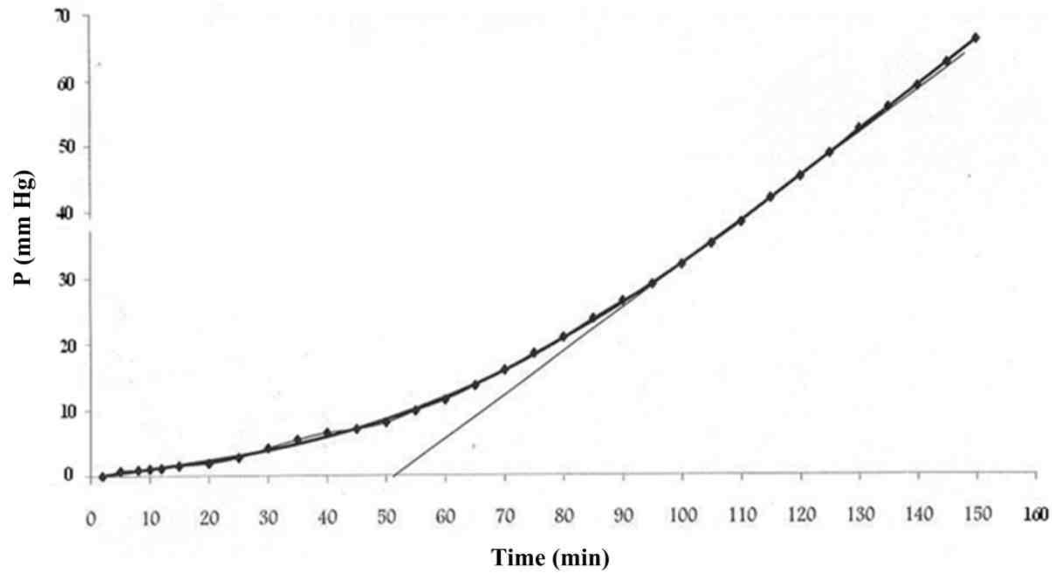


Figure 8: Oxygen consumption as a function of time using 0.001 moles ethoxylated (12 ethylene oxide units) alkyl imidazoline in cumene oxidation (25 ml) in the presence of 0.35 g of AIBN at 60 °C

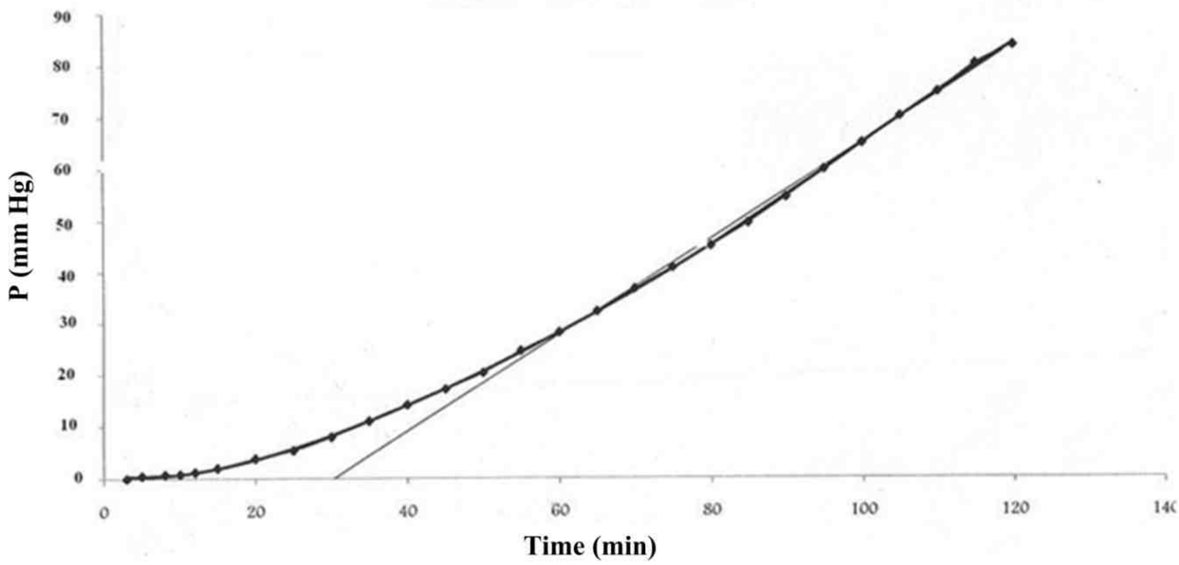


Figure 9: Oxygen consumption as a function of time using 0.001 moles ethoxylated (18 ethylene oxide units) alkyl imidazoline in cumene oxidation (25 ml) in the presence of 0.35 g of AIBN at 60 °C

RESULTS AND DISCUSSION

As previously mentioned, Alkyl imidazolines can be used as corrosion inhibitors, antirust, anti gum formation, and dispersing agents for various media in storage tanks and pipelines in hydrocarbon products such as fuels, gasoline, gasoil, etc. In the current work, ethoxylated alkyl imidazolines are used as antioxidants for the first time. The results obtained show that ethoxylated alkyl imidazolines containing 12 EO units are almost twice as effective as the commercial Lubrizol ZDDP.

Increasing ethoxylation chain length results in a higher HLB value which decreases oil solubility; this seems to inversely affect oxidation retardation. Based on the initial results and considering the relationship between the solubility of ethoxylated alkyl imidazolines and alkyl chain length, ethoxylation degree, and the specifications of hydrocarbon media, the design of a high performance antioxidant is plausible depending on hydrocarbon type.

CONCLUSIONS

A commercial alkyl imidazoline was used to prepare the ethoxylated derivatives with different ethoxylation degrees and the products thus obtained were investigated as antioxidants in hydrocarbon media. Alkyl imidazolines was highly reactive in the ethoxylation reaction. The antioxidancy performance of the ethoxylated alkyl imidazolines with an appropriate ethoxylation degree was satisfactory compared to ZDDP and its oxidation inhibition time was about twice as long as that of ZDDP.

A limitation in the application of ethoxylated alkyl imidazolines is the degree of ethoxylation. The higher the degree of ethoxylation is, the lower the oil solubility and antioxidancy performance of the product become. Considering the simplicity of ethoxylation and the availability of ethylene oxide, it is therefore recommended that this compound should be field tested as an antioxidant.

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