

Oxidative Stability improvement of diesel fuel during the storage

Y. Mesbah^{1,3}, K. Rahawi², S. Cheikh¹, H. Benmabrouka¹ and B. Hamada^{1,*}

¹Laboratory of petrochemical synthesis, Faculty of Hydrocarbons and Chemistry, University M'hamed Bougara of Boumerdès - Algeria;

²University of Mossul, College of Petroleum and Mining Engineering University of Mosul - Iraq

³Sonatrach - Algeria

*Corresponding author: bou.hamada@univ-boumerdes.dz ; Tel.: +213 24 79 51 56; Fax: +213 24 79 51 56

ARTICLE INFO

Article History :

Received : dd/mm/yyyy

Accepted : dd/mm/yyyy

Key Words:

biobased additive;
antioxidant; epoxidation;
transesterification; oxidation
test.

ABSTRACT/RESUME

Abstract: In this work a biobased material which is an antioxidant additive for diesel fuel during the storage was synthesized. Pomace olive oil extracted by maceration with hexane as raw material was chosen in the experimental process. Further, olive pomace wastes were fetched from a traditional oil mil. The involved processes were epoxidation by oleic acid of the pomace olive oil, opening of the oxirane ring, and esterification; respectively. The structures of the products were characterized and identified by both FTIR spectroscopy and by physic-chemical analysis methods. The effectiveness of our biobased antioxidant additive was tested by realizing an accelerated oxidation test (AOT) on the Algerian diesel of first by catalytic cracking without additive (blank) and further by testing diesel with different additive concentrations such as 2000, 3000, 4000 and 5000 ppm, respectively. The oxidative degradation of diesel with or without antioxidant was followed by sediment contents according to ASTM D2274. Diesel stability with antioxidant additive compared with the blank confirms the inhibition of the oxidation phenomena. Further the best antioxidant additive efficiency was recorded at the optimal concentration of 4000ppm.

I. Introduction

Currently, chemistry is moving to the replacement of products derived from oil because they are not renewable and do not fit the policy of durable development. Moreover, the industry must be adapted to restrictions related to environmental problems and thus find satisfactory solutions for the protection of the environment, therefore developing new materials from natural products idea was released [1].

For that, natural oils were chosen as initial products. This type of oils which are the subject of different studies are usually used after a chemical modification such as epoxidation, esterification, copolymerization with other synthesis monomers, and later as reactive diluents.

In addition to olive-oil which is the main product, also an important quantities of wastes defined by pomace and margins [2]. It is important to highlight that the valorization of such type of residues is widely important in both ecology and economy. During storage process, diesel fuel can be extremely sensitive to oxidation and thermal degradation. In the presence of oxygen, the diesel would undergone, even at ambient temperature, oxidation process leading to the formation of viscous products is called gums. However, the oxidative stability can be improved by the use of antioxidant additives [3]. Our work research experience consists in, first, to eliminate the principal pollutants of the oleiculture which is the olive pomace by transforming it into added value. The second step aims, to synthesize diesel fuel additives from renewable resources such

as oil olive pomace. particular interest is attributed to the antioxidant additives which have the principal function of inhibiting formation from hydroperoxides during storage.

Petroleum products additives are substances that are mixed with lubricants and fuel with well-defined proportions to enhance either their natural properties or give their new physical or chemical properties [3, 4]. The antioxidant additives called also inhibitors of oxidation guarantee the storage stability by avoiding the formation of sediments and of gums in the tanks within reservoirs and further clog the filters [3].

II. Materials and methods

II.1. Materials

Pomace olive oil is used as an initial raw material for the synthesis and the fractions of the diesel. catalytic cracking are characterized according to standards' in force (add reference). Formic acid (88%) was obtained from Fisher Scientific (add reference). All other chemicals reagents and solvents are obtained from Aldrich Chemical (add reference). Materials are used without further purification, and organic extracts are dried using anhydrous magnesium sulfate (Aldrich Chemical).

II.2. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a BRUKER Alpha-T Spectrophotometer (add reference).

II.3. Extraction of fatty acids (oleic acid)

Olive pomace wastes are fetched from a traditional oil mil. The pomace olive oil extracted by maceration with hexane is an acid (56%) presenting the profiles of fatty acids that are mainly made up with acids defined as : oleic (82%), palmitic (8%), and linoleic (7%). The oil is totally saponified by soda and decomposed with a strong acid into free fatty-acids.

II.4. Triester synthesis

II.4.1. oleic acid Epoxidation from pomace olive oil (EOA)

Hydrogen peroxide solution (30%, 8.0 mL) was added slowly into a stirred solution of oleic acid (OA) (90%, 15 g) in formic acid (88%, 14 mL) at 4°C (ice bath) and the combined reaction allowed us to proceed at room temperature with vigorous stirring (900 rpm) until the formation of a white, powdery solid (between 2 and 5 hours h). The obtained solid was collected via vacuum filtration, washed with H₂O (chilled, 3 x 10 mL) [5 -6], and placed under high vacuum for 12 h, yielding deoxidized oleic acid (EOA) as a colorless, powdery solid [5-7].

II.4.2. Synthesis of hydroxy-10-acyloxyoctadecanoic acid (HYAODA)

5 g of p-toluenesulfonic acid (PTSA), toluene (70 mL), and palmitic acid (6 g) were added to a the EOA mixture (31 g) for one and half hour 1.5 h. The mixture was also kept in a thermostat for one and half hour in order to keep the mixture at a temperature under 70 or 80°C. The reaction mixture was subsequently heated up to 90–100 °C and refluxed for 3 h. In the end of the reaction, heating was stopped and the mixture was left to stand overnight at ambient room temperature. The mixture was washed with the water next day. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using the vacuum evaporator [6-7].

II.4.3. Synthesis of butyl 9-hydroxy-10-acyloxyoctadecanoate (BHYAOD)

Sulfuric acid (conc. H₂SO₄, 10 mol%) was added into a stirred suspension of HYAODA (3.35 mmol) in iso-butanol (3.35 mL). The suspension was heated with stirring at 60 °C for 10 h. Hexane (5 mL) was then added. The solution was washed with NaHCO₃ (sat. aq., 1 x 0.5 mL) and brine (2 x 1 mL), dried using MgSO₄, filtered, concentrated in vacuuous and placed for 6 h under a vacuum to yield the desired product [5-7].

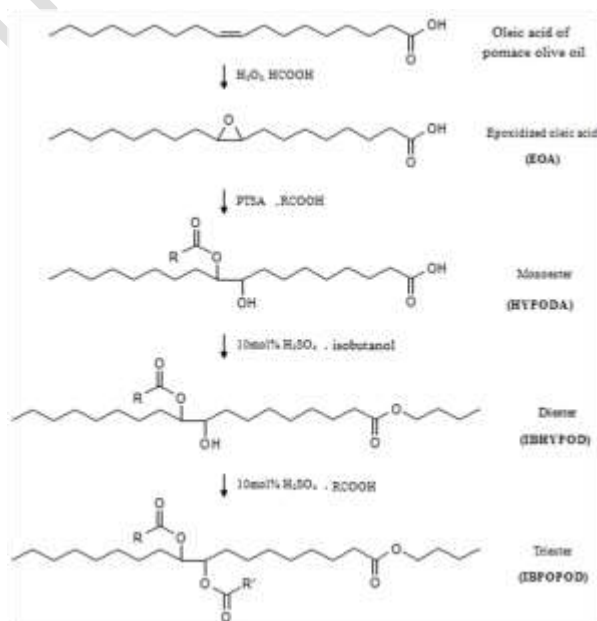


Figure 1. Triesters formation. RCOOH: CH₃(CH₂)₁₄COOH.

II.4.4. Synthesis of butyl 9-(octadecanoyloxy) 10-(acyloxy) octadecanoate (BOOAOD)

Palmitic acid (5 g) was added to a the solution of diesters butyl 9-hydroxy-10-acyloxyoctadecanoate

(5g) and sulfuric acid (10%) in a 2-neck round-bottomed flask equipped with a magnetic stir bar at room temperature; the mixture was heated to 50°C, then the reaction mixture was refluxed with stirring for 10 h. After the reaction was transferred to a separatory funnel, the lower aqueous phase was removed, and hexane (20 mL) was added to the upper oily phase. The organic phase was then washed with NaHCO₃ (sat. aq., 2 × 5 mL) and brine (2 × 5 mL), dried over anhydrous magnesium sulfate, filtered, concentrated in vacuum, and placed under high vacuum for 6h to provide with clear oils, which were stored over molecular sieves to mitigate potential hydrolysis.

II.5. Accelerated oxidation test (AOT)

Initial experiments consist in studying the oxidation resistance of various samples of taken from the Algerian diesel of catalytic cracking, undergone under different conditions and its response to the antioxidant action of synthesized triester in order to assess its quality as well as its antioxidant activity. These tests would provide quantitative and qualitative information regarding the oxidation resistance of the different diesel samples without and with a bio-based antioxidant, therefore, tests are performed according to the standard methods. These samples are tested in accordance with the standards which define its oxidative stability. The used standards in our experimental work are defined as:

II.5.1. ASTM D2274 [8] (gravimetric analysis)

ASTM D2274 is the only method adopted for evaluation diesel stability. It was used to determine the oxidation resistance of diesel with and without antioxidants. A 350 ml volume of filtered blend was aged at 95°C (203°F) for 16 h. Oxygen was bubbled through the sample at a rate of 3 L/h. After aging, the sample was cooled to approximately room temperature before filtering to obtain the filterable insolubles quantity.

Adherent insolubles were then removed from the oxidation cell and associated glassware with trisolvent (a mixture of equal parts toluene, acetone and methanol). The trisolvent was evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles, expressed as milligrams per 100 ml, was reported as total insolubles.

Accelerated oxidation test was applied to samples from diesel by catalytic cracking without additive (blank); commercial diesel; diesel with 2000, 3000, 4000 and 5000ppm of the synthesized bioadditif.

II.5.2. ASTM D 1500 [9] (color scale)

It is a classical colorimetric technique which is based on visual determination of the color of the product by comparison with colored standards where the scale ranges from 0.5 to 8. Generally, the level should not be greater than 5 (orange-brown color); most often it will target levels of 1 to 2 (yellow straw). The evolution of product color towards to a dark color oftenly represents a chemical deterioration [3].

III. Results and discussion

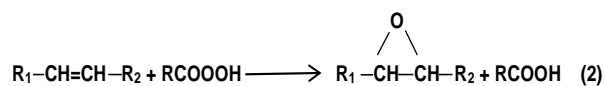
III. 1. Epoxidation and Esterification

In this part, we describe the synthesis of ester derivatives (mono-, Di- and triester) by: the epoxydation of the acid oleic of from pomace olive oil followed by the opening of ring of oxiranein with the presence of a Paratoluene sulfonic acid (PTSA) that results to a monoester (HYPODA). The process was followed by the esterification of carboxylic acid group with isobutanol to afford diester products (IBHYPOD), and further by esterification of the resulting α -hydroxy group in into diester with palmitic acid in order to find out the triester (IBPOPOD). We note that The presence of catalysts is necessary to accelerate the reactions.

In order to characterize and identify products obtained from each step of the synthesis monitored structural changes was realized using FTIR spectroscopy [7] and the physico-chemical analysis was done in to confirm the results obtained by FTIR.

Epoxidation of vegetable oil with carboxylic acid in the presence of suitable catalyst such as peracetic acid formation is an acid-catalyzed reaction [10].

This reaction is usually used to find out olefins by oxidation with a peracid [11]. The obtained olefins can be added directly with its commercial form, it can also be formed from peroxide and carboxylic acid, example of the hydrogen peroxide and formic acid to form performic acid [12].



Excess reagents can react with the epoxy rings to evoke unwanted side reactions [11] as depicted below:

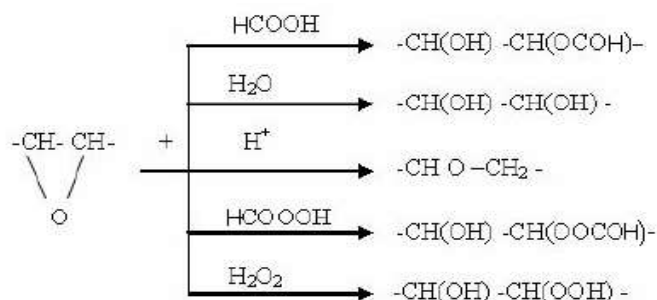


Figure 2. Epoxidation side reactions[13-14].

By analyzing the FTIR spectra of the acid 9,10-epoxyoctadecanoic and in comparison with that of the oleic acid of pomace olive oil which showz the appearance of two new peaks to 894cm-1 and 825cm-1. These new peaks approve to the presence of the epoxy function in the product [5-15]. the disappearance of the peaks corresponds to the double bond, such as: 3005 cm-1 (=CH), 1689 cm-1 (C=C), 1413 cm-1 (=CH) and 938 cm-1 (HC=CH).

In the second step of the synthesis we took advantage of the high reactivity of the epoxide function to graft a long carbon chain. in fact, the opening of the oxirane ring in the presence of palmitic acid allows us to have at the end of the reaction product a relatively high number carbons.

On the FTIR spectra of HYPODA we can clearly see the disappearance of the peaks of the epoxide function (825 cm-1 and 894 cm-1) and the appearance of sizeable peaks corresponding to the ester[6]. An absorption band at 1730 cm-1 represents the C=O bond and those at 1109 cm-1,1177cm-1,1248cm-1,corresponds to the C-O bond of the ester functional group formed after the graft palmitic acid at the oxirane group [5].The appearance of another peak at 3486cm-1, corresponds to the hydroxyl groups (-OH) appearing after ring opening[13-14].

Synthesis of diester IBHYPOD one sought to graft on the function carboxyl of the preceding product of HYAODA. a A isobutyl grouping by esterification reaction, explains the total disappearance of the peaks of absorption corresponding to the grouping carboxyl defined by: a peak of O-H to 2674 cm-1, a peak of C=O to 1710 cm-1 and a peak of CO to 1290 cm-1 and thus increase in theintensity of the peaks corresponding to the groupings ester. The function ester is characterized by an intense absorption band at 1737 cm-1 of the connection (C=O). an other significant bands like 1247 cm-1, 1105 cm-1 and to 1173 cm -1 corresponds to CO grouping [6].

The synthesis of triester consists in grafting a carboxylic group on the hydroxyl function of the preceding product of BHYAOD. For that an

esterification between a BHYAOD and a molecule of palmitic acid was realized. This reaction can also be carried out by acylation.

We note that in the spectrum of (IBPOPOD) the total disappearance of the peaks corresponding to the OH bond (3460 cm⁻¹)after the scribing of the fatty acid. The increase in absorbance of the ester function at 1244 cm⁻¹, 1174 cm⁻¹, 1106 cm⁻¹ (CO) and 1735 cm⁻¹ (C = O) [6] confirms that the reaction has occurred.

III.2. Characterization of the additive triester (IBPOPOD)

The Figure 3 presents the FTIR spectra of the antioxidant additive.

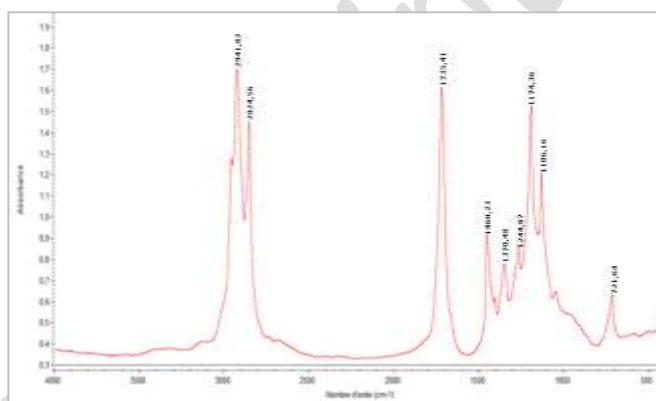


Figure 3. FTIR spectra of triester additive.

Table 1. The physicochemical properties of the synthesized products.

| Products | Yield (%) | Density (g/cm ³) | iodine Index (g of I ₂ /100g) | ester Index (mg KOH/g) |
|--------------------|-----------|------------------------------|--|------------------------|
| Oleic acid epoxide | 89 | 0.804 | 9 | 0 |
| Monoester | 92 | 0.840 | 0 | 96 |
| Diester | 75 | 0.890 | 0 | 178 |
| Triester | 77 | 0.960 | 0 | 189 |

III.3. Effectiveness of the antioxidant additive test on the diesel fuel

To follow the sediment content (mg / 100 ml) in the diesel before and after the application of our antioxidant additive with various concentrations, oxidation test(ASTM D2274) was realized on: diesel without additive (blank); commercial diesel (used as reference); diesel with 2000,3000,4000 and 5000 ppm of the additive.

Sediment content calculation (mg / 100 ml) of different diesel samples after the oxidation test (ASTM D2274) was done. Similarly, the color was determined by comparison with the color standards

before and after the test. The obtained results are represented in the histogram below (Figure 4).

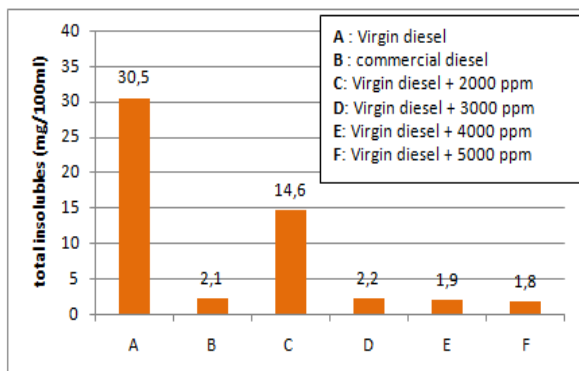


Figure 4. Tota linsolubles after accelerated oxidation test (ASTM D2274).

These samples were tested according to ASTM D2274 which defines the oxidation stability of the fuel to ASTM D1500 and determines the color change after the diesel oxidation. We noticed that the content of sediments for the virgin diesel is maximum compared to the various diesels with various concentration of 2000, 3000, 4000 and 5000 ppm of additive, respectively. These could be explained by the cracking phenomena of heavy products initially, which supports the formation of the light products having relatively low boiling points. On the other hand for the diesel formula, the content of sediment decreases with the increase in the concentration of the synthesized product.

This decrease can be explained the decomposition of the relatively heavy hydrocarbons in a the first stage. As the cracking is carried out according to a radical mechanism, diesel is cracked form intermediate compounds called radicals which react with derivatives bioadditif to yield molecules having a high boiling point and a good thermal stability.

The diesel with additive acted against oxidation as a model diesel (commercial diesel) once adding a concentration of 3000 ppm of bioadditif.

The evolution of diesel color until the darker shade often translates chemical deterioration of the product [3]. We note that, the color development is influenced by the presence of the antioxidant additive, which implies that the presence of the latter slows down the oxidation of diesel and than, minimizes chemical deterioration phenomena.

IV. Conclusion

This work aims to the respect of the new restriction binding of petrochemical products to the environment, the biodegradability, the not-toxicity and the not-emission of gases that have effect of the greenhouse, further, to promote vegetable oils unfit for consumption. Our research was mainly focused upon the olive pomace oil acid. Antioxidant additive for diesel fuel was synthesized and the obtained products. Were characterized by FTIR spectroscopy. Obtained results in these steps are interesting and showed a clear reduction of the content of sediments, which was followed in accordance with the standard D2274. This reduction confirms the inhibition of the oxidation phenomena and thus of the good efficiency of our bioadditive synthesized.

Acknowledgements

The authors acknowledge Naftal Society (Distribution of Algerian Petroleum Products) for their material help.

V. References

1. Brito, J.; dos Santos, R.; Branco, F.A. Environmentally sound concrete release agents, *Magazine of Concrète Research* (2000)n265-273
2. Nefzaoui, A. contribution à la rentabilité de l'oléiculture par la valorisation optimale des sous-produits, *OLIVAE IV Tunisie* (1987).
3. Guibet, J.C. Carburants et moteurs: technologies, énergie, environnement, éditionstechnip, Volume 1 (1994).
4. Chaithongdee, D.; Chutmanop, J.; Srinophakun, P. Effect of Antioxidants and Additives on the Oxidation Stability of Jatropha Biodiesel. *Kasetsart Journal – Natural Science* (2010) 44, 243-50.
5. Salimon, J.; Salih, N.; Yousif, E. Chemically modified biolubricantbasestocks from epoxidized oleic acid: Improved low temperature properties and oxidative stability. *Journal of Saudi Chemical Society* (2011) 15, 195–201.
6. Sharma, B.K.; Kenneth, M. D.; Sevim, Z. Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties, *Bioresource Technology* 99 (2008) 7333–7340.
7. Salih, N.; Salimon, J.; Yousif, E. Synthetic biolubricantbasestocks based on environmentally friendly raw materials. *Journal of King Saud University – Science* (2012) 24, 221–226.
8. ASTM D 2274 norme : test d'oxydation accéléré .
9. ASTM D 1500 norme : echelle de couleurs.
10. Saurabh, T.; Patnaik, M. B.; Bhagt, S.L.; Renge, V.C. Epoxidation of vegetable oils, *International journal of advanced engineering technology, a review*, (2011) 0976-3945.
11. Snezana, S.F.; Milovan, J.; Zoran, S.P. Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin, *Journal of the American Oil Chemists' Society*, 1 (2001) 78.
12. Petrovic, Z.S. Zlatanac, A.; Lava, C.C.; Sinadinovicfise, S. Epoxidation of soya bean oil in toluene with peroxyacetic acid and peroxyformic acids-kinetics and side reactions. *European Journal of Lipid Science and Technology*, 104 (2002) 293-299.

13. Saurabh, T.; Patnaik, M.; Bhagt, S.L.; Renge, V.C. Epoxidation of vegetable oils: a review, *International Journal of Advances in Engineering & Technology*, 2 (2011) 491-501.

Please cite this Article as:

Y. Mesbah, K. Rahawi, S. Cheikh, H. Benmabrouka and B. Hamada., Oxidative Stability improvement of diesel fuel during the storage, *Algerian J. Env. Sc. Technology*, X:X (YYYY) XX-XX

accepted manuscript