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# Comparison of the Effects of Different Biofuels on the Oxidation Stability of a Hydrocarbon Fuel

Zaki El-Sayah, Pierre-Alexandre Glaude, René Fournet, and Baptiste Sirjean

## Abstract

In this work, the effects of the addition of biofuels belonging to different chemical families on the oxidation stability of a conventional fuel surrogate (*n*-decane) have been investigated. Experiments have been performed in a PetroOxy apparatus, which is one of the reference Rapid Small Scale Oxidation Test of the ASTM 7545 methods. When the pressure in the cell of the device decreases by 10% of the maximum pressure recorded, the time measured to reach this target value defines the Induction Period (IP). IP constitutes a quantitative measure of the oxidation stability of the fuel. In addition to the IP measurements for each biofuel / hydrocarbon fuel blend, organic peroxides produced in the liquid sample were quantified at the IP, using iodometric titration and ultraviolet–visible spectrophotometry.

Different oxygenated biofuels have been studied in this work: diethyl ether, *n*-butanol, and cyclopentanone. Cyclohexane addition has also been considered to probe the effects of a non-oxygenated additive. For each type of biofuel, the proportion added to *n*-decane, the surrogate fuel, was varied from 0.2 to 20% vol. For each blend, the IP and the total peroxide content in the liquid have been systematically measured.

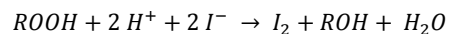
This study demonstrates an unexpected diversity of the effects of oxygenated biofuels: *n*-butanol strongly enhances the oxidation stability of the surrogate fuel (up to a factor of 6) while diethyl ether and cyclopentanone decrease the stability of *n*-decane. The experimental results show also that variations in the proportions of biofuel additives lead to non-linear variations in the measured IPs. Organic peroxide measurements confirmed that a similar reaction mechanism underpins the oxidation of all the biofuel/fuel surrogate blends.

## Introduction

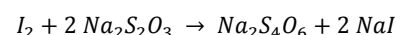
Oxidation stability of fuels is a major issue in the fields of transport and energy. It is indeed crucial that fuels remain stable over their entire chain of use, from storage to combustion. Historically, the oxidation stability of conventional fuels has been studied using different experiments that allowed to understand variations in macroscopic properties, induced by the liquid phase oxidation [1], [2]. These studies showed that the fuel auto-oxidation induces changes in a variety of chemical and physical characteristics, such as colour, viscosity, and chemical composition. The fuel aging also alters combustion properties and the compatibility with other fuels, and can favour the development of soluble / insoluble gum. The liquid phase oxidation of alkanes, the main components of conventional fuels, has been intensively investigated in the literature, such as in the work of Rust [3], Brown and Fish [4], Van Sickle et al.

[5], Cullis et al. [6] and Chatelain et al. [7]. These studies aimed to understanding the fundamental oxidation mechanism and the deposit formation pathways. Nowadays, the fundamental mechanism of the oxidation of alkanes is well established, [8]-[13] and takes place according to a chain reaction mechanisms that is similar to that found in gas phase combustion [14]. However, if a large body of work has been performed on the oxidation stability of alkanes, the knowledge of the impact of biofuel addition on their stability remains largely unknown. Apart from studies on biodiesel molecules (fatty acid alkyl esters), the effect of potential next-generation biofuels addition on the stability of hydrocarbon fuels remains to be determined.

The goal of this work is to investigate the effect of potential new biofuels on the oxidation stability of hydrocarbon fuels. *n*-Decane considered as the lightest alkane for which no initiator is needed to catalyse its liquid phase reaction has been selected as a surrogate to represent the real hydrocarbon fuels [6]. The first part of this study is dedicated to the oxidation of *n*-decane and to the impact of the addition of different types of oxygenated biofuel molecules as well as the effect of a non-oxygenated additive, in different proportions (0.2 – 20 %), on its stability. The oxidation stability of these blends is determined by measurement of an induction period (IP) in a PetroOxy device, as a function of the volume percentages of additive. The effect of different types of additive (alcohol, ether, ketone and cycloalkane) has been studied at two different temperatures (408 and 413 K). It has been shown in the literature that hydroperoxides are key products of the liquid phase oxidation of alkanes [5], [18]. The mixtures containing organic peroxides are usually difficult to analyse by means of conventional techniques because of the unstable nature of these compounds [25]. Numerous analytical techniques such as Gas Chromatography (GC) [26], High-Performance Liquid Chromatography (HPLC) [27], [28], Thin Layer Chromatography (TLC), polarography [29] and NMR techniques [30] have been developed to determine the organic peroxides (ROOHs). These methods are expensive, time consuming and require a control of ambient oxygen [31]. The standard method to quantify the total quantity of hydroperoxides in conventional fuels consists in the oxidation by ROOHs of iodide ions  $I^-$  to iodine  $I_2$  which is then quantified by titration with a sodium thiosulfate solution in presence of starch as a colour indicator [32] [33]:

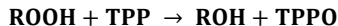


(Colourless) (Yellow-Reddish)



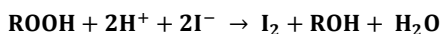
(Yellow-reddish) (Colourless)

An alternative method proposed to quantify organic peroxides involves the reaction of ROOH with triphenylphosphine (TPP). In this method, TPP is used as titrant and react with ROOH to lead to the formation of the corresponding alcohol (ROH) and triphenylphosphine oxide (TPPO) as presented in the equation below:

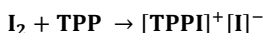


Thereafter, the measurement of the TPPO allows the quantification of original ROOH by the mean of different analytical methods like GC-mass spectrometry [34][36]. The measurement of TPPO by this method is performed only at high peroxide level and seems to be not reproducible at low quantity of ROOH [37].

Recently, a new analytical method has been proposed by Roohi and Rajabi [31]. They used TPP as a titrant for the iodine liberated from the reaction of peroxides with iodide ions. In the first step, ROOH reacts with iodide ions from potassium iodide in absolute ethanol in presence of acetic acid to produce coloured  $\text{I}_2$  as presented in the equation below:



Then, TPP is added to react with  $\text{I}_2$  producing an uncoloured complex  $[\text{TPPI}]^+[\text{I}]^-$  as shown in the equation given below:



This paper presents the first quantitative results measuring the effect of adding *n*-butanol, diethyl ether (DEE), cyclopentanone and cyclohexane on the oxidation stability of *n*-decane. Quantification of peroxides produced during the auto-oxidation of these blends, at the IP, was systematically performed using the latest iodometric titration method of the literature (with TPP) [31].

## Experimental

### PetroOxy device

Experiments have been performed in a PetroOxy apparatus from Petrotest Instruments GmbH & Co. KG, which is one of the reference Rapid Small Scale Oxidation Test of the ASTM 7545 methods [38]-[43]. In these experiments, a small amount, 5ml, of the liquid fuel is placed in a cell, which is pressurized with pure  $\text{O}_2$  under 7 bar at room temperature. The cell is thereafter heated to the test temperature and the evolution of the pressure is recorded as a function of time. Tests were conducted at 408 and 413 K. When the pressure decreases by 10% of the maximum pressure recorded, the time measured to reach this target value defines the Induction Period, which characterizes the oxidation stability of the fuel. An example of typical pressure vs time plots recorded in the PetroOxy is given in Figure 1.

The measurement uncertainty of PetroOxy device follows a linear relationship with IP ( $h$ ) = +/- 0.097 ( $h$ ). This value is based on repeatability tests measured on 10 fuel samples at same temperature and pressure. For each identical test, the same volume of the sample (5 mL) was introduced in the PetroOxy device and after each test, the joint (Viton) of the cell was changed to insure a better reproducibility of the measurement.

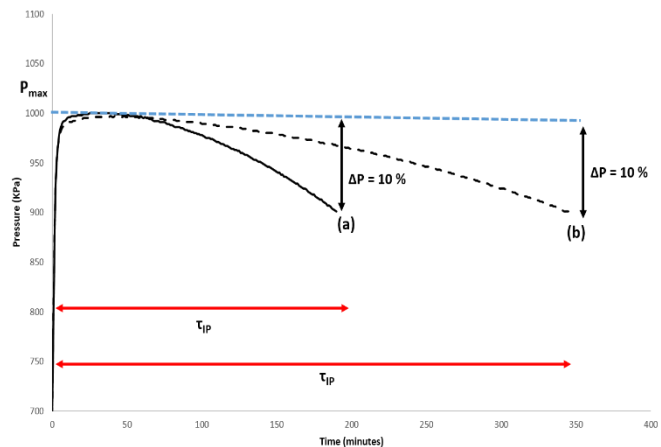
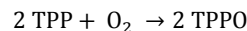


Figure 1. Typical induction period measurement with PetroOxy device. Results correspond to *n*-decane at (a) 413 K, (b) 408 K and 700 kPa of molecular oxygen.

### Hydroperoxide quantification

The organic peroxides produced during the oxidation of the different blends were quantified by triphenylphosphine iodometric titration, based on the new method proposed by Roohi and Rajabi [31]. In this method, TPP solution was used as titrant for iodine liberated from the reaction of peroxide with iodide ions. After consuming all of the iodine, the solution becomes colourless indicating the end point of the reaction. For more precision on the peroxide value, the end point detection has also been done by UV-visible spectrophotometry. The absorbance of the solution is measured at 359 nm.

The reagents for this titration were used without further purification, except TPP. Since TPP is known to undergo a slow oxidation by air to give TPPO as in the equation below, it was important to purify it before using it.



A recrystallization of organic TPP from a solution in hot ethanol at 80 °C is recommended to remove the impurity [31]. The TPP titrant solution (0.08 M in *n*-decane) was prepared by adding 2.10 g of purified TPP and 0.01 g of antioxidant Butylated hydroxytoluene (BHT) to avoid air oxidation, into a 100 mL volumetric flask. Then, the flask was filled with *n*-decane. To prepare the peroxide titration solution, 0.5 g of KI and 0.5 mL of acetic acid were added to 25 mL of absolute ethanol in a 50 mL volumetric flask. The mixture is then kept boiling at (70 – 73 °C) for 5 min under slow stirring. At the end, 0.3 g of the oxidized sample from PetroOxy test containing organic hydroperoxides ROOH was added at the same temperature without cooling. Once ROOH have reacted with iodide ions, the mixture turned to bright yellow and few second later to yellow-reddish depending on the ROOH amount in the mixture. During the titration, TPP in decane is added drop by drop and reacts with the iodine liberated from the reaction of ROOH with iodide until a colourless mixture appears. The percentage by mass (wt. %) of ROOH in the sample was calculated by the following formula [31]:

$$\% \text{ROOH} = \frac{(S - B) \text{CM}_w}{1000 \text{ G}} \times 100$$

S (mL) and B (mL) are the equilibrium volume of the titrant TPP solution and the volume used for blank titration, respectively. C (mol. L<sup>-1</sup>) is the molar concentration of TPP in the titrant TPP/decane and M<sub>w</sub> (g. mol<sup>-1</sup>) is the peroxide molecular weight. G (g) is the sample weight.

When the solution containing KI, acetic acid and absolute ethanol (blank solution) without presence of any trace of peroxide was titrated with TPP/decane solution, no colour change of the solution has been detected. The solution remained colourless since absolute ethanol does not easily oxidize in the air and thereafter there was no need to correct the titrant volume for the different samples titrated.

Potassium iodide (KI), anhydrous. Diethyl ether (≥ 99.7 %), *n*-decane (≥ 99 %), 1-butanol (99.8 %) and cyclohexane (99.5 %) were all anhydrous and purchased from Sigma Aldrich. Butylated hydroxytoluene (BHT) (≥ 99 %) triphenylphosphine, reagent plus (99 %) and acetic acid (≥ 99.8 %) were also purchased from Sigma Aldrich. Cyclopentanone (> 99 %) came from Acros organic and absolute ethanol, anhydrous, was obtained from Carlo Erba.

The present work covers a wide range of fuel surrogate (*n*-decane) mixed with different percentage of different families of biofuels. Up to 42 tests of blends *n*-decane/biofuel, in different proportions, were prepared, 21 of them tested at 408 K and the other 21 at 413 K.

## Result and Discussion

The oxidation of *n*-decane in the liquid phase was studied at 408 and 413 K with an initial oxygen pressure of 700 kPa. The induction period of pure *n*-decane at 413 K was 189 min and 349 min at 408 K as shown earlier before in Figure 1. Figure 2-7 show the changes recorded in the oxidation stability of *n*-decane, mixed with different percentages of the different oxygenated additives.

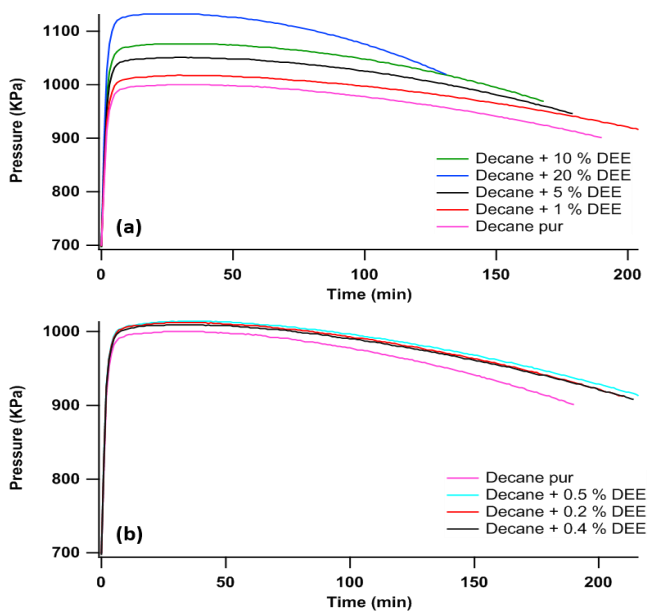


Figure 2. Induction period measurements of various proportions of DEE in *n*-decane at 413 K and under 700 kPa.

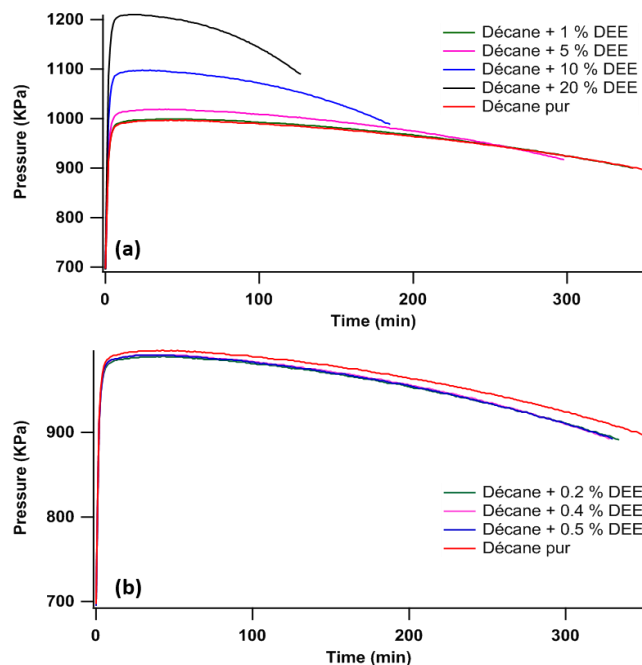


Figure 3. Induction period measurements of various proportions of DEE in *n*-decane at 408 K and under 700 kPa.

Results of oxidation stability of *n*-decane doped with DEE (0.2 – 20 %) at 408 and 413 K presented in Figure 2 and Figure 3 show a decrease of the IP for DEE amounts higher than 1 % at both temperatures. At 413K, the addition of 5% of DEE to *n*-decane leads to a decrease of the IP of 10.97 minutes, compared to pure *n*-decane (IP = 189 min). 20% of DEE decreases the stability of the hydrocarbon by 58.3 minutes. Additions of DEE in proportions below 1% slightly increases the stability on *n*-decane by about 20 minutes. The fundamental phenomena that explain these opposite behaviours as a function of the percentage of additive remains to be unravelled.

The increase of the initial pressure of blends containing DEE compared to pure *n*-decane, which is larger for an increased % of DEE, can be related to an increased quantity of diethyl ether in the gas phase during the auto-oxidation of the biofuel blend.

The induction period of *n*-decane / *n*-butanol blends with different percentages of *n*-butanol are depicted in Figure 4 and Figure 5.

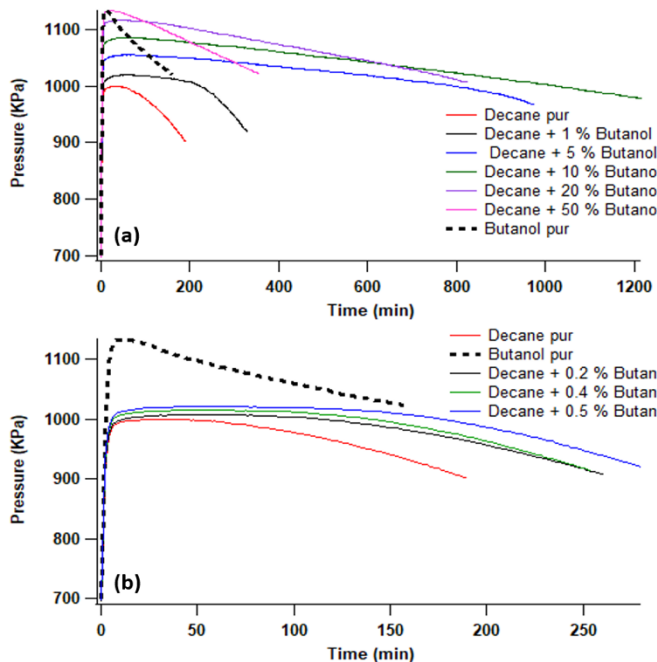


Figure 4. Induction period measurements of various proportions of *n*-butanol in *n*-decane at 413 K and 700 kPa.

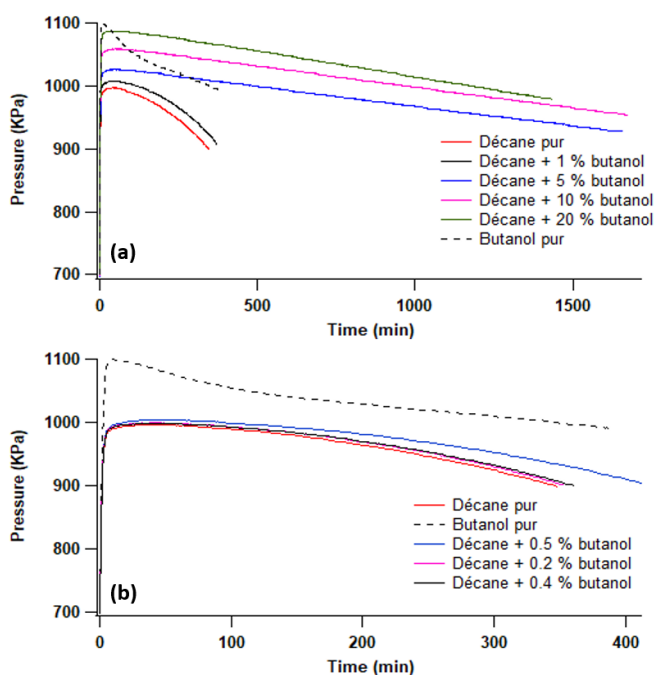


Figure 5. Induction period measurements of various proportions of *n*-butanol in *n*-decane at 408 K and 700 kPa.

All results obtained with *n*-butanol added to *n*-decane at 408 and 413 K presented in Figure 4 and Figure 5 show that for all proportions of *n*-butanol, ranging from 0.2 to 20 %, a noticeable increase of the induction period of the blend is obtained. IP increases from 349 min and 190 min in case of pure *n*-decane to 1700 min and 1214 min at 408 and 413 K, respectively, after addition of 10% *n*-butanol. This behaviour is surprising as the IP of pure *n*-butanol is only a few minutes higher than that of pure *n*-decane. Strong synergistic effects

are therefore observed and further studies deserve to be performed to understand this strong antioxidant behaviour of *n*-butanol when it is added in proportions greater than 5%. It is also noticeable that the IP of decane starts to decrease for proportions of *n*-butanol higher than 10 % added at both temperatures.

An oxygenated biofuel containing a carbonyl function C=O was tested with *n*-decane at 408 and 413 K to study its influence on the oxidation stability of *n*-decane. The IPs of *n*-decane containing cyclopentanone at different doping levels are presented in Figure 6 and Figure 7.

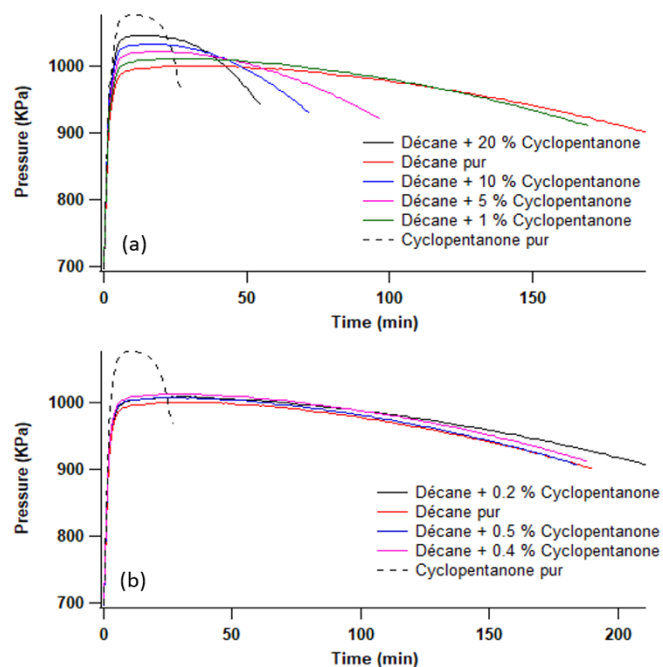


Figure 6. Induction period measurements of various proportions of cyclopentanone in *n*-decane at 413 K and under 700 kPa.

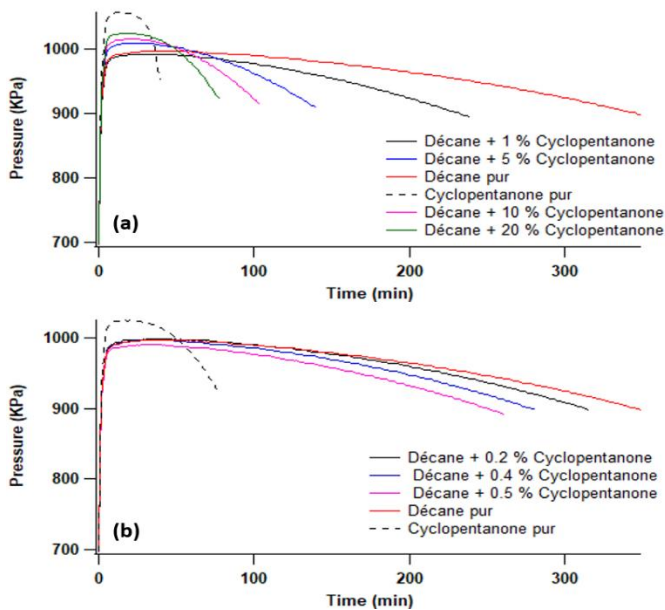


Figure 7. Induction period measurements of various proportions of cyclopentanone in *n*-decane at 408 K and under 700 kPa.

The effect of cyclopentanone added in different amounts on the oxidation stability of *n*-decane shows a similar behaviour to results obtained with DEE. Figure 7 shows that IP decreases when adding cyclopentanone at portions higher than 1 %. For cyclopentanone < 1 % there was no significant effect detected on the oxidation stability. The influence of the temperature and of the proportion of additives on the oxidation stability of *n*-decane is illustrated in Figure 8 and Figure 9.

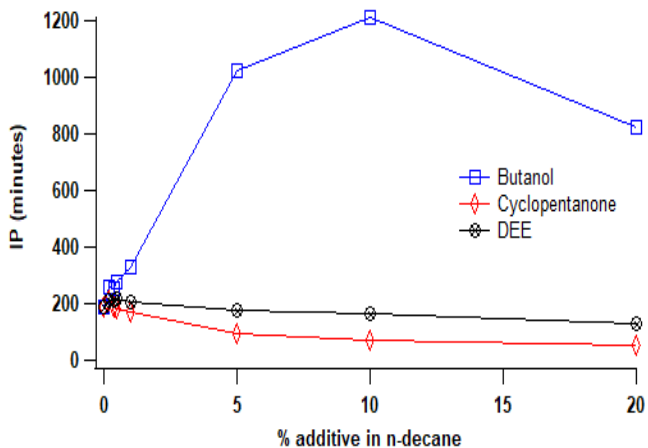


Figure 8. Induction period measurements as a function of vol. % of additives. Results correspond to % DEE, *n*-butanol and cyclopentanone in *n*-decane at 413 K and under 700 kPa.

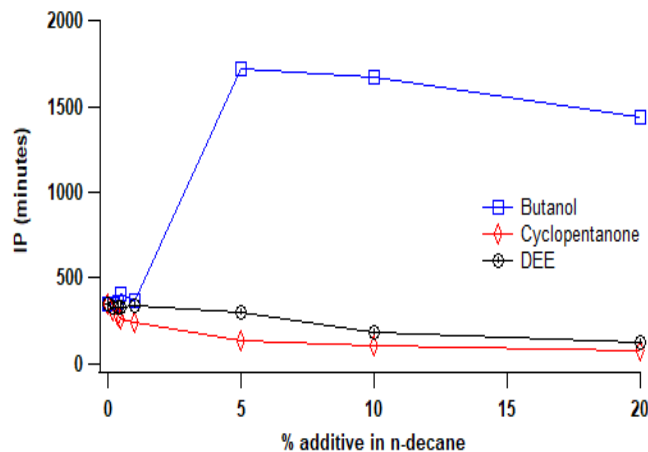


Figure 9. Induction period measurements as a function of vol. % of additives. Results correspond to % DEE, butanol and cyclopentanone in decane at 408 K and under 700 kPa.

The results obtained for the oxidation of *n*-decane in presence of DEE presented in Figure 8 and Figure 9 shown that for different doping levels of DEE at 408 and 413 K, a decrease in the IP value is observed. The small increase of the IP for % DEE less than 1 % at 413 K remains in the uncertainty of the PetroOxy device. The effect of addition of cyclopentanone to *n*-decane at 408 and 413 K leads to a degradation of the oxidation stability of *n*-decane, more noticeable than in the case of the doping with DEE. The slight increase of the IP at 0.2 % at 413 K can be related to the uncertainty of the device. Results obtained for blends of *n*-decane with *n*-butanol at 408 and 413 K show that for any percentage of *n*-butanol added to *n*-decane, an increase of the IP is observed with a maximum IP reached at 5 and 10 % butanol. DEE and cyclopentanone can be considered as oxidation enhancers for *n*-decane oxidation at both temperatures, while *n*-butanol strongly enhance the oxidation stability of the fuel surrogate, up to a factor of 6.

The impact of cyclohexane was also tested in the PetroOxy with *n*-decane at 408 and 413 K, for comparison and to better understand the role of non-oxygenated additive on the oxidation stability of *n*-decane. The results obtained for this test are shown in Figure 10 and Figure 11.

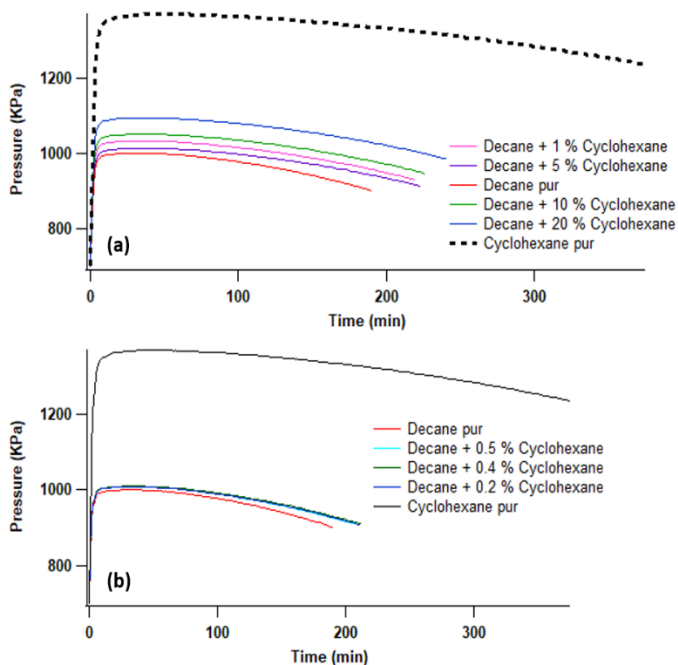


Figure 10. Induction period measurements of various proportions of cyclohexane in *n*-decane at 413 K and under 700 kPa.

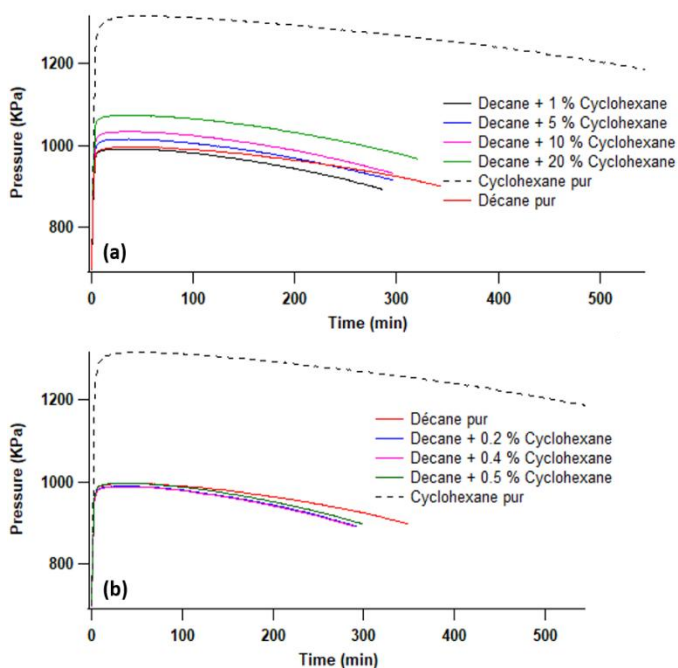


Figure 11. Induction period measurements of various proportions of cyclohexane in *n*-decane at 408 K and under 700 kPa.

As shown in Figure 10 (a) and (b), the addition of cyclohexane in different proportions increases the induction period of *n*-decane at 413 K and therefore cyclohexane has increased the oxidation stability of the hydrocarbon fuel at higher temperature. However, Figure 11 (a) and (b) show that for the lowest temperature, 408 K, a decrease in the induction period was observed after addition of different proportions of cyclohexane.

Opposite impacts on the oxidation stability of *n*-decane are therefore observed for the addition of cyclohexane at 408 and 413 K. Figure 12 and Figure 13 presents the IPs as a function of the vol. % cyclohexane additive at two different temperatures.

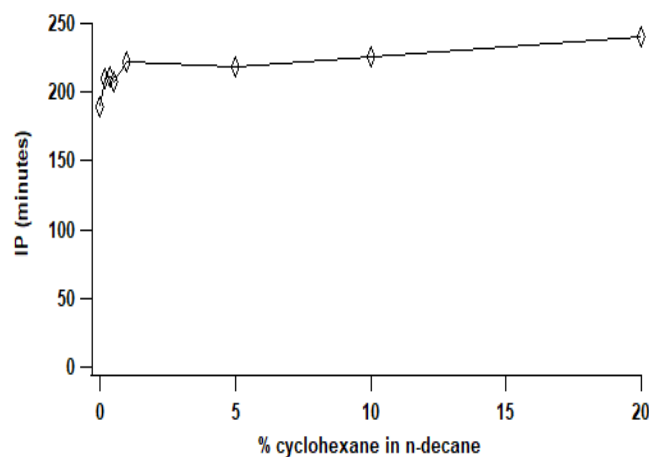


Figure 12. Induction period measurements as a function of vol. % cyclohexane in *n*-decane at 413 K and under 700 kPa.

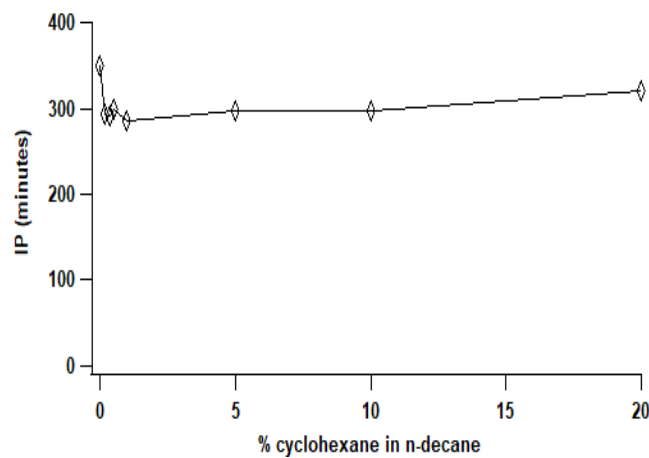


Figure 13. Induction period measurements as a function of vol. % cyclohexane in *n*-decane at 408 K and under 700 kPa.

Adding cyclohexane in different portions to *n*-decane at 413 K increases the induction period as presented in Figure 12. As shown in Figure 13, blends on *n*-decane with 0.2 – 20 % cyclohexane decreases the induction period of the fuel and, therefore, it could accelerate its oxidation at 408 K. Thus, adding a non-oxygenated additive to *n*-decane could help to increase its oxidation stability at higher temperature while it could be considered as accelerator for the oxidation process at lower temperature.

The oxidation of a mixture of hydrocarbons proceeds via a free radical chain reaction mechanism, which leads to oxygenated hydrocarbon such as alcohols, carboxylic acid and carbonyls in addition to ROOH via radical terminations pathways [44]. The main goal of this part of the work was to determine the concentration of ROOHs after the oxidation of the fuel.

The weight mass percentages as well as the equivalence volumes of ROOH founded after titration with TPP solution of different blend of

*n*-decane / additives oxidized at 413 K under oxygen pressure of 700 kPa are given in Table 1. For all calculations,  $M_w$  represented the peroxide molecular weight issued from decane peroxide which should be in the majority in all samples.

Table 1. Yields of peroxides at the IP for different amounts of additives in *n*-decane. Temperature of the test 413 K and oxygen pressure 700 kPa.

Sample name	Iodometric titration (TPP in decane) 0.08 M	
	Equivalence volume (mL)	Wt. % ROOH
Pure decane – C10	0.6	2.59
C10 + 0.2 % DEE	0.9	4.10
C10 + 0.4 % DEE	0.9	4.13
C10 + 0.5 % DEE	0.9	4.17
C10 + 1 % DEE	0.8	3.60
C10 + 5 % DEE	0.8	3.54
C10 + 10 % DEE	0.8	3.70
C10 + 0.2 % <i>n</i> -butanol	0.8	3.70
C10 + 0.4 % <i>n</i> -butanol	0.8	3.52
C10 + 0.5 % <i>n</i> -butanol	0.8	3.53
C10 + 1 % <i>n</i> -butanol	0.9	4.16
C10 + 5 % <i>n</i> -butanol	0.6	2.74
C10 + 10 % <i>n</i> -butanol	0.6	2.76
C10 + 0.2 % cyclopentanone	0.7	3.09
C10 + 0.4 % cyclopentanone	0.8	3.55
C10 + 0.5 % cyclopentanone	0.7	3.22
C10 + 1 % cyclopentanone	0.7	3.23
C10 + 5 % cyclopentanone	0.8	3.63
C10 + 10 % cyclopentanone	0.8	3.57
C10 + 0.2 % cyclohexane	0.8	3.70
C10 + 0.4 % cyclohexane	0.9	3.93
C10 + 0.5 % cyclohexane	0.8	3.49
C10 + 1 % cyclohexane	0.8	4.39
C10 + 5 % cyclohexane	0.7	3.04
C10 + 10 % cyclohexane	0.9	4.06

Results presented in Table 1 show that the order of magnitude of ROOH in different mixtures *n*-decane / additive remains the same after auto-oxidation of different blends. The quantity of peroxides found seems to be almost the same in different mixtures, which is logic since the same amount of pure oxygen is consumed at the IP, during the auto-oxidation of the mixtures in the PetroOxy.

## Summary/Conclusions

The oxidation stability of a fuel surrogate, *n*-decane, blended with different potential biofuels has been investigated. The standard IP of *n*-decane at 413 K and 408 K, at a 700 kPa pressure of pure oxygen is 190 min and 349 min, respectively. Adding *n*-butanol at different percentages to *n*-decane strongly increases the induction period of the fuel and thereafter improves its oxidation stability under the same conditions of temperature and pressure. Conversely, adding diethyl ether or cyclopentanone, deteriorates the oxidation stability of *n*-decane. Studying the auto-oxidation of these blends at different

temperatures showed that the temperature does influence the effect of the additive but for a slightly lower temperature an important increase of the induction period or the blend is observed.

The new technique proposed in the literature to determine the peroxide concentrations in organic mixture was successfully used in case of *n*-decane / additives. In this technique, the iodine liberated from the reaction of ROOH with iodide ions was titrated with TPP diluted in decane (organic solution) therefore there was no need for an aqueous medium to determine the quantity of peroxides. This method is simple, easy to establish, inexpensive and with a good precision.

## References

- [1]. Pradelle, F., Braga, S. L., Martins, A. R. F., Turkovics, F., and Pradelle, R. N. C., "Gum Formation in Gasoline and Its Blends: A Review," *Energy Fuels*, 29, 12, 7753-7770, 2015.
- [2]. Morris, R. E., Hazlett, R. N., and McIlvaine III, C. L., "The Effects of Stabilizer Additives on the Thermal Stability of Jet Fuel," *Ind. Eng. Chem. Res.*, 27, 1524-1528, 1988.
- [3]. Rust, F. F., "Intramolecular Oxidation. The Autoxidation of Some Dimethylalkanes," *J. Am. Chem. Soc.* 79, 15, 4000-4003, 1957.
- [4]. Brown, D. M., and Fish, A., "The Extension to Long-Chain Alkanes and to High Temperatures of the Hydroperoxide Chain Mechanism of Autoxidation," *Proc. R. Soc. Lond. A* 308, 547-568, 1969.
- [5]. Van Sickle, D. E., Mill, T., Riayo, F. R., Richardson, H., and W.Gould, C., "Intramolecular Propagation in the Oxidation of *n*-Alkanes. Autoxidation of *n*-Pentane and *n*-Octane," *J. Org. Chem.*, Vol. 58, No. 26, 4435, 1975.
- [6]. Cullis, C. F., Hirschler, M. M., and Rogers, R. L., "The Oxidation of Decane in the Liquid and Gaseous Phases," *Proc. R. Soc. Lond. A* 375, 543-563, 1981.
- [7]. Chatelain, K., Nicolle, A., Ben Amara, A., Catoire, L., Starck, L., "Wide Range Experimental and Kinetic Modeling Study of Chain Length Impact on *n*-Alkanes Autoxidation," *Energy Fuels*, 30, 2, 1294-1303, 2016.
- [8]. Bacha, K., Ben-Amara, A., Vannier, A., Alves-Fortunato, M., and Nardin, M., "Oxidation Stability of Diesel/Biodiesel Fuels Measured by a PetroOxy Device and Characterization of Oxidation Products," *Energy Fuels*, 29 (7), pp 4345-4355, 2015.
- [9]. Kapilan, N., Ashok Babu, T. P., and Reddy, R. P., "Technical Aspects of Biodiesel and its Oxidation Stability," *International Journal of ChemTech Research*, Vol.1, No.2, pp 278-282, April-June 2009.
- [10]. Zuleta, E. C., Baena, L., Riosa, L. A., and Calderón, J. A., "The Oxidative Stability of Biodiesel and its Impact on the Deterioration of Metallic and Polymeric Materials: a Review," *J. Braz. Chem. Soc.*, Vol. 23, No. 12, 2159-2175, 2012.
- [11]. Kumar, N., "Oxidative stability of biodiesel: Causes, effects and prevention," *Fuel*, Volume 190, Pages 328-350, 15 February 2017.
- [12]. Monyem, A., Van Gerpen, J. H., "The effect of biodiesel oxidation on engine performance and emissions," *J. Biomass and Bioenergy*, 20, 317-325, 2001.
- [13]. Sicard, M., Boulicault, J., Coulon, K., Thomasset, C., Ancelle, J., Raepsaet, B., and Ser, F., "Oxidation stability of jet fuel model molecules evaluated by rapid small scale oxidation



- tests,” IASH 2013, The 13th International Conference On Stability, Handling and Use of Liquid Fuels Rhodes, Greece 6-10 October 2013.
- [14]. Pollard, R. T., “Hydrocarbons, Comprehensive Chemical Kinetics,” Gas-Phase Combustion, Edited by Bamford, C. H., and Tipper, C. F. H., Volume 17, Pages 249-367, 1977.
- [15]. Pullen, J., Saeed, K., “An overview of biodiesel oxidation stability. Renewable Sustainable Energy,” 16 (8): 5924–5950, 2012.
- [16]. McCormick, R. L., Ratcliff, M., Moens, L., and Lawrence, R., “Several factors affecting the stability of biodiesel in standard accelerated tests,” Fuel Process, Technol, 88 (7): 651–657, 2007.
- [17]. Botella, L., Bimbela, F., Martín, L., Arauzo, J., and Sánchez, J. L., “Oxidation stability of biodiesel fuels and blends using the Rancimat and PetroOXY methods. Effect of 4-allyl-2,6-dimethoxyphenol and catechol as biodiesel additives on oxidation stability,” Frontiers in Chemistry | Chemical Engineering, Volume 2, Article 43, July 2014.
- [18]. TWIGG, G. H., “The mechanism of liquid-phase oxidation,” Special Supplement to Chemical Engineering Science, Vol. 3, 1954.
- [19]. Hong, J., Maguhn, J., Freitag, D., and Kettrup, A., “Determination of H<sub>2</sub>O<sub>2</sub> and organic peroxides by high-performance liquid chromatography with post-column UV irradiation, derivatization and fluorescence detection,” Fresenius J Anal Chem 361: 124–128, 1998.
- [20]. Steinberg, S. M., “High-performance liquid chromatography method for determination of hydrogen peroxide in aqueous solution and application to simulated Martian soil and related materials,” Environ Monit Assess, 185: 3749–3757, 2013.
- [21]. Gimeno, M. P., Mayoral, M. C., and Andrés, J. M., “A potentiometric titration for H<sub>2</sub>O<sub>2</sub> determination in the presence of organic compounds,” Anal. Methods, 5, 1510, 2013.
- [22]. Funk Jr, M. O., and Baker, W. J., “Determination of Organic Peroxides by High Performance Liquid Chromatography with Electrochemical Detection,” Journal of Liquid Chromatography, 8(4), 663-675, 1985.
- [23]. Richard Wagner, J., Lier, J. E., Berger, M., and Cadet, J., “Thymidine Hydroperoxides: Structural Assignment, Conformational Features, and Thermal Decomposition in Water,” J. Am. Chem. Soc., Vol: 116, No. 6, 1994.
- [24]. Csoregi, E., Gorton, L., and Marko-Varga, G., “Peroxidase-Modified Carbon Fiber Microelectrodes in Flow-Through Detection of Hydrogen Peroxide and Organic Peroxides,” Anal. Chem., 66, 3604-3610, 1994.
- [25]. Baj, S., “Quantitative determination of organic peroxides,” Fresenius J Anal Chem 350: 159-161, 1994.
- [26]. Hong, J., Maguhn, J., Freitag, D., and Kettrup, A., “Determination of organic peroxides by gas chromatography with cold on-column injection,” Journal of high resolution chromatography, Vol 22: Num 8, pp 475-476, 1999.
- [27]. Steinberg, S. M., “High-performance liquid chromatography method for determination of hydrogen peroxide in aqueous solution and application to simulated Martian soil and related materials,” Environ Monit Assess 185: 3749–3757, 2013.
- [28]. Calandra, M. J., Impellizzeri, J., and Wang, Y., “An HPLC method for hydroperoxides derived From limonene and linalool in citrus oils, using post-column luminol-mediated chemiluminescence detection,” Flavour Fragr. J, 30, 121–130, 2015.
- [29]. Molnár, S., and Péter, F., “Polarographic investigations of organic peroxides,” Journal of Electroanalytical Chemistry and Interfacial Electrochemistry Volume 22, Issue 1, Pages 63-68, July 1969.
- [30]. Cavalli, L., and Cancellieri, G., “Quantitative Evaluation of Peroxides, Hydroperoxides and Alcohols of m-Diisopropylbenzene by Nuclear Magnetic Resonance Spectroscopy,” Analyst, Vol: 100, pfi. 46-50, January, 1975.
- [31]. Roohi, H., and Rajabi, M., “Iodometric Determination of Hydroperoxides in Hydrocarbon Autoxidation Reactions Using Triphenylphosphine Solution as a Titrant: A New Protocol,” Ind. Eng. Chem. Res., 57, 6805–6814, 2018.
- [32]. ASTM D3703: “Standard Test Method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels,” Annual Book of ASTM Standards. Vol. 05.01, 5 p, 2018.
- [33]. ASTM E298: “Standard Methods for Assay of Organic Peroxides,” American national Standard Z159.3- 1969.
- [34]. West, Z. J., Zabarnick, S., and Striebich, R. C., “Determination of Hydroperoxides in Jet Fuel via Reaction with Triphenylphosphine,” Ind. Eng. Chem. Res., 44, 3377, 2005.
- [35]. Pinkernell, U., Effkemann, S., and Karst, U., “Simultaneous HPLC Determination of Peroxyacetic Acid and Hydrogen Peroxide,” Anal. Chem., 69 (17), 3623, 1997.
- [36]. Hiatt, R., Smythe, R. J., and Coleman, C., “The Reaction of Hydroperoxides with Triphenylphosphine,” Canadian Journal of Chemistry, 49, 1707, 1971.
- [37]. Dulog, L., and Burg, K. H., “Bestimmung Organischer Peroxide,” Fresenius' Z. Anal. Chem., 203, 184, 1964.
- [38]. Machado, Y. L., Teles, U. M., Neto, D., Dantas, A. A., Fonseca, T. N. C., and J. L. C., “Determination of antioxidant depletion kinetics using ASTM D 7545 as the accelerated oxidation method,” Fuel, 112, 172–177, 2013.
- [39]. Marteau, C., Ruyffelaere, C. F., Aubry, J. M., Penverne, C., Favier, D., and Nardello-Rataj, V., “Oxidative degradation of fragrant aldehydes. Autoxidation by molecular oxygen,” Tetrahedron, 69 (10), 2268–2275, 2013.
- [40]. Dantas, M. B., Albuquerque, A. R., Barros, A. K., Rodrigues Filho, M. G., Antoniosi Filho, N. R., Sinfrônio, F. S. M., Rosenhaim, R., Soledade, L. E. B., Santos, I. M. G., and Souza, A. G., “Evaluation of the oxidative stability of corn biodiesel,” Fuel 90 , 773–778, 2011.
- [41]. Hartikka, T., Kiiski, U., Kuronen, M., and Mikkonen, S., “Diesel Fuel Oxidation Stability: A Comparative Study,” Downloaded from SAE International by Big Ten Academic Alliance, Wednesday, August 01, 2018.
- [42]. Neumann, A., Jebens, T., and Wierzbicki, V., “A Method for Determining Oxidation Stability of Petrodiesel, Biodiesel, and Blended Fuels,” American laboratory, February 18, 2008.
- [43]. Jain, S., and Sharma, M. P., “Review of different test methods for the evaluation of stability of biodiesel,” Renewable and Sustainable Energy Reviews 14, 1937–1947, 2010.
- [44]. Toribio, P. P., Gimeno-Gargallo, A., Capel-Sanchez, M. C., de Frutos, M. P., Campos-Martin, J. M., and Fierro, J. L. G., “Ethylbenzene oxidation to its hydroperoxide in the presence of N-hydroxyimides and minute amounts of sodium hydroxide,” Appl. Catal, A, 363, 32, 2009.

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## Definitions/Abbreviations

**C10** *n*-decane

<b>DEE</b>	Diethyl ether
<b>IP</b>	Induction Period (min)
<b>TPP</b>	Triphenylphosphine
<b>BHT</b>	Butylated hydroxytoluene