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**OXIDATION STABILITY OF JET FUEL MODEL MOLECULES EVALUATED BY
RAPID SMALL SCALE OXIDATION TESTS**

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ABSTRACT

Jet fuel, besides its fuel role, can be used as a coolant for aircraft subsystems and thus it may be exposed to temperatures above 200 °C. Between 140 and 300 °C, an autoxidation phenomenon occurs due to the presence of 70 ppm of dissolved dioxygen in jet fuel resulting in the formation of oxidized products and solid deposits.

The aim of this work is to study the behavior of jet fuel model molecules in order to highlight their oxidation sensitivity and the solid products formed. A rapid small scale oxidation test (RSSOT) is used. Within the RSSOT's test chamber, 5 mL of fuel is combined with oxygen, at 700 kPa, and heated up to 150 °C. This initiates a fast oxidation process. As the fuel oxidizes, it consumes the dioxygen resulting in a pressure drop that is recorded. Different tests are carried out and stopped at various values of time. Gaseous and liquid samples are recovered and analyzed by gas chromatography.

In the case of n-dodecane, its consumption is observed up to a pressure drop of 64 %. At the same time, oxidized products are formed among which are alcohols, ketones and carboxylic acids. The gas analysis shows that all the dioxygen has been consumed. Oxidation reactions stop and new reactions appear. They are aldehyde decarbonylations and condensation reactions. Heavy products like esters and lactones are formed.

KEYWORDS: hydrocarbons, thermal-oxidation stability, RSSOT

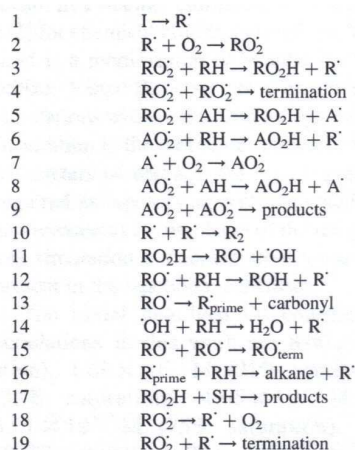
INTRODUCTION

Thermal stability of the jet fuel becomes a very important parameter in modern aircraft. Jet fuel, besides its fuel role, can be used as a coolant for aircraft subsystems and thus it may be exposed to temperatures above 200 °C in the fuel system and injection devices.¹⁻³ This thermal stress combined with the presence of dissolved oxygen can lead to the formation of gums and solids, causing fouling of nozzles and heat exchangers.⁴⁻⁶

A lot of parameters like temperature⁴⁻⁷, fuel flow,⁸ fuel composition,^{3,9-15} presence of

heteroatoms (sulfur^{16,17} and nitrogen¹⁸) have a significant influence on the fuel autoxidation process.

In order to explain the products obtained during the oxidation of the fuels, various autoxidation mechanisms have been proposed.^{1,19-22} Among them, Kuprowicz *et al.*²³ have proposed the following detailed mechanism:



The standard test method used to estimate the thermal oxidation stability of aviation turbine fuels is the JFTOT Procedure (ASTM D3241²⁴/IP 323). This test method covers “the procedure for rating the tendencies of gas turbine fuels to deposit decomposition products within the fuel system.” The results of these tests can normally assess the level of formed deposit when the fuel is in contact with a heated surface. Suitable for the characterization of aviation jet fuel derived from crude oil, its limitations became evident in the characterization of alternative jet fuels. All the fuels tested in the Swafea project pass the test. In order to get more information on the oxidation behaviour of fuels or hydrocarbon models it is necessary to choose a test method more discriminating. In this work, we propose to evaluate the sensibility to oxidation of the n-dodecane using the Rapid Small scale Oxidation Test (RSSOT) also named PetroOXY test. This test method measures the induction period, under specified conditions, which can be used as an indication of the oxidation stability of middle distillate fuels. This test was approved by ASTM D02.14 committee as ASTM D7545.²⁵

The aim of this work is to study the oxidation behaviour of the n-dodecane chosen as model molecule.

EXPERIMENTAL SECTION

PetroOxy RSSOT Apparatus²⁶

A 5 mL fuel sample is placed into a small hermetically sealed test chamber (Figure 1). The chamber is pressurized with oxygen to 700 kPa and possibly heated up to 160 °C. As the sample warms up to the desired temperature, the pressure increases up to a maximum. The temperature initiates a fast oxidation process resulting in consumption of oxygen and a pressure decrease. The induction period method is defined as the time needed to observe a pressure drop of 10 % below the observed maximum pressure (Figure 2). The length of the induction period is directly linked to the oxidation sensitivity of the fuel.



Figure 1 - Photography of Apparatus for Rapid Small Scale Oxidation Test

Besides giving an easy-to-understand result (time), the apparatus shows an interesting flexibility. Thus, it is possible, for example, to work at different temperatures, to modify the length of the test, to collect the gas after the test. In this study, the tests were performed mainly at 150 °C and the oxygen initial pressure was 700 kPa. The test was stopped for pressure drop values from 10 to 80 %.

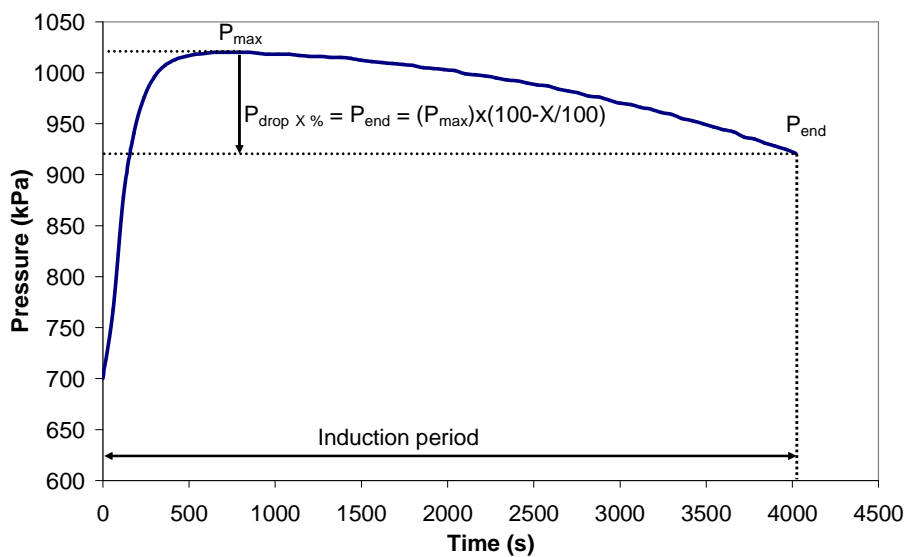


Figure 2 – Definition of the induction period

Analysis techniques

Gas chromatography studies on liquid products were performed on a Varian 3900 chromatograph equipped with an autosampler 8410, a factor four fused silica capillary column (phase type: VF-5 ms, length: 60 m, internal diameter: 0.25 mm, phase thickness: 1 μ m) and a Flame Ionization Detector (FID). The carrier gas is helium. GC/MS investigations were carried out with a VARIAN 450GC/320MS. The column used is identical to the one of the Varian 3900.

A Varian 4900 micro-GC was used to perform gas analysis. It contains four analysis blocks, all with a Thermal Conductivity Detector (TCD). The analysis blocks, the corresponding columns, the identified products and the carrier gas are summarized in Table 1.

Table 1 – Description of the 4 analysis blocks of the VARAIN 4900micro-GC

| Block number | Column type | Identified molecules | Carrier gas |
|--------------|--------------------------------|--|-------------|
| 1 | Al ₂ O ₃ | Short alkanes from C ₂ to C ₅ | He |
| 2 | COx | H ₂ , CO, CO ₂ , CH ₄ | Ar |
| 3 | CP sil-5CB | Short oxidized molecules (alcohols, aldehydes, ketones...) | He |
| 4 | M5A | N ₂ , O ₂ | He |

The consumption of the parent hydrocarbon is followed by GC. Standards are prepared by mixing a volume of n-dodecane and n-decane. Each sample or standard is injected at least twice and the chromatographic peak's area must have a difference below 2 %.

The evolution of the formed products is plotted in term of the surface of their chromatographic peaks.

As it can be seen in the mechanism of the autoxidation²³ (see above eq. 3), hydroperoxides are the key reaction intermediates. In order to quantify them, a method inspired from the ASTM D3703 is used.

Model molecule

n-dodecane (99+%) was purchased from Lancaster. This hydrocarbon was chosen because it is often present in significant quantity in operational hydrocarbon jet-fuels. N-dodecane is liquid at room temperature and colorless.

RESULTS

Characterization of n-dodecane

The GC analysis shows one main peak corresponding to the n-dodecane (Figure 3). Some very small peaks can be seen due to impurities (not shown).

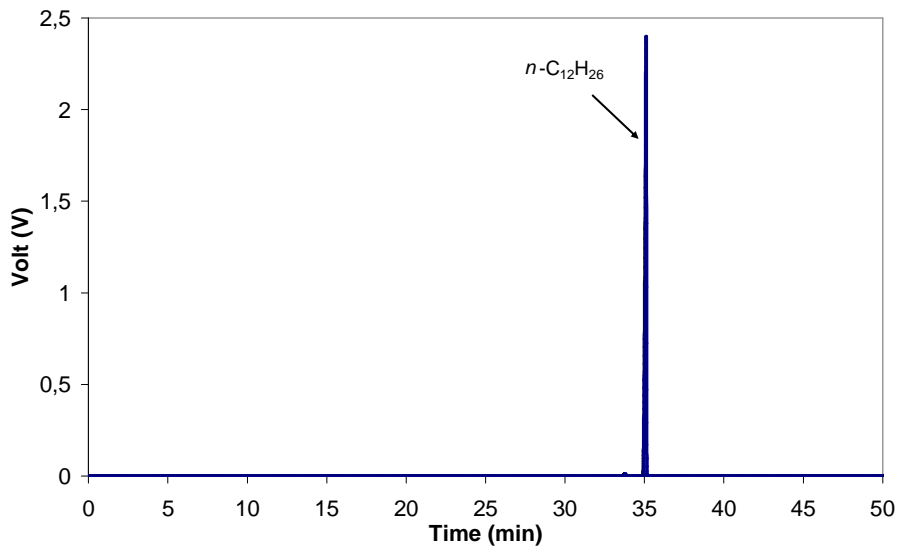


Figure 3 – GC chromatogram of the n-dodecane

Evolution of the pressure

The tests are performed at 150 °C with an initial O₂ pressure of 700 kPa. Maximal pressure, around 1010 kPa is obtained after 7 min as soon as 150 °C is reached. Temperature is maintained with oscillation of 0.5 °C. The first drop (zone 1) has a parabolic shape (Figure 4) and reached a pressure decrease of 64 % (measured value: 366 kPa) in 143 minutes, then the pressure bounces (zone 2). This brief pressure bounce, which represents around 80 kPa, is followed by a slow and continuous pressure reduction (zone 3). The induction period (10 % pressure drop) is obtained after 67 minutes of test.

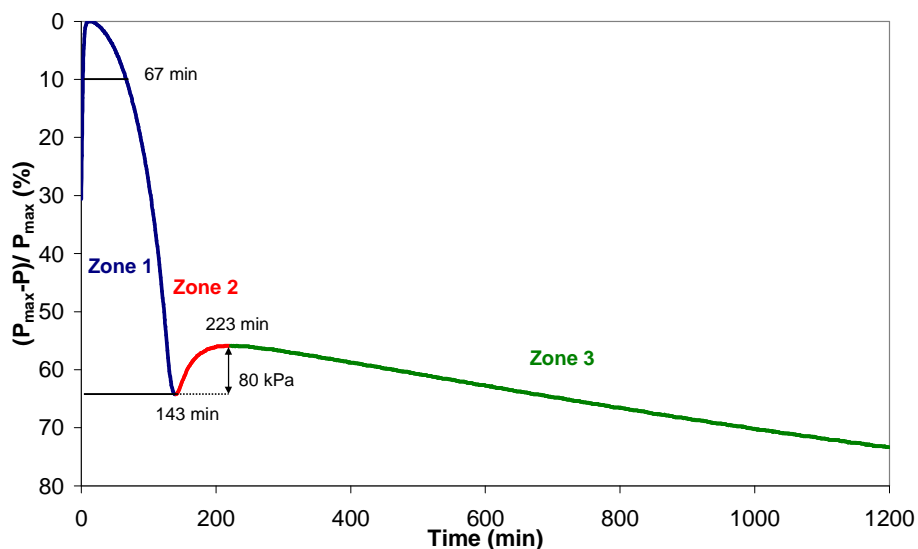


Figure 4 – Evolution of normalized pressure drop versus time

Table 2 – Correspondance between presure drop (%) and time (min) in the first pressure drop zone (zone 1)

| | | | | | | |
|-------------------|----|----|-----|-----|-----|-----|
| Pressure drop (%) | 10 | 20 | 30 | 40 | 50 | 60 |
| Time (min) | 67 | 89 | 103 | 113 | 123 | 131 |

Consumption of n-dodecane

Liquid analysis permits to measure n-dodecane consumption, after GC calibration. It shows that there is a parabolic consumption during the entire initial pressure drop zone, around 20% of n-dodecane is consumed at this point (Figure 5). At the moment of the pressure bounce, there seems to be a formation of n-dodecane, around 2-3%, and then its level stays stable up to the end of the test.

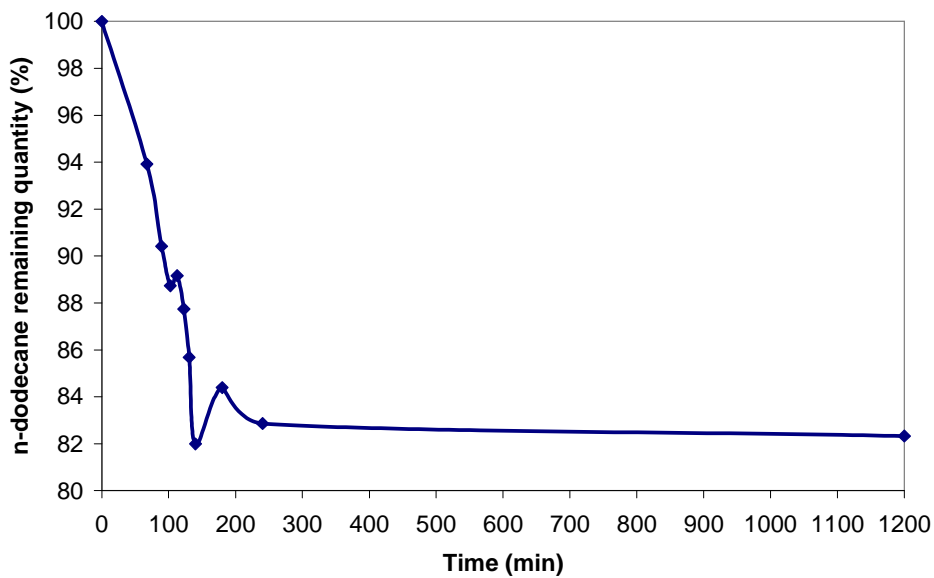


Figure 5 – Consumption of the n-dodecane during the test

Analysis of the gaseous products

During the first pressure drop zone (zone 1), gases analyses reveal an increasing presence of dihydrogen, carbon monoxide, carbon dioxide, ethylene and some oxidized products like acetaldehyde, acetone, alcohols (Figure 6a). At the same time, the dioxygen is consumed and the quantity of gas collected after each test drops. At the end of the first important pressure decreasing (143 min) the chamber pressure is 336 kPa, but when this chamber is cooled at 20 °C the internal pressure is around 20 kPa (700 kPa at the beginning of the test). Pressure increase at 150 °C is due to species which become liquid at ambient temperature. This fact combined with the diminution of its percentage by volume indicates that there is quite no more dioxygen at this point (Figure 6b).

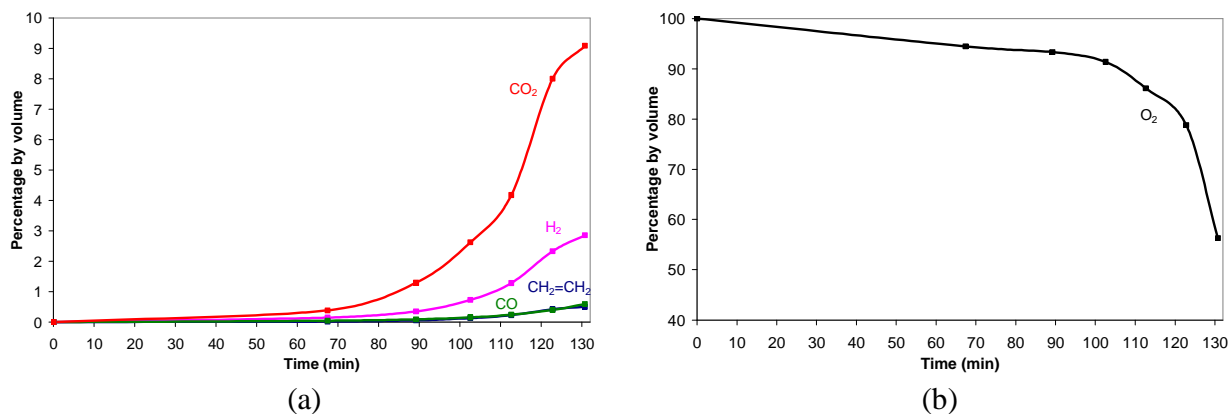


Figure 6 – Evolution of the percentage by volumique of the gaseous products (zone 1)

At the moment when the pressure bounce occurs, between 143 and 250 min, there is an important formation of carbon monoxide and dihydrogen. Alkanes like methane, ethane, propane and butane appear (Figure 7).

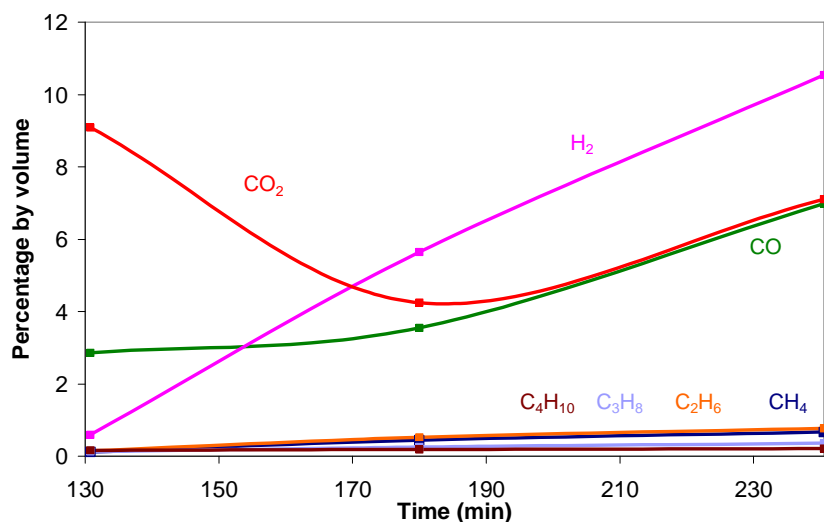


Figure 7 – Evolution of the percentage by volume of the gaseous products (zone 2)

After 250 min, all the gaseous products are progressively consumed. There is quite no more gas for the test which lasts 1200 min.

Analysis of the liquid products

The liquid phase stays colourless during the first quick drop (zone 1) and becomes pale yellow few time after the pressure bounce, some tiny water drops are detected until this point but disappear after.

Elemental analysis of the solution shows that at the end of the first quick drop (143 min), the liquid contains around 6% mass of oxygen.

Zone 1

Characterization of the liquid phase shows that dodecanones and dodecanols isomers are the main species formed. Dodecanones isomers and dodecanols have similar retention times. Some of these products are co-eluted (Figure 8).

Even if it is difficult to identify each compound, because they have nearby elution times, it seems that peaks' areas are similar for each one of these oxidized products. Dodecanal is not detected; we suppose that this compound is directly oxidized into dodecanoic acid, detected with a longer retention time.

Light compounds appear. They are mainly ketones, carboxylic acids. There are also aldehydes, alkanes, some alcohols, γ -butyrolactones with an alkyl substitute and esters. For all the products without exception, all chain's lengths are identified. Ketones, from acetone to undecanone, are only functionalised on position 2, there are very few alcohols. Nevertheless, methanol to dodecanol are characterized, all are primary alcohols. The formation of aldehydes can easily be explained as they are intermediates between alcohols and carboxylic acids. Few weak signals corresponding to γ -butyrolactones with an alkyl substitute and some esters, resulting to combination of acids and alcohols characterised below, are also identified.

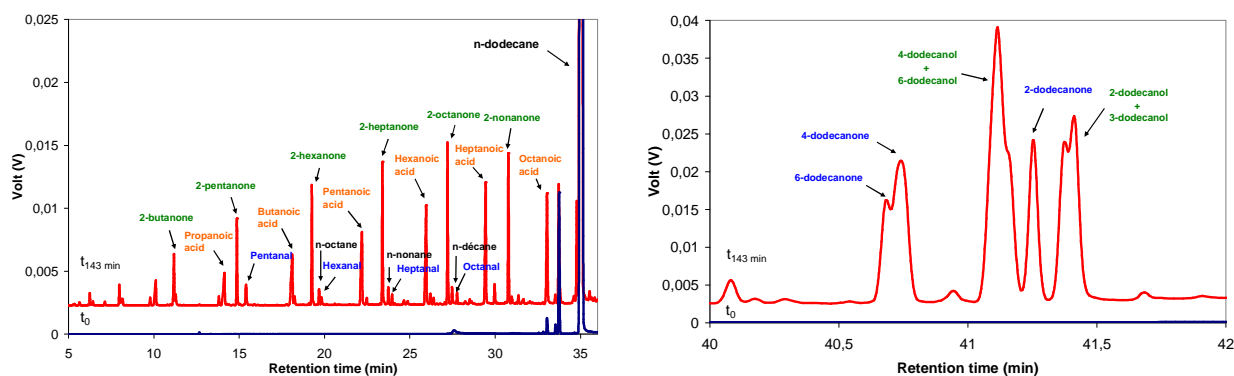


Figure 8 – Chromatograms of the initial *n*-dodecane (t_0) and the liquid phase after 143 minutes of test ($t_{143 \text{ min}}$)

Zone 2

The main differences with the previous product distribution are the formation of *n*-alkanes and the decrease of the quantities of aldehydes (Figure 9).

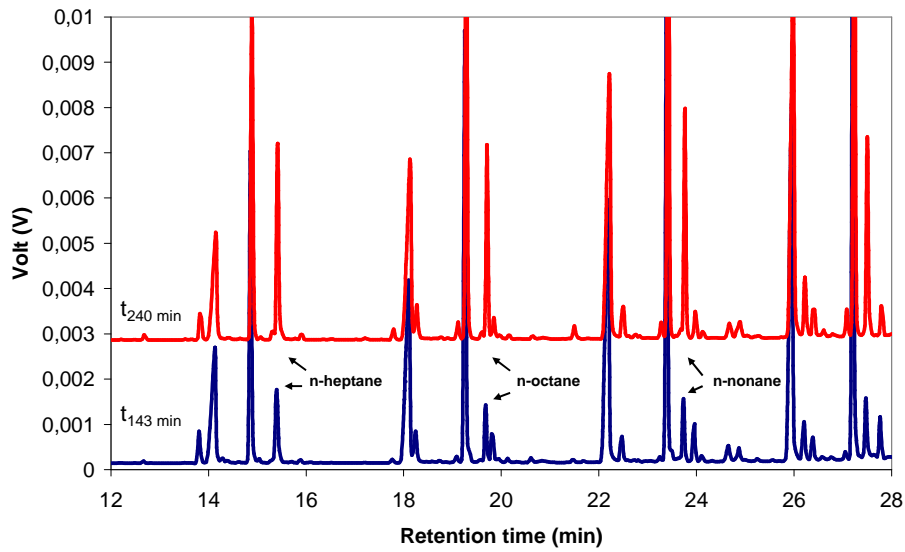


Figure 9 – Chromatograms of the liquid phases after 143 minutes ($t_{143 \text{ min}}$) and 240 minutes of test ($t_{240 \text{ min}}$)

Zone 3

The last period of time is characterized by:

- a consumption of the previously formed oxidized products: carboxylic acids, alcohols, ketones (Figure 10a);
- a formation of heavy products corresponding to heaviest compounds than dodecanoic acid (Figure 10b). Their identification is not possible due to the weakness of their signals, and to the random combination structures which make their spectrum difficult to interpret. Nevertheless, they seem to be products like esters and lactones.

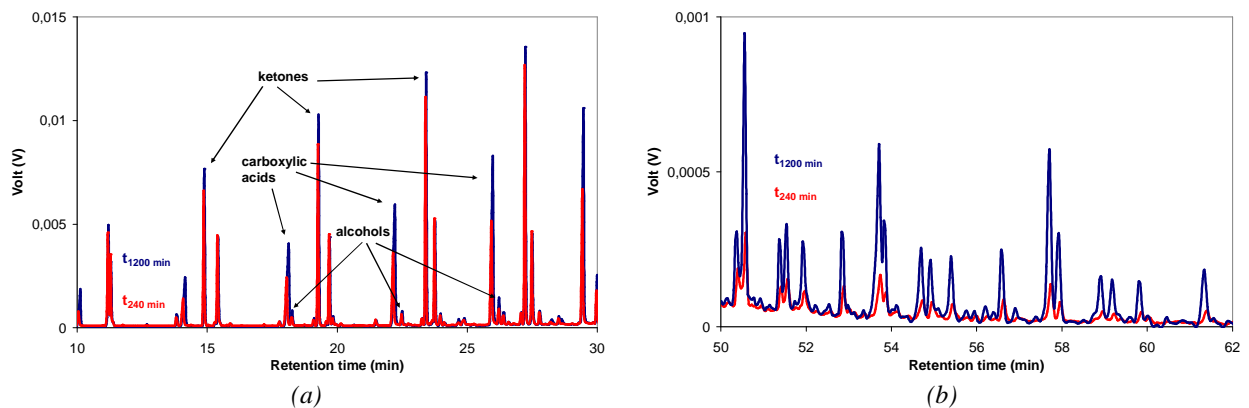


Figure 10 – Chromatograms of the liquid phases after 240 minutes ($t_{240 \text{ min}}$) and 1200 minutes of test ($t_{1200 \text{ min}}$)

Discussion

Behaviour of species is different depending on families. Thus, the quantities of acids, ketones or alcohols increase during the first period, whereas alkanes are revealed by some tiny signals without any progression. Alkanes are punctually produced at the moment when the pressure bounces but are neither produced nor consumed after this point.

For all the oxidized products (carboxylic acids, alcohols...), there is a diminution of their quantity during the entire second zone where a pressure decrease is observed (zone 3). At the same time, we notice appearance of numerous small peaks corresponding to heavy compounds.

During the zone 1, the n-dodecane is consumed and a lot of different products are obtained (alcohols, acid carboxylic, ketones). Oxidation reactions occur. To confirm this explanation, the evolution of the concentration of the peroxide compounds is measured (Figure 11). The peroxide quantity increases during all the first period, it explains why the hydrocarbon consumption has a parabolic shape, the more the amount of peroxide is, the faster the oxidation reactions are.

The decrease of the quantity of gas collected after the tests and the diminution of the concentration of dioxygen leads to conclude that there is no more oxygen at the end of the first pressure drop. The peroxide concentration falls dramatically and remains then nil. The peroxides are formed by reaction of a radical with a molecule of dioxygen. Their formation is impossible if there is no more dioxygen. Thus, the oxidation reactions stop.

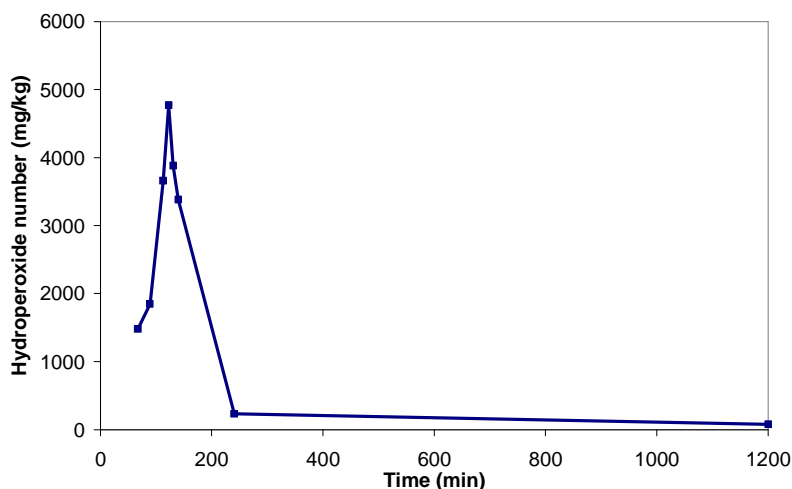


Figure 11 – Evolution of the concentration of peroxides

The second period (zone 2) is characterized by a decrease of the quantity of aldehydes and the production of alkanes, hydrogen and carbon monoxide. As the quantity of dioxygen decreases significantly and there are more and more hydrogen, carbon monoxide and dioxide, it is supposed that the reaction medium goes from oxidizing environment to reducing conditions. It is assumed that aldehyde decarbonylations occur.

The formation of heavy products observed during the last period (zone 3) could be explained by condensation reactions between the oxidized products formed during the zone 1. They seem to be esters, lactones...

CONCLUSION

The aim of this work was to evaluate the sensibility to oxidation of the n-dodecane using the Rapid Small Scale Oxidation Test (RSSOT) also named PetroOXY test. Normally, this test method is used to measure an induction period, under specified conditions, which is an indication of the oxidation stability. Nevertheless, besides giving an easy-to-understand result (time), the apparatus shows an interesting flexibility. It is possible to modify different parameters like temperature, pressure, duration of the test... In this study and in order to better understand the n-dodecane behaviour under oxidative conditions, the parameter modified was the test duration.

The tests were performed at 150 °C with an initial O₂ pressure of 700 kPa. A test can last up to 1200 minutes. The evolution of the pressure is monitored. A first pressure drop (zone 1) with a parabolic shape was observed, then the pressure bounces (zone 2). This brief pressure bounce is followed by a slow and continuous pressure diminution (zone 3). The induction period (10 % pressure drop) is obtained after 67 minutes of test.

During the zone 1, the n-dodecane is consumed, around 20%, and a lot of different products are obtained (alcohols, acid carboxylic, ketones). Oxidation reactions occur. At the end of the first pressure drop, there is no more oxygen. Oxidation reactions stop.

From then, new reactions appear. They are aldehyde decarbonylations and condensation reactions. Heavy products like esters and lactones are formed.

The results obtained with the PetroOXY are very interested. It is possible with this device to study the degradation of hydrocarbons. The products obtained during the first pressure drop were characteristic of oxidation reactions.

Other molecules will be studied alone or blended in order to identify their interactions between each others.

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