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# 1 Oxidative stability of hydrocarbons produced by pyrolysis of 2 polypropylene

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8

9 **Key words:** Fuel stability, Pyrolysis oils, Polypropylene, Antioxidant, PetroOxy, Waste  
10 management.

## 11 Abstract

12 The instability of liquid oils issued from the pyrolysis of plastics usually leads to the  
13 degradation and the deterioration of their different properties. In this study, the stability of oils  
14 produced from the pyrolysis with and without reflux of polypropylene (PP) was investigated in  
15 a standard test device called PetroOxy. This work compares the stability of PP liquid oils with  
16 kerosene throughout their induction period and hydroperoxide (ROOH) content, two well-  
17 known stability parameters. Moreover, experimental investigations of the impact of a  
18 stabilizer (BHT=butylated hydroxytoluene) on the same stability parameters were achieved.  
19 A titration method and GC-MS were used to quantify ROOHs and to identify the oxidized  
20 liquid compounds, respectively.

21 PetroOxy tests with BHT showed an enormous influence of BHT on the oxidation stability  
22 compared to all other oxidative tests. Adding 500 ppm of BHT multiplied the induction period  
23 by 5.9, 4.3, 10.7 and 6.7 for reflux liquid oils, no-reflux liquid oils mixed with kerosene, reflux  
24 liquid oils mixed with kerosene and pure kerosene respectively. The ROOH concentration  
25 was divided by up to 16.9 for reflux liquid oil when BHT was used.

26 Based on the results, it can be concluded that the liquid oils obtained by pyrolysis with reflux  
27 are less stable than without reflux, and both of them are less stable than kerosene used as  
28 reference model. But using kerosene as solvent mixed with liquid oils obtained by pyrolysis  
29 with and without reflux increases their oxidative stability. The use of BHT as an antioxidant  
30 contributes to make these oils compatible for use as fuels.

31

## 32 **1. Introduction**

33 The production and use of plastics have exploded over the last decades in the world. The  
34 amount of plastic solid wastes produced in Europe is estimated to increase four-fold by 2050  
35 [1] despite the continuous efforts to reduce, re-use, recycle and recover. Therefore, recycling  
36 methods are generally necessary for a long-term solution.

37 However, one of the promising alternatives to classic treatment of plastic waste recycling can  
38 be pyrolysis. It has received a lot of attention from the scientific community [2-7], not only  
39 because it is a rather eco-friendly technology but also because the process can produce oil  
40 considered as fuels and chemicals up to 80 wt.% at an easily achievable temperature of  
41 about 500 °C [8]. The converted products could be integrated in standard petrochemical or  
42 petroleum refining industry operation, and the recovered monomer can be used to produce  
43 new polymer, fuel and detergent.

44 Nevertheless, during the entire lifetime of oil issued from pyrolysis of plastics, from when it is  
45 first produced in the laboratory or the refinery, until the moment when it is transformed to new  
46 polymer or fuel, the problem of fuel instability exists. Since several contaminants are present  
47 in these oils, their presence can also affect the oil oxidative properties if they are not  
48 removed and their degradation can also cause engine failure and malfunction that affect the  
49 engine performance. Low stability can lead to increased maintenance problems and  
50 maintenance costs, equipment vulnerability, decreased reliability, and numerous other  
51 problems which may result in profit losses [9,10].

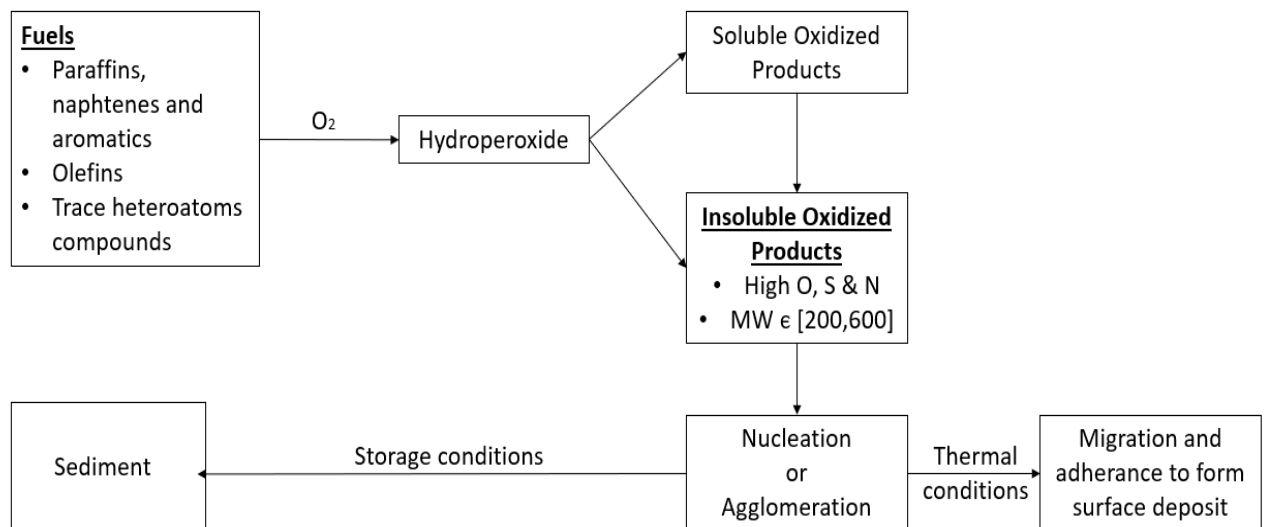
52 The term of liquid stability refers to the general resistance of a liquid to change its properties.  
53 Two types of stability exist in this context: “storage stability” which refers to the ability of a  
54 liquid to remain in storage over extended periods of time under ambient conditions and  
55 without significant deterioration; “thermal stability”, which refers to the ability of a liquid to  
56 resist to relatively high temperatures for short periods of time without significant deterioration.  
57 This change or degradation in liquids can be seen in a variety of ways, including the change  
58 of color (the change occurs as a deepening or darkening in color), change in physical  
59 properties (such as viscosity or density that tends to reduce the quality of an oil which then  
60 does not comply with the specifications and the standards anymore), change in chemical  
61 properties (such as formation of peroxides or hydroperoxides), and therefore change in  
62 combustion properties (such as autoxidation that leads to changes in burning efficiency,  
63 changes in the heat of combustion and ignition qualities of the liquid), change in compatibility  
64 with other types of hydrocarbon liquids and fuels, particle formation followed by sediment and  
65 deposits (which may solidify in tanks, fuel heaters, plug strainers, and cause pump  
66 breakdowns and plug lines), appearance of soluble and/or insoluble gum that may be  
67 troublesome in engine performance, and appearance of coke and clogging materials in  
68 engine filters [10].

69 Several researchers have reviewed, studied and investigated fuel stability since the  
70 beginning of the 19<sup>th</sup> century and they confirmed that the stability of fuels depends on factors  
71 such as the fuel hydrocarbon composition, source of crude oil, boiling range, type and  
72 severity of the refining process, and storage conditions [9–17]. They reported that the  
73 stability decreases in the increasing order of paraffins, naphtenes, aromatics, olefins, and  
74 diolefins. They also emphasize that there are some conditions that play a key role in fuel  
75 stability such as temperature, pressure, oxygen content, storage time, light intensity and  
76 wavelength, and type of storage. Low stability will then result from high temperature, high  
77 oxygen content, exposure to light, or extended storage time [10]. These effects justify the  
78 existence of regulation regarding these parameters for the use of oil as a fuel. For the

79 induction period, an international standard ASTM 7525 characterizes the stability of gasoline  
80 and Diesel fuels. This data is often linked to another standard regarding the total content of  
81 hydroperoxides in fuels ASTM D3703 [18].

82 The influence of the complexity of the recovery process of fuel or liquid oil issued from the  
83 pyrolysis of plastics is not negligible. There is not a single explanation for all the phenomena  
84 and processes associated with fuel degradation. However, most researchers agree that the  
85 instability of fuel is highly linked to the oxidation reactions in the liquid phase. Reactive  
86 organic compounds involving sulfur, nitrogen, and oxygen atoms in the feedstock are also  
87 responsible for the deterioration and instability. Catalytic effects during the pyrolysis  
88 experiment could also lead to degradation of the fuel when the storage time is not negligible.

89 An overall conceptual process of fuel instability is proposed in Fig.1 [19].



90

91 **Fig 1.** Overall conceptual process of fuel instability [19].

92

93 This article focuses on the study of the stability of liquid oil produced from the pyrolysis of  
94 polypropylene (PP), one of the most produced commodity plastics [20]. This choice of

95 polymer is highly supported by the achievement of our previous study which investigated the  
96 pyrolysis of PP in a detailed framework with and without reflux [21].

97 The principle of reflux is to separate the gas mixture in the reflux zone by selectively  
98 condensing the liquid and continuously removing heat. Reflux condensation works as  
99 described in our previous work [21]. Heavy components are continuously removed from the  
100 mixed vapor upstream, and the reflux liquid stream is enriched in these components. The  
101 principle of reflux is similar to conventional distillation. When the boiling point of the gas  
102 mixture is higher than the temperature of the reflux zone, the gas condenses and the liquid  
103 flows downward along the wall of the reactor condensation tube, while the range of light  
104 compounds with a boiling point lower than the temperature of the reflux zone remains in the  
105 gas phase and escapes from the reactor [21].

106 Previous pyrolysis results of PP [21] showed that the use of reflux condenser greatly affects  
107 the decomposition of PP. Propylene was the main gas detected in all experiments, followed  
108 by butadiene. GC-MS/FID characterization of the liquid product showed that when the reflux  
109 temperature was 125°C, the main compounds were the C<sub>9</sub> hydrocarbons, and their fraction  
110 was 71.2 wt% of the liquid oil. Characterization of the liquid product by FT-ICR MS showed  
111 that hydrocarbons formed by pyrolysis without reflux can reach up to 65 carbons, while  
112 hydrocarbons formed by reflux pyrolysis do not exceed 35 carbons and most of them are  
113 shorter than 20 carbons. Nevertheless, the Double Bond Equivalent slightly increases by  
114 using the reflux.

115 The stability tests on these oils were achieved with and without stabilizer in a  
116 microprocessor-controlled automatic test device called PetroOxy under pure oxygen, then  
117 the different liquids obtained were analyzed by GC-MS to identify the components of oxidized  
118 liquid oils and an iodometric titration was used to quantify hydroperoxides.

119 To the best of our knowledge, this article presents the first oxidative study of the stability of  
120 hydrocarbons produced by plastics recycling and more specifically by a thermochemical

121 method (pyrolysis of polypropylene).The main objective of this research is to test the stability  
122 of the liquid oils issued from the pyrolysis of polypropylene with and without reflux and to find  
123 a practical solution to avoid the degradation and the deterioration of the oils by keeping their  
124 different properties (chemical, physical, color...).

125

## 126 **2. Materials and methods**

### 127 **2.1. Materials**

128 Oil was produced from the pyrolysis of virgin PP [21] which was provided by Total  
129 Petrochemicals (PPH9020) in the form of pellets (2-3 mm) and with the following properties:  
130 melting point of 165°C and density of 0.905 g/cm<sup>3</sup>. Dichloromethane (DCM) with a purity  
131 above 99.8 mol% was used as solvent and was purchased from Fluka. 1-Decanol with a  
132 purity above 98 mol% was purchased from Sigma Aldrich and chosen as the internal  
133 standard. O<sub>2</sub> provided by Messer (purity above 99.995 mol%) was used to feed the  
134 PetroOxy. Butylated hydroxytoluene (BHT), also known as dibutylhydroxytoluene with a  
135 purity above 98 mol% was purchased from Sigma Aldrich and chosen as stabilizer  
136 (antioxidant). Liquid kerosene was purchased from Sigma Aldrich. It was used as fuel  
137 reference since the boiling points and the composition are similar to those of the pyrolysis oil  
138 and it has the following properties: kinematic viscosity of 1.43 cSt (at 40 °C), density of 0.758  
139 g/cm<sup>3</sup> (at 15.6°C), storage temperature of 2-30°C and a distillation range between 65°C and  
140 230°C. Since the oil without reflux was highly viscous, liquid oils from 1 g to 5 g were mixed  
141 with 25 mL of kerosene otherwise the oxidation tests could not be performed for liquid oil  
142 without reflux.

143 Triphenylphosphine used for iodometry (TPP reagent plus 99 mol%) and acetic acid (≥ 99.8  
144 mol%) were purchased from Sigma Aldrich. n-Decane used as the solvent of the titrant was  
145 purchased from ACROS Chemicals.

146

147

## 2.2. Experimental apparatus and procedure

148

### 2.2.1. PetroOxy

149

PetroOxy, a RSSOT (Rapid Small-Scale Oxidation Test) device developed over the last few

150

decades as an alternative to traditional oxidation stability testing methods, based on

151

reflectance and less accelerated oxidation (45°C) for long time period (ASTM D6468), was

152

used (Fig.2). It is a microprocessor-controlled automatic batch reactor for the rapid and

153

reliable measurement of the oxidation. The experimental apparatus has been described in

154

detail previously by Zabarnick et al [9,22,23]. It measures the induction period of fuels under

155

accelerated oxidation conditions with an uncertainty of 10%. A typical test is carried out with

156

a small sample volume of  $5 \pm 0.01$  mL which is introduced into a test chamber charged with

157

oxygen at  $700 \pm 3$  kPa at a starting temperature of 25°C. The measurement begins by

158

heating the test chamber to  $130 \pm 1$ °C and lasts until the endpoint is reached, which is

159

defined as a pressure drop of 10% below the maximum test pressure. The induction period is

160

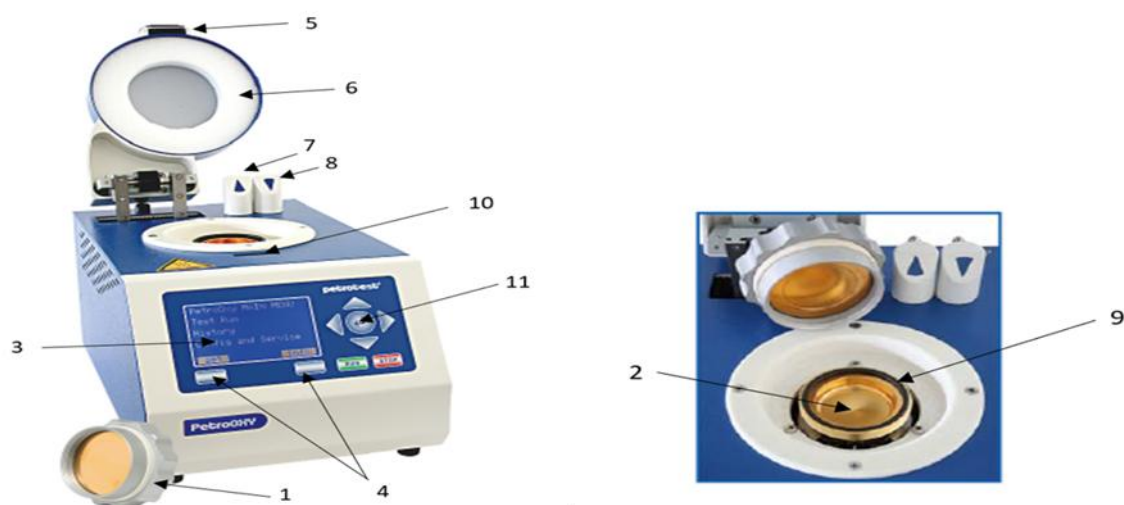
specified as the time from the start of the test chamber heating procedure to the endpoint

161

( $P_{\max} - 10\%$ ), which is usually measured in minutes and a good representative indicator of the

162

fuel stability.



163



164 **Fig 2.** Front and top view of the PetroOxy [44].

165 (1) Screw cap for closing the test chamber; (2) Test chamber; (3) Display; (4) Softkeys;  
166 (5) Latch to lock/ unlock the safety hood; (6) Insulated safety hood; (7) Oxygen outlet;  
167 (8) Oxygen inlet; (9) Oxygen inlet/outlet of the test chamber; (10) Locking latch for the  
168 safety hood; (11) Enter key and arrow keys

169

### 170 **2.2.2. Experimental parameters and conditions**

171 Each PetroOxy experiment was carried out at least three times and the result expressed in  
172 this study is the average with standard deviation. The experiment 1, which was also called «  
173 experiment without reflux », was performed with the oil obtained by pyrolysis with a reflux  
174 zone heated at the same external temperature than the feedstock zone [21]; this experiment  
175 consisted of 5 sub-experiments with different no-reflux (NR) liquid oil masses that have been  
176 mixed with 25 mL of kerosene to study its effect as an additive. These experiments were  
177 performed in order to analyze and study the effect of the mixture of different masses of the  
178 liquid oil and the kerosene on the induction time of the oxidation tests. It should be noticed  
179 that the no-reflux liquid oil is too viscous to be used pure in the PetroOxy device. The  
180 experiment 2 consisted of 2 g of liquid oil obtained by pyrolysis with reflux at 200 °C (AR\_2g)  
181 and mixed with 25 mL of kerosene. This experiment was performed in order to study and  
182 compare the influence of the reflux over the oxidation stability of the produced oil, and  
183 especially when the oil is used as an additive in the kerosene. The experiment 3 was  
184 performed with oil obtained by pyrolysis with a reflux temperature of 200°C in order to see  
185 the influence of the reflux on the yielded oil stability.

186 The experiment 4 which is also called “reference experiment” was performed using kerosene  
187 model to compare its stability with the oil produced from the pyrolysis of PP. The experiments  
188 5, 6, 7 and 8 were performed with BHT stabilizer to visualize its influence during the oxidation  
189 tests and to be compared with the experiments 1, 2, 3 and 4.

190 The BHT was chosen as a stabilizer because it is widely used to prevent free radical-  
 191 mediated oxidation in organic fluids (e.g. fuels, oils) and other materials, and it is recognized  
 192 as safe and noncarcinogenic. Moreover, BHT is proved to be the more effective antioxidant  
 193 during PetroOxy test compared to other antioxidants such as 2,4,6-tris isopropylbenzoic  
 194 hydrazide and benzoic hydrazide [24]. For reference, 500 ppm of BHT was used for all  
 195 PetroOxy tests with antioxidant.

196 **Table 1.** Description of the oxidation experimental tests.

Use of antioxidant	Name of the experiment		Description of the experiment
No BHT	Experiment 1	NR_1g	Different masses of oil without reflux and with kerosene
		NR_2g	
		NR_3g	
		NR_4g	
		NR_5g	
	Experiment 2	AR_2g	2 g of oil with reflux at 200°C and with kerosene
	Experiment 3	AR	Oil with reflux (200°C)
	Experiment 4	Kero	2 g of kerosene
With BHT	Experiment 5	NR_2g_BHT	2 g of oil without reflux and with kerosene
	Experiment 6	AR_2g_BHT	2 g of oil with reflux at 200°C and with kerosene
	Experiment 7	AR_BHT	Oil with reflux (200°C) with BHT
	Experiment 8	Kero_BHT	2 g of kerosene with BHT

197

198 **2.3. Analytical methods after PetroOxy tests**

199 **2.3.1. Analysis of liquid oil by GC-MS**

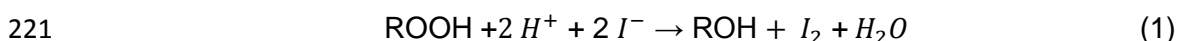
200 After oxidation tests, liquid oils were analyzed using a GC-MS and were dissolved in DCM.  
201 Other solvents were tested, but the extracted oil was soluble only in DCM [25]. The internal  
202 standard was 1-decanol because it is a linear carbon chain alcohol that cannot be produced  
203 by polyolefins and comes out halfway through the GC-MS analysis. Therefore, it could be  
204 easily distinguished in the chromatogram.

205 For the qualitative analysis, a GC-MS was used to identify unknown compounds in the liquid  
206 products. Shortly, the experimental conditions of the GC-MS method for the pyrolysis  
207 products were similar to our work for polypropylene (PP) [21]. An Agilent 7890A Gas  
208 Chromatography system coupled to an Agilent 5975C TAD (Triple-Axis Detector) Series  
209 GC/MSD (Mass Selective Detector) system was used. The solution was injected with a split  
210 ratio of 50 into an Agilent HP-5MS (diphenyl 5%, dimethylpolysiloxane 95%, non-polar, 30 m  
211 × 250 μm × 0.25 μm) column. The GC oven temperature was stabilised at 50 °C for 5 min,  
212 then increased with a 5 °C/min ramp to 320 °C and held at this temperature for 10 min.  
213 Different previous research studies provide also more details for this section [26,27].

214 **2.3.2. Analysis of the liquid oil by titration method**

215 The total hydroperoxide content of oxidized liquids was determined by iodometric titration,  
216 with triphenylphosphine in n-decane titrant, [28] and the titration endpoint was measured with  
217 a G10S Compact potentiometric titrator (Mettler Toledo).

218 The reaction between ROOHs and iodide is widely known since this reaction is the basis of  
219 the ASTM D3703 method [18]. The iodine liberated from the reaction of ROOHs with iodide  
220 ions was titrated with a standardized TPP solution thanks to the equations below.

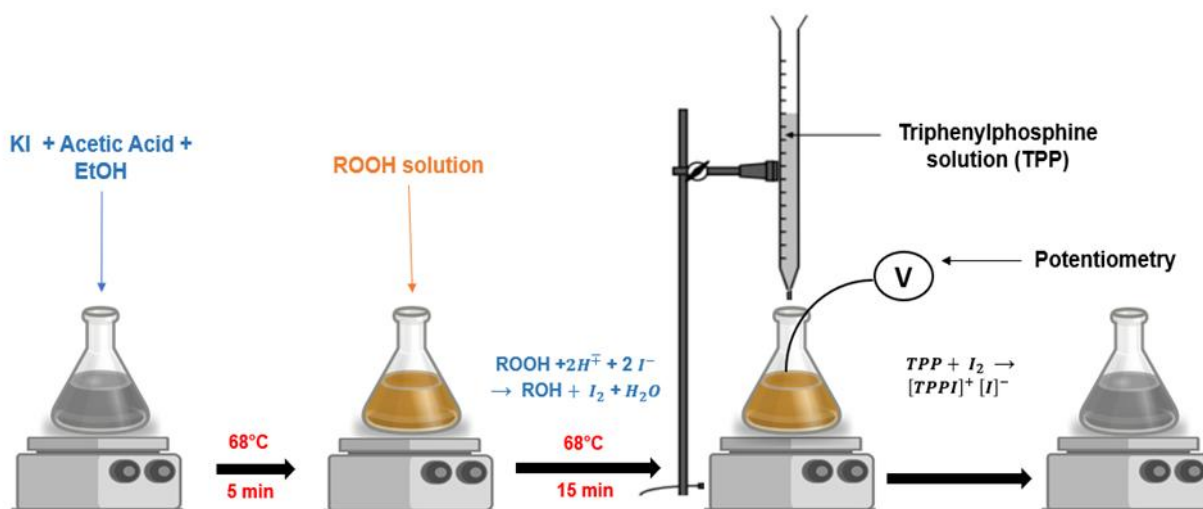


223

224 The titration method used in this study is a potentiometric method that is known to be more  
225 precise and more effective for the detection of ROOHs than other titration methods [28,29].  
226 The total ROOH concentration in the samples was then calculated. The uncertainty of the  
227 hydroperoxide concentration through this method is 9% of the final result, corresponding to  
228 95% of the confidence interval [29].

229 The experimental protocol observed in Fig.3 consisted in heating the solvent mixture  
230 including solid potassium iodide in the presence of acetic acid for 5 min at a temperature of  
231 68 °C to get a saturated solution of iodide ions. Then, without cooling, 1 mL of the sample  
232 containing the ROOHs was added and was kept at a temperature of 68°C for 15 min. At this  
233 stage, the reaction of ROOHs with iodide ions was complete and iodine was released. The  
234 amount of iodine released is equal to the stoichiometric amount of ROOHs present in the  
235 sample, and the iodine was titrated with TPP solution. It is predicted that a colorless charge  
236 transfer (CT) complex  $[TPPI]^+ [I]^-$  is formed from titration of the produced iodine with TPP as  
237 given below.

238 The proposed titration method had a clear endpoint, and the type of potentiometric endpoint  
239 detection was based on the visible changes of the potential of the solution by the complex  
240 formation.



241

242 **Fig.3.** Scheme of the iodometric method using triphenylphosphine solution and potentiometry  
243 [22].

244

### 245 **3. Results and discussion**

#### 246 **3.1. Oxidation stability tests results**

247 The kerosene and the oils issued from the pyrolysis of PP are composed of a wide range of  
248 hydrocarbons; during their oxidation tests, the reactions proceed via a free radical chain  
249 reaction mechanism [9,22,30], leading to the formation of a mixture of ROOHs and  
250 oxygenated hydrocarbon derivatives (alcohols, ketones, carboxylic acids...) via radical  
251 termination pathways [9,22,30].

252 In the first series of measurements shown in Table 2, the effect of the addition of different  
253 quantities of liquid oil, produced without reflux, to kerosene was investigated. Then an  
254 oxidative test of liquid oil produced with reflux was performed to compare the influence of the  
255 reflux on the stability of these oils. An additive concentration of 2.2 mmol/kg was chosen for  
256 BHT. This concentration corresponds to approximately 500 ppm. BHT was then added in a  
257 series of further tests to point out the relevance of the antioxidant effect.

258 **Table 2.** Results of oxidative analysis by PetroOxy tests and triphenylphosphine iodometric  
259 titration.

<b>Use of antioxidant</b>	<b>Name of the experiment</b>		<b>PetroOxy induction period (min)</b>	<b>Concentration of ROOHs (mmol/L)</b>
No BHT	Experiment 1	NR_1g	170.5 ± 6.7	87.8 ± 12.7
		NR_2g	157.9 ± 8.4	66.4 ± 9.8
		NR_3g	127.4 ± 5.2	67.4 ± 9.4
		NR_4g	106.9 ± 4.1	61.9 ± 8.7

		NR_5g	90.9 ± 3.9	56.8 ± 8.1
	Experiment 2	AR_2g	60.6 ± 2.7	90.5 ± 12.9
	Experiment 3	AR	12.2 ± 1.7	174.2 ± 18.5
	Experiment 4	Kero	150.5 ± 5.9	81.8 ± 11.8
With BHT	Experiment 5	NR_2g_BHT	681.6 ± 13.8	57.7 ± 7.3
	Experiment 6	AR_2g_BHT	650.8 ± 12.1	31.3 ± 3.4
	Experiment 7	AR_BHT	71.9 ± 2.2	10.3 ± 1.1
	Experiment 8	Kero_BHT	1011.2 ± 12.6	36.2 ± 5.5

260

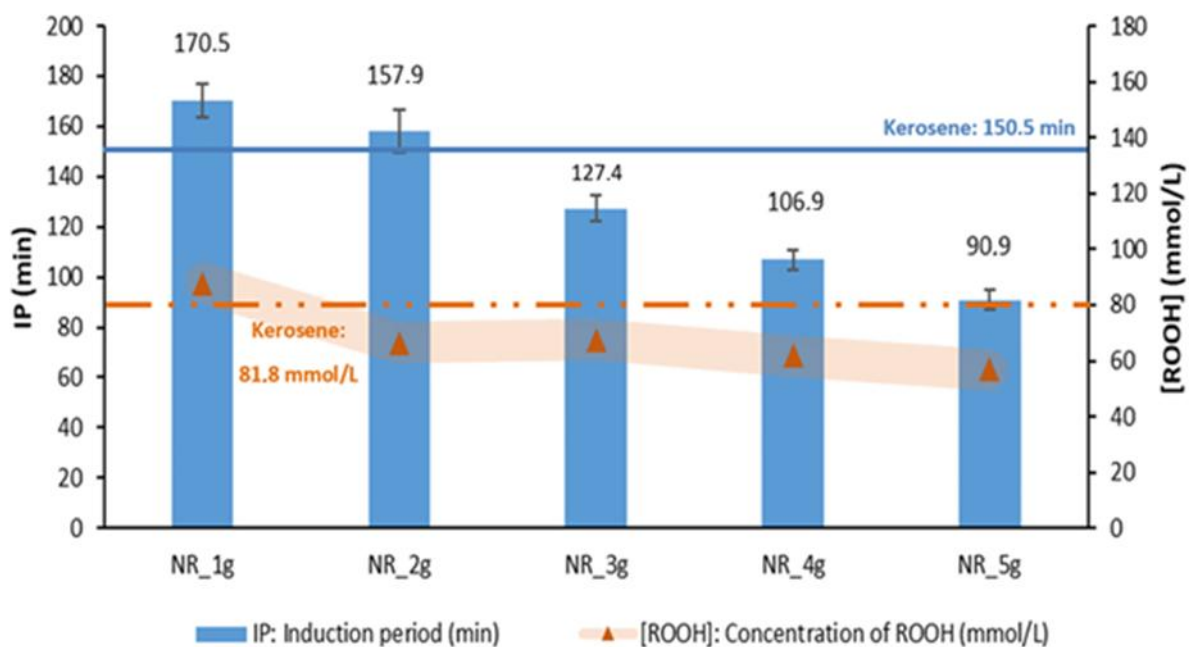
261 Under the investigated conditions and without BHT, the oil produced by pyrolysis with reflux  
 262 (AR) presented the lowest induction period of 12.2 min. Also, experiment 2, where 2 g of AR  
 263 is added to the kerosene, showed a low induction period of 60.6 min compared to the  
 264 experiment 1.2 (2 g of NR blended with the kerosene, IP of 157.9 min) and all the sub-  
 265 experiments of the experiment 1.

266 Based on these results, we can conclude that the liquid oils obtained by pyrolysis with reflux  
 267 are less stable than liquid oils obtained without reflux. Also, using kerosene as solvent mixed  
 268 with liquid oils obtained with and without reflux can help to stabilize these oils and increase  
 269 their oxidation stability.

270 Oils issued from plastics pyrolysis do not contain any antioxidants and therefore they exhibit  
 271 a poor stability towards oxidation. This effect can be explained through the composition of  
 272 the pyrolysis oils. Indeed, the plastic pyrolysis oils contain a large amount of linear  
 273 carbonated chains with an average number of  $C_{10}$ , and the literature shows that these  
 274 hydrocarbons are stable [30]. However, the presence of alkenes drastically changes the  
 275 oxidation chemistry of these oils. The reactions between alkenes and oxygen are easier than  
 276 those for linear alkanes, which leads more rapidly to the formation of unstable compounds  
 277 such as ketones and aldehydes [31]. So, when an oxidative stress occurs, the oil is less  
 278 stable than the kerosene since the kerosene composition is mainly alkanes which are known

279 to be rather stable products. Moreover, the pyrolysis oil obtained with reflux exhibits a higher  
 280 Double Bond Equivalent (DBE) than without reflux [21], which explains the lower stability of  
 281 oil obtained with reflux than that obtained without reflux. Indeed, without reflux, most  
 282 compounds have a DBE of 2, whereas with reflux, the DBE of most compounds is between 2  
 283 and 4, with a high proportion of DBE of 3 and 4. Note that the DBE of the  $C_cH_hO_o$  ions has  
 284 been calculated according to the general formula  $1 + c - h/2$ , and the molecular formulas  
 285 have been previously determined by GC-MS/FID and FT-ICR MS [21].

286 Fig.4 show the effect of the addition of NR oil on kerosene model on the induction period and  
 287 on the ROOH content of the aged fuel blend.



288  
 289 **Fig.4.** Influence of the mass of NR liquid oil added to kerosene on the PetroOxy induction  
 290 period and the concentration of ROOHs (error of [ROOH] represented as orange cloud).

291  
 292 The results in Fig.4 showed that mixing a low quantity of plastic pyrolysis oil can increase the  
 293 oxidation stability of the pure kerosene model since its IP increased from 150.5 min to 170.5  
 294 min and 157.9 min when we mixed it with 1 g and 2 g of NR liquid oils respectively. However,  
 295 the addition of high quantities of plastic pyrolysis oil lowered the induction period drastically;

296 the induction period decreased from 170.5 min to 90.9 min when the quantity of NR liquid oil  
297 added increased from 1 to 5 g. So, a low quantity has a positive effect on stability, which  
298 could be due to the production of stabilized allyl radicals from alkenes, but when the quantity  
299 increases the inhibition effect is lost, since alkenes are very sensitive to oxidation.

300 For comparative purposes, experiment 2 was performed (oil produced by pyrolysis with reflux  
301 added to kerosene) and results showed that its IP is the lowest compared to experiment 1  
302 (Fig.4) and experiment 4 (pure kerosene), although it is better than for pure oil produced with  
303 reflux. However, it will be difficult to conclude on the relative stability of the oils with and  
304 without reflux by comparing their mixture with kerosene [29].

305

## 306 **3.2. Characterization of the oxidized liquid oils**

### 307 **3.2.1. Analysis by GC-MS**

308 The PetroOxy oxidized liquid oils obtained from the pyrolysis of PP were dissolved in  
309 dichloromethane and semi-quantitatively analyzed to identify their chemical compositions.

310 The major compounds identified in some oxidized oils obtained by pyrolysis with and without  
311 reflux and antioxidant are presented in the supplementary material. All the oils identified  
312 consisted of alkanes, alkenes and small quantities of ketones. No hydroperoxides and  
313 carboxylic acids were detected in all the oils analyzed. Since ketones were detected in all  
314 oxidized liquid oils except kerosene and kerosene mixed with NR liquid oils, it can be  
315 confirmed that the oxidation process was rather advanced in the oxidized oils obtained by  
316 pyrolysis with reflux. Nevertheless, the GC-MS could not identify and quantify the  
317 hydroperoxides and oxidation compounds due to their fragility.

318 The major compounds included a range of hydrocarbons from C<sub>6</sub> to C<sub>10</sub> when the reflux was  
319 used, with and without BHT. For kerosene and all NR liquid oils (1, 2, 3, 4 and 5 g) mixed  
320 with kerosene, no significant change was noticed, and the major compounds included a  
321 range of hydrocarbons from C<sub>6</sub> to C<sub>14</sub>. Small amounts of ketones and alcohols such as



322 C<sub>8</sub>H<sub>18</sub>O, C<sub>9</sub>H<sub>20</sub>O, C<sub>10</sub>H<sub>16</sub>O and C<sub>10</sub>H<sub>18</sub>O were detected in the oxidized oil obtained by  
323 pyrolysis with reflux.

324 Regarding the abundance, it was observed that when the NR oil mass increased from 1 g to  
325 5 g, it drastically decreased between a retention time of 10 to 20 min and it slightly increased  
326 between 20 to 35 min, due to the increase of the concentration of hydrocarbons of high  
327 molecular weight [21].

328 To overcome some GC-MS limitation (identification of all the liquid oil compounds in the  
329 NIST bibliography and decomposition of ROOHs in the column), a titration method was  
330 necessary to determine the hydroperoxide (ROOH) concentration in all the oxidized oils.

### 331 **3.2.2. Analysis by titration method**

332 In order to control the laboratory and industrial production processes of ROOHs, it is required  
333 to know their concentration during the oxidation reactions and processes.

334 As presented in the experimental protocol in Fig.3 (section 2.3.2), iodometric titration  
335 methods for the quantification of ROOHs are simple, rapid, and need only simple laboratory  
336 equipment. TPP method was water-free and was suitable for organic ROOH quantification.  
337 Iodine released from the reaction of iodide ions with ROOHs was completely soluble in an  
338 organic media and formed a charge transfer complex with TPP in an organic solvent [32].

339 Results of ROOH quantification with TPP iodometric methods using the acetic acid and EtOH  
340 as solvent and KI as an iodine source are given in Table 2. The interpretation of ROOH  
341 concentration should be done cautiously, since a low ROOH concentration could indicate,  
342 either a rather stable oil or an oil in an advanced state of oxidation. Indeed, first ROOHs  
343 accumulate and then decompose to produce other oxidized compounds. ROOHs produced  
344 from PP pyrolysis oil are particularly unstable since they contain double bonds. So, it could  
345 be difficult to compare the concentration of ROOHs produced from kerosene (mostly  
346 alkanes), from oil obtained by pyrolysis without reflux, and from oil obtained by pyrolysis with  
347 reflux (higher DBE).

348 Nevertheless, some comments can be proposed. Liquid oil obtained by pyrolysis with reflux  
349 (AR) presented the lowest oxidation stability and it showed the highest concentration of  
350 ROOHs at the end of the induction period with 174.2 mmol/L. Also, experiment 2 showed  
351 that the second highest hydroperoxyde concentration with 90.5 mmol/L compared to the  
352 experiment 4 and all the sub-experiments of the experiment 1. Based on these results, we  
353 can confirm again that the liquid oils obtained with reflux are less stable than liquid oils  
354 without reflux and kerosene model.

355 Moreover, the results of liquid oils obtained by pyrolysis without reflux showed that mixing  
356 high quantities of plastic pyrolysis liquid oil lowered the concentration of ROOHs; it  
357 decreased from 87.8 mmol/L to 56.8 mmol/min when the quantity of NR liquid oil added  
358 increased from 1 to 5 g. Regarding the oxidative test with only kerosene (experiment 4-Kero),  
359 it presented a concentration of 81.8 mmol/L. The oxidation stability got impoverished by  
360 unsaturated and polyunsaturated compounds present in NR liquid oil [22]. These  
361 compounds tend to initiate a classical free radical chain reaction mechanism (autoxidation)  
362 [35].

363

### 364 **3.3. Antioxidant effect of BHT in liquid oils**

365 The antioxidant effect of BHT depends on the chemical structure of the hydrocarbon oils.  
366 During the oxidation of hydrocarbons in the liquid phase, a specific mechanism of formation  
367 of hydroperoxides is involved. Le et al. [36] summarized it in Fig.5. The H-atom abstractions  
368 by peroxy radical ( $\text{ROO}\cdot$ ) and alkoxy radical ( $\text{RO}\cdot$ ) represent the main consumption channels  
369 of an alkane (RH) in order to yield the main alkyl radical  $\text{R}\cdot$  that reacts with dissolved  $\text{O}_2$  and  
370 produces the corresponding peroxy radical  $\text{ROO}\cdot$ .

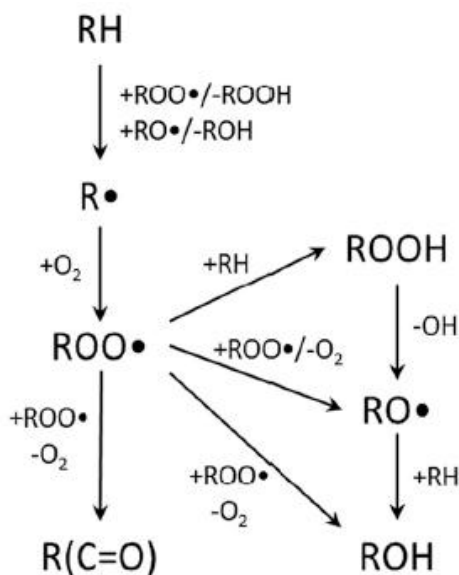
371 Then, the peroxy radical  $\text{ROO}\cdot$  produces the peroxide  $\text{ROOH}$  via H-atom abstractions from  
372 the reactant in a main consumption reaction and the remaining non-consumed  $\text{ROO}\cdot$   
373 involves self-reactions ( $\text{ROO}\cdot + \text{ROO}\cdot$ ) to produce a ketone (or aldehyde) ( $\text{R}(\text{C}=\text{O})$ ) in a

374 termination step by the Russell mechanism and an alcohol (ROH) or two alkoxy radical RO•  
375 and O<sub>2</sub> [36–38].

376 In alkanes, ROOHs are entirely decomposed into a hydroxyl radical OH• and an alkoxy  
377 radical RO• that subsequently produce an alcohol ROH by H-atom abstraction from the  
378 reactant RH by the alkoxy radical RO•. After that, ROH is oxidized into ketone (or aldehyde)  
379 R(C=O) by some successive reactions, which follow a similar scheme to that of the alkanes.

380 Yehye et al. [36] and Jia et al. [40] had described deeply the influence of the BHT in the  
381 thermal oxidation stability of fuels and they confirmed that BHT interrupts the chain  
382 propagation of the fuel auto-oxidation by reacting with peroxy radicals via H-atom abstraction  
383 reactions by the hydrogen atom of phenolic group. These reactions are favored as the  
384 radicals produced from hindered phenols are relatively stable thanks to the electron  
385 delocalization due to the resonance effect.

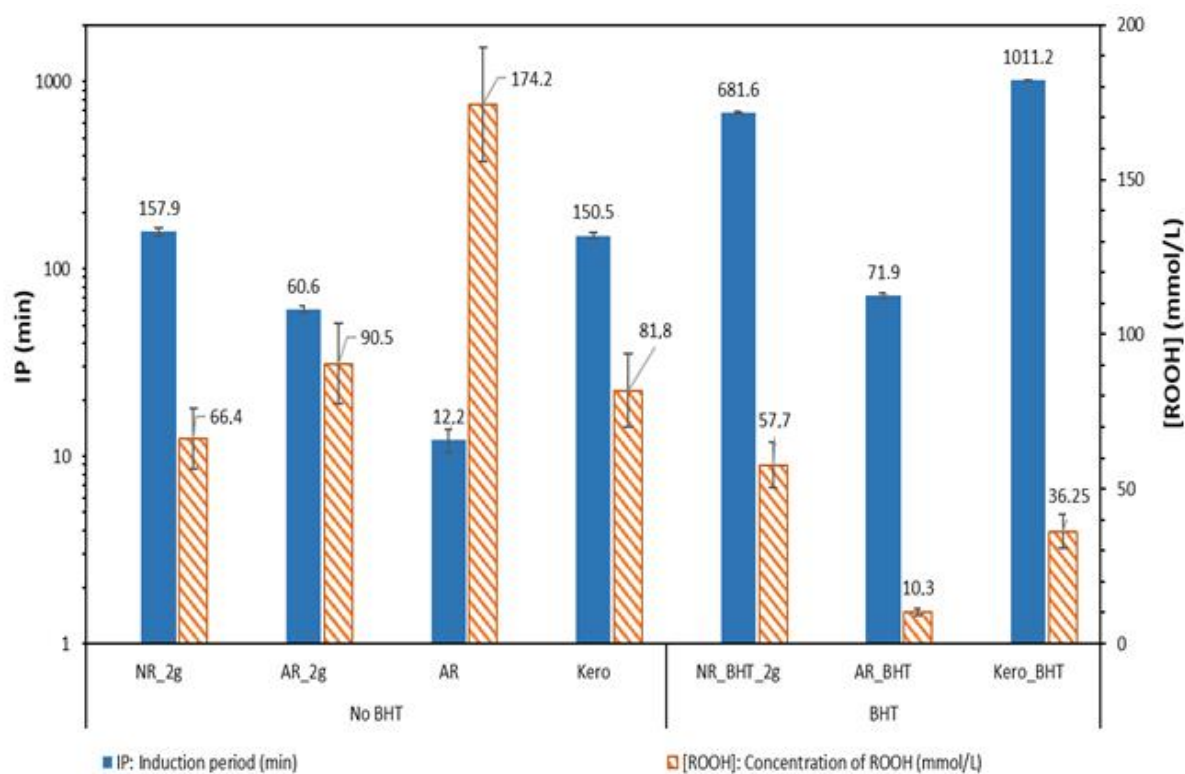
386 These reactions are in competition with H-atom abstractions from parent fuel and then  
387 slowdown the liquid-phase reactivity.



388  
389 **Fig. 5.** Simplified reaction pathway of an alkane RH in the liquid phase.  
390 (R• is an alkyl radical, ROO• a peroxy radical, RO• an alkoxy radical, ROOH a hydroperoxide,  
391 ROH an alcohol, and R(C=O) an aldehyde or a ketone) [36].

392

393 The PetroOxy tests with BHT showed (Fig.6) a huge stability compared to all other oxidative  
394 tests. However, BHT increased the induction period of 59.7 min (ratio of 5.9) for liquid oils  
395 with reflux, 523.7 min (ratio of 4.3) for liquid oils without reflux mixed with kerosene (NR\_2g),  
396 590.2 min (ratio of 10.7) for liquid oils with reflux mixed with kerosene (AR\_2g) and 860.7  
397 min (ratio of 6.7) for kerosene. Regarding the concentration of ROOHs, it was divided by  
398 16.9 (from 174.2 to 10.3 mmol/L), 2.6 (from 81.8 to 36.2 mmol/L), 2.9 (from 90.5 to 31.3  
399 mmol/L) and 1.2 (from 67.4 to 57.7) for liquid oil with reflux (AR), kerosene (Kero), liquid oil  
400 with reflux mixed with kerosene (AR\_2g) and no-reflux liquid oil mixed with kerosene  
401 (NR\_2g) respectively when BHT was used.



402

403 **Fig.6.** Influence of BHT on the PetroOxy induction period and the concentration of ROOHs  
404 on NR, AR and kerosene liquid oils

405

406 The overall analysis of the results showed significant influence in the stability towards  
407 oxidation when BHT was used as an antioxidant. A number of studies showed that oxidation  
408 conditions such as temperature and oxygen partial pressure have a substantial impact on the  
409 efficiency of antioxidants but whatever the chosen antioxidant, the stability towards oxidation  
410 is always highly improved [24,41–43]. Nevertheless, adding BHT to pyrolysis oils mixed with  
411 kerosene is less efficient than adding BHT to pure kerosene, although the stability of pure  
412 kerosene is about the same or worse than that of kerosene mixed with small amounts of  
413 pyrolysis oil obtained without reflux. Developing the detailed mechanism of oxidation in both  
414 cases could help to understand these phenomena.

415 Based on the results it can be confirmed that the addition of a highly effective BHT  
416 antioxidant is then strongly recommended to increase long-term stability.

#### 417 **4. Conclusion**

418 The stability of hydrocarbons produced by pyrolysis of PP was investigated in a  
419 microprocessor-controlled automatic test device called PetroOxy in an oxygenated  
420 environment. This study provides a highlight on the induction period under accelerated  
421 oxidation conditions and a quantitative analysis of the concentration of ROOH compounds in  
422 all oxidized oils. It has been shown that PP pyrolysis oils are less stable than kerosene, due  
423 to the double-bonds they contain, especially for the oils obtained by PP pyrolysis with reflux.  
424 Mixing small amounts of oils with kerosene increases their stability towards oxidation. This  
425 might be due to the production of stabilized allyl radicals which lead to an inhibition effect, but  
426 the inhibition effect is lost when the amounts of alkenes present in the mixture increase,  
427 since alkenes are very sensitive to oxidation. Further research is needed to confirm this  
428 hypothesis. Moreover, the use of BHT increased the induction period from 12.2 to 174.2 min  
429 for oils obtained by pyrolysis with reflux (AR), from 157.9 to 681.6 min for oils obtained  
430 without reflux mixed with kerosene (NR\_2g), from 60.6 to 650.8 min for oils obtained with  
431 reflux mixed with kerosene (AR\_2g) and from 150.5 to 1011.2 min for pure kerosene (Kero).

432 Regarding the concentration of ROOHs, it decreased from 174.2 to 10.3 mmol/L, from 81.8  
433 to 36.2 mmol/L, from 90.5 to 31.3 mmol/L and from 67.4 to 57.7 for oil produced with reflux  
434 (AR), kerosene (Kero), liquid oil with reflux mixed with kerosene (AR\_2g) and no-reflux liquid  
435 oil mixed with kerosene (NR\_2g) respectively, when BHT was used, although it could be  
436 difficult to precisely interpret these results, especially between different types of oil, since a  
437 low ROOH concentration could indicate, either a rather stable oil or an oil in an advanced  
438 state of oxidation.

439 Previous experiments had demonstrated that the reflux allows to narrow the molecular  
440 weight distribution range of the liquid obtained by PP pyrolysis, yielding interesting molecules  
441 corresponding to the naphtha cuts. The present results showed that combining BHT  
442 antioxidants to the liquid oils obtained by PP reflux pyrolysis increases a lot their stability,  
443 although they remain much less stable than kerosene, for instance. Further research may be  
444 useful to improve the stability of these liquid oils. Nevertheless, adding BHT contributes to  
445 preserve the narrow molecular weight distribution of the liquid oils obtained by reflux  
446 pyrolysis, increases their long-term stability, and contributes to make them compatible for  
447 use as fuels.

448

## 449 **Declaration of Competing Interest**

450 The authors declare that they have no known competing financial interests or personal  
451 relationships that could have appeared to influence the work reported in this paper.

452

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