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1 **An Experimental and Detailed Kinetic Modeling of the Thermal Oxidation Stability of *n*-decane**  
2 **as a Jet Fuel Surrogate Component**

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10

11

12 **Abstract**

13 Thermal oxidation stability of liquid jet fuels remains a significant scientific challenge in the development  
14 of modern aviation. This study aims at experimentally and numerically investigating the autoxidation of  
15 *n*-decane, which is used as a component of jet fuel surrogates in the literature. Induction periods (IP) of  
16 *n*-decane were measured in a PetroOxy device under 7 bar of oxygen and cell temperatures varying from  
17 403 to 418 K. IPs give a quantitative measure of the oxidation stability of a fuel. In addition to IPs  
18 measurements, the total hydroperoxides content at the end of the IP test was quantified using two  
19 iodometric titration methods: colorimetry and potentiometry. In order to simulate the oxidation of the  
20 homogeneous liquid phase as a batch reactor, we developed a physical model based on the so-called  
21 gamma-phi thermodynamic approach to calculate the compositions of liquid- and gas-phases at the set  
22 temperatures and pressures. Based on a state-of-the-art method to capture solvent effects, a detailed  
23 kinetic model for the *n*-decane autoxidation was developed. The simulations are consistent with  
24 experimental data from this study (IP and hydroperoxides concentration profiles) and from the  
25 literature. The proposed model is validated to simulate the thermal oxidation stability of liquid *n*-decane,  
26 for conversions up to 15%. Kinetic analyzes highlight the central role played by hydroperoxides  
27 decomposition and the self-termination of peroxy decyl (ROO·) radicals in the autoxidation of *n*-decane.

28

## 29 1. Introduction

30 The rapid growth of worldwide aviation requires intense research efforts to optimize aircraft engines to  
31 achieve better energy efficiency and emission reductions [1]. Aviation liquid fuels, also called jet fuels,  
32 are used as the main energy carrier in aircraft engines but also have a role in the cooling system, which is  
33 specific to them [2]. Indeed, if their primary role is to provide energy through the combustion in jet  
34 engines, their second role is to act as a coolant, which ensures the normal operation of several parts  
35 including, the hydraulic and the lubrication systems, the combustor and the airframe and environmental  
36 control system [2]. Due to their use as a heat sink, jet fuels undergo thermal stresses [3]. For example, in  
37 commercial aircrafts, it can be exposed to temperature of 393 to 433 K for several seconds under cruise  
38 conditions [4-6]. During their logistic operations, from their storage to the jet engine injectors, jet fuels  
39 are in contact with air under various pressure and temperature conditions. Dissolved oxygen from air in  
40 the fuel promotes the liquid phase oxidation of the fuel, also called autoxidation. This phenomenon is  
41 the source of major issues in aircrafts as it forms undesired products including gums and deposits.  
42 Nowadays, the formulation of jet fuels, including additives, allows them to remain stable throughout  
43 their use as coolant in commercial aircrafts, but to temperatures up to 433 K [4]. In order to increase the  
44 efficiency of future turbine engines and design supersonic aircrafts operating at higher speed it is  
45 necessary to improve the thermal oxidation stability of jet fuel so that it can be stable up to  
46 temperatures as high as  $\approx 573$  K [7]. Comprehensive studies on jet fuel autoxidation are therefore  
47 essential to understand, predict and optimize their thermal oxidation stability.

48 Jet fuels are blends of hundreds of hydrocarbons. To facilitate jet fuel studies, including numerical and  
49 experimental works, researchers proposed several jet fuel surrogates [8]. A jet fuel surrogate is a mixture  
50 of pure compounds combined to mimic physical and ignition characteristics of real jet fuels. *n*-decane is  
51 commonly used as a mono-component surrogate or included in multi-component surrogate for jet fuels  
52 [9-12]. Thus, the development of a kinetic model of autoxidation of *n*-decane, validated against  
53 experiments, is a first step towards a jet fuel surrogate kinetic model. Kinetic modelling of *n*-decane

54 autoxidation is also of great interest to understand lubricant degradation [13]. This remains a challenge  
55 in the literature as liquid phase detailed kinetic models are at their early stages of developments  
56 compared to gas-phase models [14, 15]. It is commonly accepted in the community that both gas-phase  
57 oxidation and liquid-phase oxidation of hydrocarbons undergo similar radical mechanisms [15]. While  
58 the gas-phase oxidation mechanism of large alkanes such as *n*-decane is well understood [16], its liquid-  
59 phase oxidation mechanism remains to be fully understood [2].

60 Several studies on *n*-decane autoxidation have been performed in the literature. Cullis et al. [17]  
61 performed *n*-decane liquid and gas phases oxidation experiments in the same temperature region. They  
62 found some notable differences in the mechanisms in the two phases: absence of C<sub>10</sub> O-heterocycles and  
63 dihydroperoxides in the liquid phase and small amounts of lower mass oxygenated compounds,  
64 compared to gas phase experiments. Experiments on the slow combustion of *n*-decane were performed  
65 in a closed reactor between 445 and 473 K and liquid phase oxidation was conducted in a semi-open  
66 reactor in which a flux of oxygen was passed into an isothermal batch reactor at 423 K containing *n*-  
67 decane. Principal products of *n*-decane autoxidation were determined as decane monohydroperoxides,  
68 C<sub>10</sub> carbonyls and alcohols.

69 Goosen and Morgan [18] studied the products obtained during the autoxidation of *n*-decane  
70 and *n*-nonane, at significant conversion. Oxygen was passed into boiling *n*-decane, in a reflux, at about  
71 451 K. In the investigated conditions, these authors described the autoxidation of *n*-decane as  
72 proceeding in three stages: the first stage involves the formation of alkyl hydroperoxides, the second  
73 stage occurs when the hydroperoxide decomposes into alcohols and ketones, and the last stage  
74 corresponds to the oxidation of the latter products in competition with the alkanes, yielding  $\gamma$ -lactones  
75 and carboxylic compounds.

76 Pfaendtner and Broadbelt [13, 19] used automated mechanism generation to study the  
77 autoxidation of *n*-decane to understand lubricant oil degradation. They proposed condensed phase

78 adapted rate rules and kinetic parameters, based on structure reactivity correlations, and were able to  
79 simulate the autoxidation of *n*-decane and *n*-octane and validated the results against experimental data  
80 of the literature. This pioneering work was the first to use detailed chemical kinetic modeling to simulate  
81 the liquid phase oxidation of alkanes. However, it is entirely based on gas-phase thermochemical data  
82 and most of the kinetic data adopted are based on gas-phase estimations.

83           Recently, Chatelain et al. [20] investigated the autoxidation kinetic of several *n*-alkanes including  
84 *n*-decane by conducting Induction Periods (IP) measurements at three different temperatures (393, 413,  
85 and 433 K) in a PetroOxy device. Liquid-phase mechanisms of these alkanes were generated thanks to an  
86 automated mechanism generator, RMG [21], and were capable of predicting IP within a factor of 3 at  
87 high temperature ( $T > 413$  K). Note that only the autoxidation kinetic models of *n*-octane and *n*-  
88 dodecane are available from this study.

89           Auzani et al.[22] assessed the effect of ethanol on the IPs of a real kerosene and three  
90 surrogates. They proposed a Python code to simulate the pressure drop in the PetroOxy measurements  
91 that solves the ordinary differential equations of a Perfectly Stirred Reactor for each species and an  
92 equation for the consumption of the number of moles of O<sub>2</sub> in the gas phase. RMG was used to generate  
93 detailed reaction mechanisms for *n*-decane, ethanol and *n*-dodecane and simulate some of their  
94 experimental results. Upon significant changes in the kinetic data of the R· + O<sub>2</sub> reactions, they were able  
95 to qualitatively simulate their experimental results. The same group also proposed a skeletal kinetic  
96 mechanism for liquid hydrocarbons autoxidation to simulate experiments on a fuel composed of five  
97 normal alkanes in a near-isothermal reactor and in a PetroOxy device [23].

98 The motivations of our study are: (1) to provide additional experimental data for the liquid-phase  
99 reactivity of *n*-decane; (2) to define a rigorous framework to model IP data measured in PetroOxy  
100 devices; (3) to develop a validated kinetic model of *n*-decane autoxidation and (4) to refine the  
101 understanding of *n*-decane autoxidation. To reach these goals, IPs of *n*-decane were measured in a

102 PetroOxy and were coupled with an experimental quantification of the total hydroperoxides (ROOH)  
103 content. These data allow us to define a rigorous criterion for the simulation of IPs which is based on the  
104 total amount of ROOH in the aged fuel. The kinetic model of *n*-decane was developed using our reaction  
105 mechanism generator (EXGAS [24, 25]) which has been adapted to automatically capture solvent effects  
106 on the thermochemical data based on corrections computed with an Equation of State (EoS) [26, 27].  
107 This approach has been validated in the case of the liquid-phase oxidation of *n*-butane [26]. The main  
108 reaction pathways of *n*-decane liquid-phase oxidation are presented and discussed in this paper.

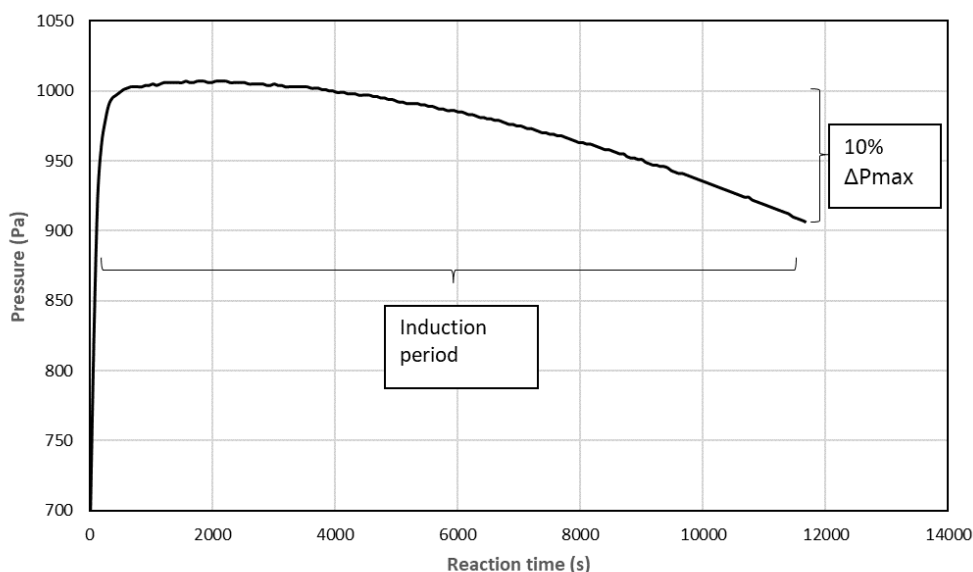
109 This work will contribute to improve the experimental kinetic studies performed in PetroOxy on jet fuels  
110 because a method to determine the liquid-vapor equilibrium in the test cell is proposed for the first time.  
111 A new approach to determine the IP from homogeneous liquid phase simulations is also proposed, based  
112 on ROOH quantification. Finally, a new detailed kinetic model is proposed, based on the calculation of  
113 hundreds of new thermochemical data adapted to *n*-decane solvent and new reaction rate rules. This  
114 model is systematically validated against all available literature data. This model will constitute a building  
115 block for the construction of detailed multi-component jet fuel surrogate models which are necessary to  
116 understand the oxidation stability of jet fuels and to allow the optimization and formulation of future  
117 aviation energy carriers.

## 118 **2. Experimental methods**

### 119 **2.1. PetroOxy description**

120 Experiments of *n*-decane autoxidation were conducted in a PetroOxy, a device that has been widely used  
121 for fuel stability studies [28-31] and employed as a reference instrument in ASTM D7525, ASTM D7545  
122 and EN 16091 tests [32]. A PetroOxy apparatus operates similarly as a closed batch reactor: it contains a  
123 gold-plated test cell, whose volume is 25 mL. The experiment begins with the introduction of 5 ml of fuel  
124 into the cell, which is then pressurized under 7 bar of pure oxygen. High-purity *n*-decane ( $\geq 99\%$ ) from  
125 Sigma-Aldrich were employed in this work. The reactor is then heated quickly (about 3 minutes) from the

126 ambient to the desired temperature and kept constant until the end of the test. The temperature in  
127 these tests ranged from 403 to 418 K. The gas-phase pressure is followed during each experiment and, as  
128 the autoxidation of *n*-decane consumes oxygen, a decrease of pressure is observed. The induction period  
129 (IP) is defined as the time corresponding to a 10% pressure drop from the maximum pressure reached at  
130 the beginning of the test (as illustrated in Figure 1).



131

132 *Figure 1. Evolution of measured pressure during a typical PetroOxy test and definition of the induction period (IP) Fuel: n-decane,*  
133 *test temperature: 413 K, initial O<sub>2</sub> pressure: 7 bar.*

134 The IP characterizes the thermal oxidation stability of a fuel and decreases with increased oxidation rates  
135 of the fuels. The maximum uncertainty observed for our experimental induction periods is 10% of IP at  
136 the lowest temperature (403 K). This uncertainty was ascribed to all measured IPs (see Table S1).

137

## 138 **2.2. Hydroperoxide quantification: iodometric method**

139 Since the simulations of the autoxidation process are performed in a homogeneous liquid-phase reactor  
140 with a constant oxygen content [14, 20, 26], it is difficult to directly simulate the, gas-phase, pressure  
141 decrease measured in the PetroOxy. In the literature [20, 33], the definition of the IP in the simulations  
142 was assumed to correspond to a conversion of 5% of the fuels oxidized in the PetroOxy. However, the

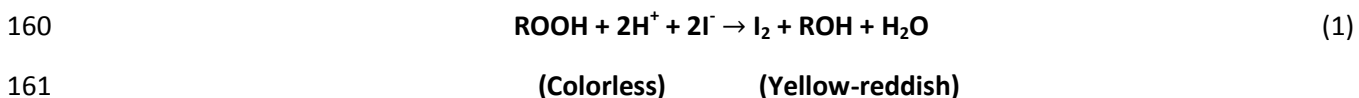


143 extent of fuel conversion at IP is fuel dependent definition is not universal and Mielczarek et al. [34]  
144 indicated that the conversion of toluene at corresponding IP was around 40%. In this work, we propose  
145 to link the IP with another experimental measure: the total hydroperoxides content at the IP. This  
146 creates a universal criterion to define the IP in the simulations, where the simulated IP is reached when  
147 the simulated total content of ROOH matches the experimental one. To quantify the total  
148 hydroperoxides concentration, two methods based on iodometric titration were used in this study.

### 149 **2.2.1. Colorimetry**

150 The iodometric titration method developed by Roohi and Rajabi [35] was used to quantify the total  
151 hydroperoxides content in aged fuels at the end of each PetroOxy test. The main advantage of this  
152 method, compared to the classic titration that uses thiosulfate in aqueous solution as titrant [36, 37],  
153 resides in the use of triphenylphosphine diluted in *n*-decane as titrant. Solubility issues of *n*-decane in  
154 water are therefore avoided in the titrant. The titration was performed in two steps:

155 1) the first step involves the oxidation of iodide anion  $I^-$  to iodine  $I_2$  by hydroperoxides at a  
156 temperature of 68 °C. A volume of 1 ml of aged *n*-decane, sampled at the end of the IP in the  
157 PetroOxy, was added to a solution of potassium iodide (KI, anhydrous 99.9%, VWR Chemicals)  
158 and acetic acid ( $\geq 99.8\%$ , Sigma Aldrich) in absolute ethanol ( $\geq 99.8\%$ , VWR Chemicals). The  
159 reaction is presented in equation (1). The resulting solution has a yellow-reddish color of iodine.



162 2) The second step involves the titration of the iodine with triphenylphosphine (TPP, 99 %, Sigma  
163 Aldrich), which produce an uncolored complex  $[\text{TPPI}]^+[\text{I}]^-$ , as presented in equation (2). The color  
164 change at the endpoint is therefore provided by the complexation of iodine. TPP was prepared in  
165 a solution of pure *n*-decane (99+%, ACROS Chemicals) at a concentration of 0.08 mol/L. The  
166 titration endpoint point was determined as a sharp color change was observed.



168 (yellow-reddish) (colorless)

169 The uncertainty of the concentration of ROOH with the colorimetric titration depends mainly on the  
170 uncertainty of the volume of the titration endpoint, which comes from different sources of errors: the  
171 reading of the burette, the uncertainty of the burette (given by the constructor), and the manipulations.  
172 The detection limit of the equivalence point depends on the size of the drop of the burette which is 0.05  
173 mL. The uncertainty calculations are presented in details in the supplementary material. The uncertainty  
174 in equivalence volumes determined via colorimetry is  $\pm 0.14$  mL, with a confidence interval of 95%.

### 175 2.2.2. Potentiometry

176 As colorimetry, potentiometry is used to quantify  $I_2$  after the iodometric reaction. The biggest difference  
177 between two methods is the considered indicator which is a sharp color change in iodometric titration  
178 and a sharp electric potential change in potentiometric titration. Potentiometry has been shown to  
179 improve the method for measuring hydroperoxides in fuels, thanks to a better determination of the  
180 endpoint compared to the visual detection of the color change in standard titration [36]. The electric  
181 potential during the titration of  $I_2$  was followed by a Mettler Toledo Compact Titrator G10S.

182 As for the colorimetry, the uncertainty on the final ROOH concentration obtained by potentiometry  
183 method mainly depends on the uncertainty of the titration endpoint volume. The use of a potentiometer  
184 allows a better detection of end points because of lowest size of the drops of the burette. Despite the  
185 uncertainty on the measured potential (given by the constructor) the global uncertainty in the titration  
186 endpoint volume remains well below the uncertainty of the colorimetric titration with a value of  $\pm 0.04$   
187 mL, with a confidence interval of 95% (see Table S2 for more details).

## 188 3. Kinetic modelling

### 189 3.1. Detailed kinetic model development

190 In a recent work [26], we presented an approach to develop a detailed kinetic model for fuel  
191 autoxidation based on the corresponding gas-phase kinetic model. In order to capture solvent effects, it  
192 is essential to include thermodynamic, diffusion and kinetic corrections. The details of the method can

193 be accessed in the work on *n*-butane autoxidation kinetics [26], and only the most important features  
194 are recalled here.

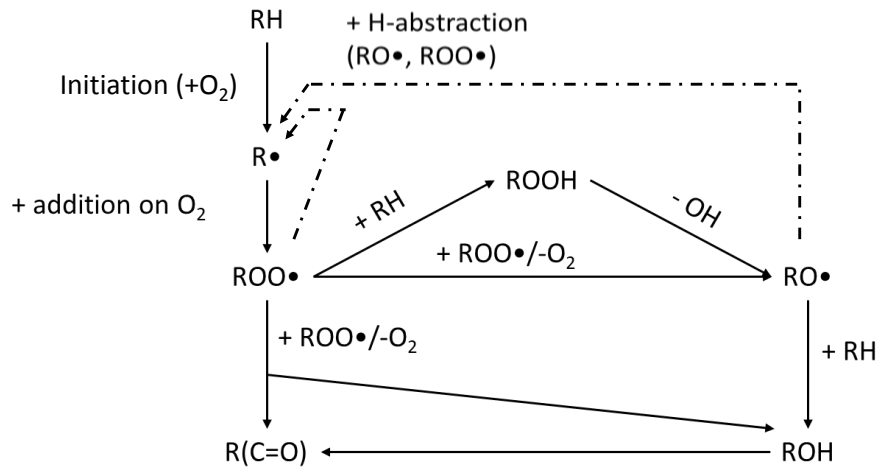
195 The first step in the development of the detailed chemical kinetic model for the autooxidation of *n*-  
196 decane was the generation of the low-temperature oxidation (gas-phase) kinetic mechanism, using the  
197 EXGAS software [24, 25]. This software has been extensively used and validated for the computer aided  
198 generation of combustion kinetics models of hydrocarbons and oxygenated fuels [24, 38-42]. The  
199 generated mechanism is composed of three parts: a primary and a secondary mechanism and a C<sub>0</sub>-C<sub>2</sub>  
200 reaction basis. In the primary mechanism, all the possible elementary reactions of the reactants, and free  
201 radicals produced, are written and leads to a large number of primary products. If the primary molecular  
202 products are larger than C<sub>2</sub>, their decomposition reactions are generated and are lumped to yield C<sub>0</sub>-C<sub>2</sub>  
203 products in order to avoid an excessive growth of the size of the mechanism. For products lower than C<sub>2</sub>,  
204 the combustion reactions are included in the exhaustive C<sub>0</sub>-C<sub>2</sub> reaction base. The details of the  
205 adaptation of the *n*-decane gas-phase model to the liquid-phase is described hereafter.

### 206 **3.1.1. Thermochemical data**

207 The gas-phase thermochemical data for all the species that do not belong to the C<sub>0</sub>-C<sub>2</sub> reaction base were  
208 generated using the THERGAS code [43] based on Benson group additivity method [44]. C<sub>0</sub>-C<sub>2</sub> species  
209 thermochemistry is taken from literature databases. The gas-phase data are then corrected by  $\Delta_{sol}G(T)$   
210 calculated at infinite dilution, using the equation of state (EoS) universal mixing rule Peng-Robinson  
211 UNIFAC (UMR-PRU) [45] to obtain the liquid-phase thermochemical data. Further details of  $\Delta_{sol}G(T)$   
212 calculation can be accessed elsewhere [26, 27, 46].

### 213 **3.1.2. Liquid-phase kinetic data**

214 The typical reaction pathways occurring during the oxidation of an alkane in the liquid phase, at low  
215 conversion, can be schematized as in Figure 2 [47].



216

217

Figure 2. Simplified reaction pathways of an alkane in the liquid phase

218 The main consumption channels of the reacting alkane (RH) are H-atom abstractions by peroxy radical  
 219 ( $\text{ROO}\cdot$ ) and alkoxy radical ( $\text{RO}\cdot$ ), all yielding the main alkyl radical  $\text{R}\cdot$ . The latter radical produces the  
 220 corresponding peroxy radical  $\text{ROO}\cdot$  upon addition on dissolved  $\text{O}_2$ . One of the main reactions of peroxy  
 221 radical  $\text{ROO}\cdot$  yields the corresponding peroxide  $\text{ROOH}$  via H-atom abstractions from the reactant. The  
 222 remaining consumption route of this radical involves the self-reactions ( $\text{ROO}\cdot + \text{ROO}\cdot$ ) that produce an  
 223 alcohol ( $\text{ROH}$ ) and a ketone (or aldehyde) ( $\text{R(C=O)}$ ) in a termination step (disproportionation) known as  
 224 Russell mechanism, or two alkoxy radical  $\text{RO}\cdot$  and  $\text{O}_2$ . Hydroperoxide  $\text{ROOH}$  entirely decomposes into  
 225 two radicals, an alkoxy radical  $\text{RO}\cdot$ , and a hydroxyl radical  $\cdot\text{OH}$ . This degenerate branching reaction is the  
 226 most important reaction governing the liquid-phase reactivity of alkanes as it transforms a molecule into  
 227 two reactive radicals.  $\text{ROH}$  is produced by both self-termination reactions of peroxide radical  $\text{ROO}\cdot$  and  
 228 H-atom abstraction of the reactant  $\text{RH}$  by the alkoxy radical  $\text{RO}\cdot$ . This alcohol  $\text{ROH}$  is then oxidized into  
 229 ketone (or aldehyde)  $\text{R(C=O)}$  by successive reactions, which follow a similar pattern as the one for  
 230 alkanes autooxidation.

231 The reaction classes in this model are bimolecular initiations, additions of alkyl radicals on oxygen,  
 232 radical decompositions by beta-scission, H-atom abstractions from the reactant by radicals, and  
 233 disproportionation. It can be noted that internal isomerization of  $\text{ROO}\cdot$  radicals are negligible in alkanes

234 autoxidation [17, 48] and that this reaction class can be ignored in the reaction mechanism [13, 26]. A set  
 235 of new reaction rate rules, adapted to the liquid-phase oxidation of *n*-decane, was established for the  
 236 self-termination reactions of peroxy radicals, and the H-atom abstractions by peroxy and alkoxy radicals  
 237 based on the corresponding reactions in the autoxidation model of *n*-butane [26]. For the other  
 238 reactions, the EXGAS reaction rate rules were adopted as the simulations demonstrated that they are  
 239 not sensitive for *n*-decane conversion and for the products formation. The most important features of  
 240 the developed mechanism are presented below.

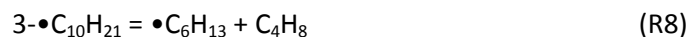
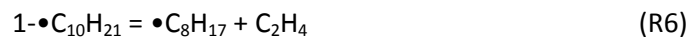
### 241 3.1.2.1 Initiations and beta-scissions

242 Bimolecular initiations involve the reactions R1-R5 of *n*-decane (*n*-C<sub>10</sub>H<sub>22</sub>) with O<sub>2</sub>. Five isomers of *n*-decyl  
 243 radicals (1-C<sub>10</sub>H<sub>21</sub>, 2-C<sub>10</sub>H<sub>21</sub>, 3-C<sub>10</sub>H<sub>21</sub>, 4-C<sub>10</sub>H<sub>21</sub>, 5-C<sub>10</sub>H<sub>21</sub>) are produced. The kinetic parameters were taken  
 244 from EXGAS rate rules (for a primary H-atom, (R1):  $k = 4.2 \times 10^{13} \times \exp(-53033 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ;  
 245 for a secondary H-atom (R2-R5) :  $k = 2.8 \times 10^{13} \times \exp(-50650 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). The influence of  
 246 diffusive rate constants on these kinetic parameters were verified and were found to be negligible. This  
 247 point is further discussed in the 3.1.3 section.



248 In the condition of low temperature oxidation, only C-C bond  $\beta$ -scissions free radicals were considered.

249 Via reactions R6-R14, decyl radicals produce smaller alkenes and alkyl radicals.





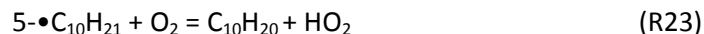
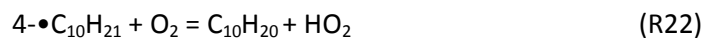
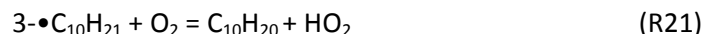
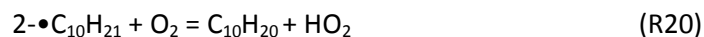
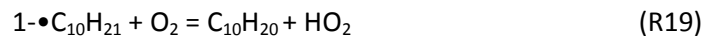
250  
 251 EXGAS rate rules were used to estimate the kinetic data of  $\beta$ -scissions. Only two structure-reactivity  
 252 correlations are needed as reactions (R6-R13) falls within two reaction classes:  $\text{R}\bullet \rightarrow \text{alkene} + \bullet\text{C}_{x>2}\text{H}_{2x+1}$   
 253 ( $k_{6,7,8,10,11,12,13} = 2.0 \times 10^{13} \times \exp(-28700/RT)$ ) and  $\text{R}\bullet \rightarrow \text{alkene} + \bullet\text{CH}_3$  ( $k_9 = 2.0 \times 10^{13} \times \exp(-31000/RT)$ ) in  
 254  $\text{cm}^3$ , mol, cal, K, s units.

### 255 3.1.2.2 Additions on oxygen and oxidations

256 The five decyl radicals ( $\text{C}_{10}\text{H}_{21}$ ) reacts with  $\text{O}_2$  to give decyl peroxy radicals,  $\text{C}_{10}\text{H}_{21}\text{OO}\bullet$  (R14-R18). EXGAS  
 257 rate rules were adopted for these reactions with the rate constant  $k_s = 1.8 \times 10^{19} \times T^{-2.5}$  for the addition of  
 258 secondary radical onto  $\text{O}_2$  (R15-R18) and  $k_p = 9.0 \times 10^{18} \times T^{-2.5}$  in the case of the primary decyl radical  
 259 (R14), in  $\text{cm}^3$ , mol, cal, K, s units. Diffusivities were calculated for these reactions (see 3.1.3) and were  
 260 found to be negligible.



261 In the model, the additions on  $\text{O}_2$  of the decyl radicals compete with the oxidation reactions, which  
 262 consist in the oxidation of decyl radicals by oxygen to form decene (R19-R23). All decene isomers were  
 263 lumped into one species ( $\text{C}_{10}\text{H}_{20}$ ) to reduce the complexity of the model.



264

265 EXGAS rate rules were used for the kinetic data.

266

### 267 3.1.2.3 *H-atom abstractions*

268 H-atom abstractions are the principal consumption flux of *n*-decane in liquid-phase oxidation, yielding  
269 five *n*-decyl radicals. These reactions involve the transfer of a H-atom from *n*-decane to radicals that are  
270 present in significant amounts. In our mechanism, these radicals are: hydroxyl (OH), hydroperoxyl (HO<sub>2</sub>),  
271 methyl ( $\bullet$ CH<sub>3</sub>), methoxy (CH<sub>3</sub>O $\bullet$ ), methyl peroxy (CH<sub>3</sub>OO $\bullet$ ), five isomers of decoxy radicals (C<sub>10</sub>H<sub>21</sub>O $\bullet$ ) and  
272 five isomers of *n*-decyl peroxy radicals (C<sub>10</sub>H<sub>21</sub>OO $\bullet$ ). In the model, the five isomers of *n*-decanol were  
273 lumped as C<sub>10</sub>H<sub>21</sub>OH and the five isomers of *n*-decyl hydroperoxide were lumped as C<sub>10</sub>H<sub>21</sub>OOH. In the  
274 experiments of *n*-decane liquid-phase oxidation [17, 20], decanol was determined as one of the major  
275 products. Most H-atom abstractions follow EXGAS rate rules except H-atom abstractions by alkoxy and  
276 peroxy radicals, which were shown to be very sensitive in *n*-butane autoxidation. In the model of *n*-  
277 decane, the rate constants of H-atom abstractions by C<sub>10</sub> peroxy radicals are estimated using an analogy  
278 with the H-abstraction from *n*-butane by butylperoxy radicals [26]. The kinetic parameters of H-atom  
279 abstraction by C<sub>10</sub> alkoxy radicals were estimated by analogy with H-atom abstractions of *n*-butane by C<sub>4</sub>  
280 alkoxy radicals based on theoretical calculations with an implicit continuum solvation model.

### 281 3.1.2.4 *Disproportionations*

282 Disproportionations are known as chain-terminating processes. In the model, these reactions are  
283 included for all important peroxy radicals. For example, decyl peroxy react with HO<sub>2</sub> as ROO $\bullet$  + HO<sub>2</sub> →  
284 ROOH + O<sub>2</sub>. Kinetic parameters of these reactions follow EXGAS rate rules.

285 Another type of disproportionation considered in the model is the self-terminations of decyl peroxy  
286 radicals. This reaction class is known crucial processes in the autoxidation of alkanes [13, 26, 48]. The  
287 self-termination of C<sub>10</sub> peroxy radicals has two exit channels: (1) producing two decoxy radicals  
288 (C<sub>10</sub>H<sub>21</sub>O $\bullet$ ) and O<sub>2</sub>, and (2) producing O<sub>2</sub>, C<sub>10</sub> alcohols and C<sub>10</sub> carbonyl compounds. In our model, isomers  
289 of C<sub>10</sub> carbonyl compounds were lumped as C<sub>10</sub>H<sub>20</sub>OK. For these two reaction classes, kinetic parameters

290 were proposed as  $k_1 = 1.0 \times 10^{11} \times \exp(2700 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_2 = 2.0 \times 10^{11} \times \exp(2700 \text{ cal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The ratio  $\alpha = k_1 / k_2$  is 0.5. It has been shown in *n*-butane liquid-phase oxidation [26]  
291 that the ratio  $\alpha$  could be between 0.5 and 1 to get reasonable simulation results. It is interesting to note  
292 that a ratio  $\alpha=1$  was used in the *n*-butane kinetic model to obtain the best agreement between  
293 simulations and experiments. In the case of *n*-decane, the  $\text{ROO}\bullet + \text{ROO}\bullet \rightarrow \text{RO}\bullet + \text{RO}\bullet + \text{O}_2$  channel is  
294 favored over the  $\text{ROO}\bullet + \text{ROO}\bullet \rightarrow \text{ROH} + \text{R}_1\text{COR}_2 + \text{O}_2$  by a factor of 2. It is difficult to find an explanation  
295 for this difference, it can be either a meaningful physical effect or a consequence of the lumping of the  
296  $\text{C}_{10}$  alcohols and  $\text{C}_{10}$  carbonyl compounds. Indeed, in the *n*-butane autoxidation model, no lumping of  
297 alcohols and ketones was used.

### 299 3.1.2.5 Decompositions of hydroperoxides

300 The unimolecular decompositions of hydroperoxides (ROOH) plays an important role as these processes  
301 generate free radicals (RO• and OH). The rate constant of the decomposition of *n*-decyl hydroperoxide is  
302  $k = 1.60 \times 10^{11} \times \exp(-31700/RT)$  in mol, cal, K, s units. This rate constant results from a regression  
303 analysis of experimental data reported in the review of Dixon [49].

### 304 3.1.2.6 Decanol sub-mechanism

305 Decanol is one of the major products quantified experimentally in *n*-decane liquid-phase oxidation [17,  
306 20]. To limit the size of the mechanism, a simplified sub-mechanism was developed for decanol,  
307 following the validated approach used for butanol in the autoxidation model of *n*-butane [26]. In the  
308 model, the lumped alcohol  $\text{C}_{10}\text{H}_{21}\text{OH}$  is consumed by H-abstraction by decyl peroxy (ROO•) and OH  
309 radicals to produce an  $\alpha$ -hydroxyl alkyl ( $\bullet\text{ROH}$ ) radical noted as RC10H21OL. In this approach, the H-  
310 abstraction is assumed to solely occur on the  $\alpha$ -site of the hydroxyl group because of a lower C-H bond  
311 dissociation energy at this position compared to other H-atoms of decanol. The  $\bullet\text{ROH}$  radical is then  
312 oxidized by  $\text{O}_2$  to form lumped  $\text{C}_{10}$  carbonyl compounds and  $\text{HO}_2$ . The associated rate constants are  
313 estimated using the proposed rate rules in the *n*-butane model [26].



### 314 **3.1.3. Diffusion correction**

315 To account for diffusive limits in the liquid phase, a diffusion rate constant ( $k_{diff}$ ) has to be combined to  
316 the intrinsic liquid-phase constant ( $k_{int,liq}$ ). This leads to the following effective rate constant ( $k_{eff}$ ) for a  
317 bimolecular reaction  $A+B \rightleftharpoons (A-B) \rightarrow Products$ :

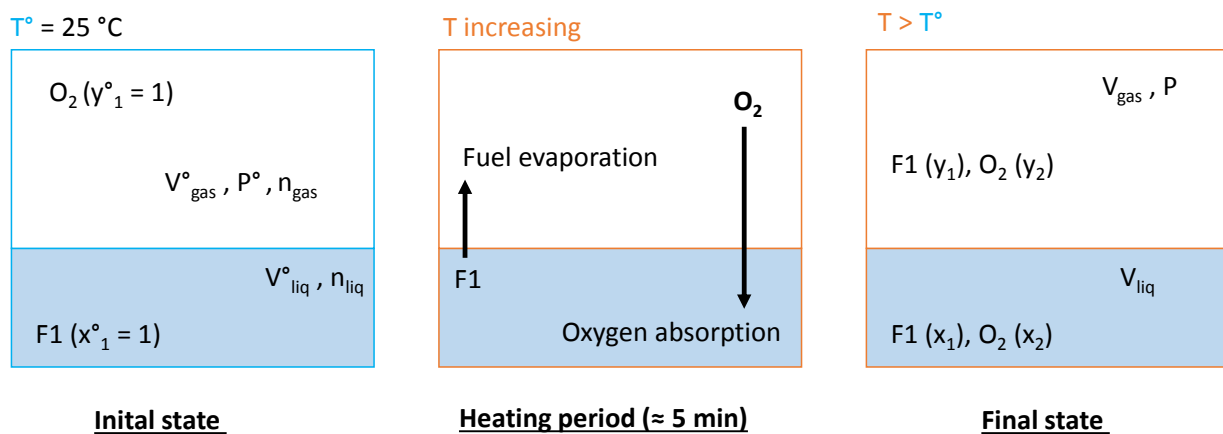
$$k_{eff} = \frac{k_{diff} \times k_{int,liq}}{k_{diff} + k_{int,liq}}$$

318  $k_{diff}$  was calculated using the Stokes-Einstein approach for diffusion of spherical particles in the liquid  
319 phase [14, 26]. In this approach, molecular radii of considered species are calculated based on the  
320 UNIFAC molecular size parameter included in UMR-PRU equation of state [27]. Temperature-dependent  
321 viscosities are read in a literature database [50]. Diffusion calculations were conducted for all the most  
322 important bimolecular reactions included in the main reaction flux of *n*-decane. It is found that the  
323 values of  $k_{diff}$  are nearly similar for the different considered reactions and increase with temperatures.  
324  $k_{diff}$  varies from  $4 \times 10^{13}$  at 300 K to about  $2 \times 10^{16} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$  at 500 K. As the values of  $k_{diff}$  of the  
325 considered reactions are very high because of the relatively low viscosity of *n*-decane (0.29 mPa.s at 400  
326 K),  $k_{eff} = k_{int,liq}$ . A similar behavior was observed for *n*-butane which has a much lower liquid viscosity  
327 (0.005 mPa.s at 400 K).

### 328 **3.2. Calculation of liquid and gas phases initial compositions in the PetroOxy**

329 The simulation of liquid-phase oxidation in the PetroOxy is performed using a homogeneous batch  
330 reactor model at fixed temperature (T), pressure (P) and volume (V) and with a constant dissolved  $O_2$   
331 concentration [14, 20, 26]. In the input, T is the target temperature (e.g. 140°C) that is used to accelerate  
332 the oxidation phenomena. However, in the PetroOxy experiments, the 25 mL cell is first filled with 5 mL  
333 of *n*-decane and sealed under atmospheric air pressure. The cell is then purged and filled with 7 bar of  $O_2$   
334 at ambient temperature and heated to the target temperature. With the increasing temperature, the  
335 compositions of the liquid and gas phases evolve. It can be noted that the heating time to reach the  
336 control temperature is a few minutes.

337 In conjunction with the temperature increase, the pressure in the cell test increases from the initial value  
 338 at 25°C (700 kPa) to a maximum value. Several competing physical phenomena affect the pressure  
 339 evolution, including the thermal expansion, the evaporation of the fuel, and the solvation of oxygen in  
 340 the liquid phase. An iterative calculation method has been developed to estimate molar compositions of  
 341 both liquid and gas phases in a PetroOxy test, when the gas pressure reaches its maximum pressure.  
 342 These molar compositions were used as inputs in IP simulations. Figure 3 presents the simplified  
 343 boundary conditions that needs to be considered in the calculations.



344 **Initial state** **Heating period ( $\approx 5$  min)** **Final state**

345 *Figure 3. Simplified scheme presenting the different steps when the temperature increases in the PetroOxy.*

346 In Figure 3, F1 is the fuel,  $x_n$  and  $y_n$  are the mole fractions of the compound  $n$  (1 for the liquid fuel and 2  
 347 for oxygen) in the liquid and gas phases, respectively. In the initial state ( $T^\circ = 25^\circ\text{C}$ ), it is assumed that  
 348 the gas phase contains only oxygen ( $\text{O}_2$ ,  $y_2^\circ = 1$ ) and the initial gas pressure ( $P^\circ$ ) is equal to the initial  
 349 oxygen pressure ( $P_{\text{O}_2}^{\text{initial}} = 7$  bar). Similarly, the liquid phase is composed only of fuel (F1,  $x_1^\circ = 1$ ). The  
 350 initial volume of the liquid phase, noted  $V_{\text{liq}}^\circ$ , is 5 mL. The transient state, represented at the center of  
 351 Figure 3, corresponds to the heating phase of the reactor and the final state corresponds to the  
 352 thermodynamic equilibrium at the test temperature.

353 The system obeys the laws of conservation during the temperature increase: volume conservation ( $V_{\text{gas}} +$   
 354  $V_{\text{liq}} = V_{\text{total}} = 25$  mL = constant) and the material balance:

$$\text{Overall balance: } n_{\text{gas}} + n_{\text{liq}} = n_{\text{total}} = \text{constant}$$

$$\text{Balance on component } i: n_{\text{gas},i} + n_{\text{liq},i} = n_{\text{total},i} = \text{constant}$$

355 where  $n_{\text{gas}}$  and  $n_{\text{liq}}$  are the mole number of the gas and liquid phases, respectively;  $n_{\text{gas},i}$  and  $n_{\text{liq},i}$  are the  
 356 mole number of the component  $i$  in the gas and liquid phases.

357 The total volume of the gas phase obeys the perfect gas law,  $V_{\text{gas}} = \frac{RT}{P}(n_{\text{gas},1} + n_{\text{gas},2})$ . The total volume  
 358 of the liquid phase is deduced from the density of the liquid ( $D_{\text{liq}}$ ) phase,  $V_{\text{liq}} = \frac{n_{\text{liq},1}M_1 + n_{\text{liq},2}M_2}{D_{\text{liq}}(T, x_1, x_2)}$ .

359 In the final state, both the gas and liquid phases contain mixtures of the fuel F1 and oxygen. The molar  
 360 compositions of both phases and the final pressure ( $P$ ) are related and are described using the so-called  
 361  $\gamma - \phi$  thermodynamic approach in which the liquid solvent is assumed to obey Raoult's law while the  
 362 liquid solute is described using Henry's law; the gas phase is considered as a perfect gas. These  
 363 assumptions are justified as long as (i) the molar fraction of the solvent in the liquid phase is nearly one  
 364 ( $x_1 \rightarrow 1$ ), (ii) the molar fraction of the liquid solute approaches zero ( $x_2 \rightarrow 0$ ) and (iii), the total pressure  
 365 remains below 10 bar (ensuring that the perfect-gas assumption is acceptable).

366

$$P \times y_1 = P_1^{\text{sat}} \times x_1 \quad (1)$$

$$P \times y_2 = H_{O_2} \times x_2 \quad (2)$$

367  $P_1^{\text{sat}}$  corresponds to the vapor pressure of the pure fuel F1 and  $H_{O_2}$  is the Henry's law constant of oxygen  
 368 in F1 solvent. Both these properties depend on temperature only.

369 Remembering that  $x_i = \frac{n_{\text{liq},i}}{n_{\text{liq},1} + n_{\text{liq},2}}$  and  $y_i = \frac{n_{\text{gas},i}}{n_{\text{gas},1} + n_{\text{gas},2}}$  ( $i = 1,2$ ), the final problem to be solved is

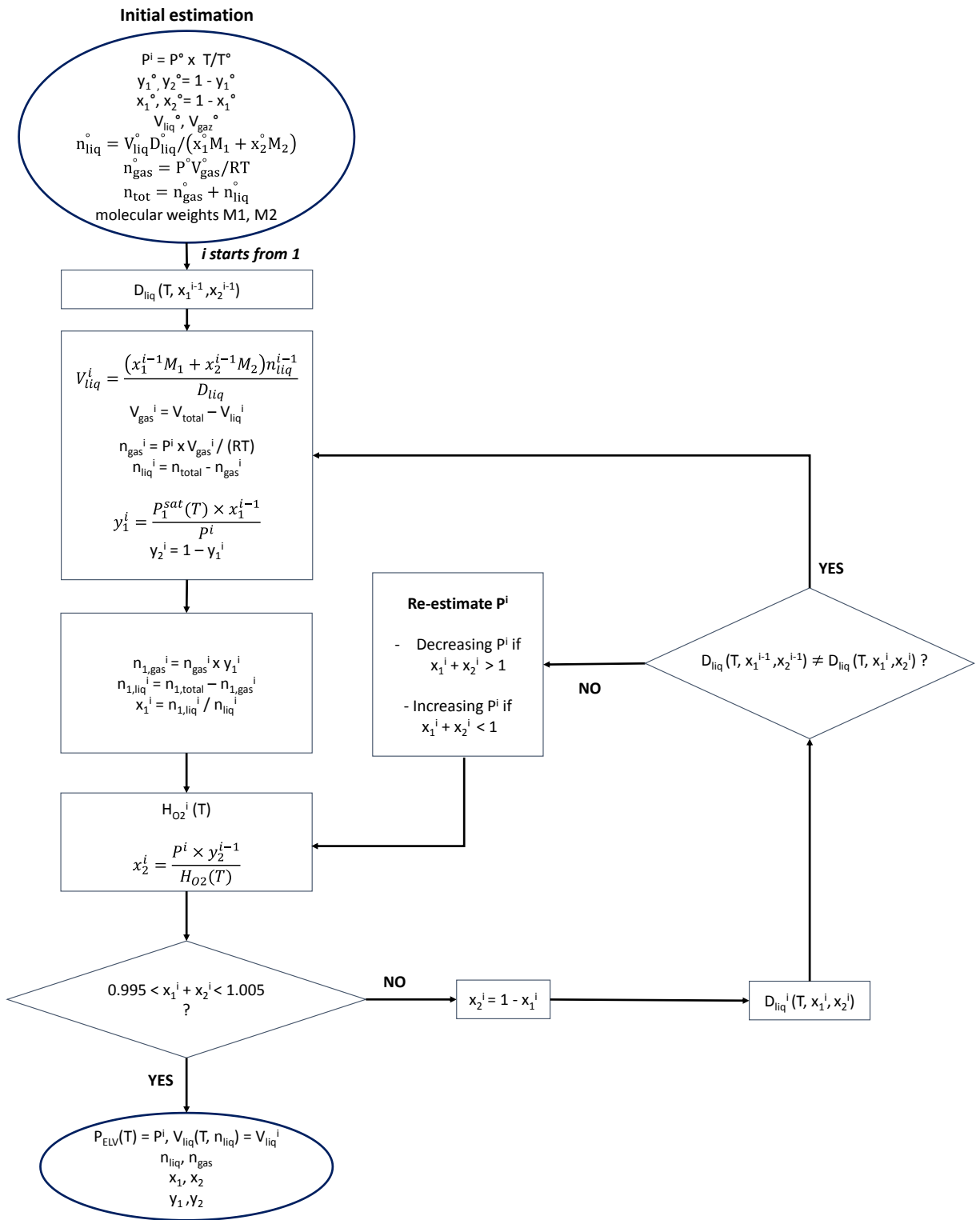
370 summarized in the following system, gathering 5 equations:

$$\left\{ \begin{array}{l} P \times y_1 = P_1^{sat}(T) \times x_1 \quad (1) \\ P \times y_2 = H_{O_2}(T) \times x_2 \quad (2) \\ V_{total} = \frac{n_{liq,1}M_1 + n_{liq,2}M_2}{D_{liq}(T, x_1, x_2)} + \frac{RT}{P}(n_{gas,1} + n_{gas,2}) \quad (3) \\ n_{total,i} = n_{liq,i} + n_{gas,i}, \quad i = 1,2 \quad (4) \\ n_{total,i} = n_{liq,i} + n_{gas,i}, \quad i = 1,2 \quad (5) \end{array} \right.$$

371  $T, V_{total}, n_{total,1}, n_{total,2}$  are input variables. The 5 unknowns are  $P, n_{gas,1}, n_{gas,2}, n_{liq,1}, n_{liq,2}$ .

372 In practice, the resolution of Eq. (1-5) is carried out using successive substitution methods. The proposed  
373 iterative calculation method consists of several steps and is presented in Figure 4. In the first step, a gas  
374 pressure in the final state is guessed based on the ideal gas law, assuming constant mole number and  
375 volume of the gas phase. Next, molar composition in the liquid phase is deduced thanks to the  
376 conservation of volume, material balance and relations (1) and (2). The thermodynamic properties  
377 involved in these equations, *i.e.*, the liquid density ( $D_{liq}$ ), vapor pressure ( $P^{sat}$ ), Henry's law constant of  
378 oxygen ( $H_{O_2}$ ) in solvent, are obtained from the Predictive SRK (PSRK) equation of state [51] implemented  
379 in Simulis software [52]. The PSRK model, capable of guesstimating the above properties, was chosen for  
380 both its flexibility and accuracy.

381 At the end of a calculation process, the sum of molar composition in the liquid phase is checked whether  
382 it is equal to 1. A tolerance of 0.005 is adopted. If the checking condition is not satisfied, a new liquid  
383 density and gas pressure are estimated and the calculation loop starts again until the validation of the  
384 checking condition.



385

386 Figure 4. Iterative calculation method to estimate the maximum pressure and molar composition in PetroOxy experiments

387

388 The iterative calculation presented in Figure 4 was used to determine the initial composition at the set  
389 temperature T in the PetroOxy experiments. This method enables the simulation of the gas pressure  
390 profiles as a function of temperature at the beginning of the tests, until the maximum pressure is  
391 reached (Figure 5).

392

393 *Figure 5.* Simulations of pressure profiles as a function of time at the beginning of PetroOxy tests (heating phase up to the set  
394 temperature T) of *n*-decane at different T: (a) 403 K, (b) 408 K, (c) 413 K, (d) 418 K. Symbols are experimental data and solid lines  
395 are simulated pressure profiles. Experimental pressure profiles of heating phases are given in Table S3.

396 In general, simulations reproduce the measured pressure profiles and are able to capture the equilibrium  
397 between the liquid and vapor phases.

398 The physical model predicts that at the end of the heating time of 5 minutes, the volume of liquid  
399 increases from 5.0 to 5.7 mL, going from 298 to 413 K. At 413 K, the mole fractions of *n*-decane and  
400 dissolved O<sub>2</sub> in the liquid phase are 0.98 and 0.02, respectively. For this condition, the corresponding gas-  
401 phase mole fractions are 0.04 for *n*-decane and 0.96 for O<sub>2</sub>.

402 The mole compositions of the liquid phase corresponding to the maximum gas pressure are also  
403 determined, at different temperatures (Table 1).

404 *Table 1.* Calculated molar composition of the liquid phase corresponding to the maximum gas pressure during PetroOxy tests of  
405 *n*-decane.

Cell temperature (K)	[ <i>n</i> -Decane] (mol/L)	[Oxygen] (mol/L)
403	4.51	8.56 x 10 <sup>-2</sup>
408	4.48	8.56 x 10 <sup>-2</sup>
413	4.45	8.75 x 10 <sup>-2</sup>
418	4.41	8.97 x 10 <sup>-2</sup>

406

407 The calculated compositions were used as concentration inputs to simulate the induction periods of  
408 *n*-decane at different temperatures. It is interesting to note that the calculated concentration of O<sub>2</sub>

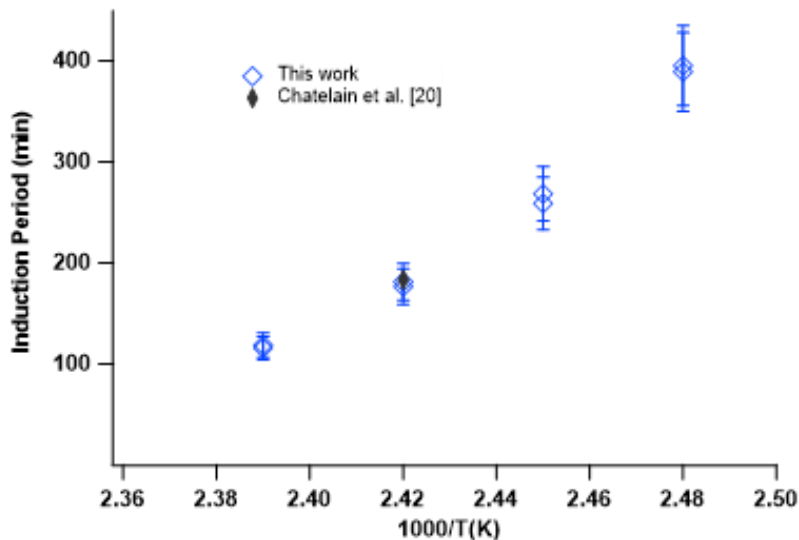
409 dissolved in *n*-decane increases with temperature. A similar behavior is well known for O<sub>2</sub> in jet fuels [6].  
410 All the simulations were performed using a homogeneous liquid batch reactor (constant T, P, and V)  
411 solver based on Chemkin II library [53] with constant O<sub>2</sub> concentration [14, 26, 34].

#### 412 4. Results and Discussions

413 Experimental results in PetroOxy are first presented, then, the simulations and the performances of the  
414 *n*-decane autoxidation model are shown. Based on the validated model, the reaction pathways of *n*-  
415 decane autoxidation are analyzed and the key reactions are highlighted thanks to a sensitivity analysis.

##### 416 4.1. Liquid-phase reactivity of *n*-decane

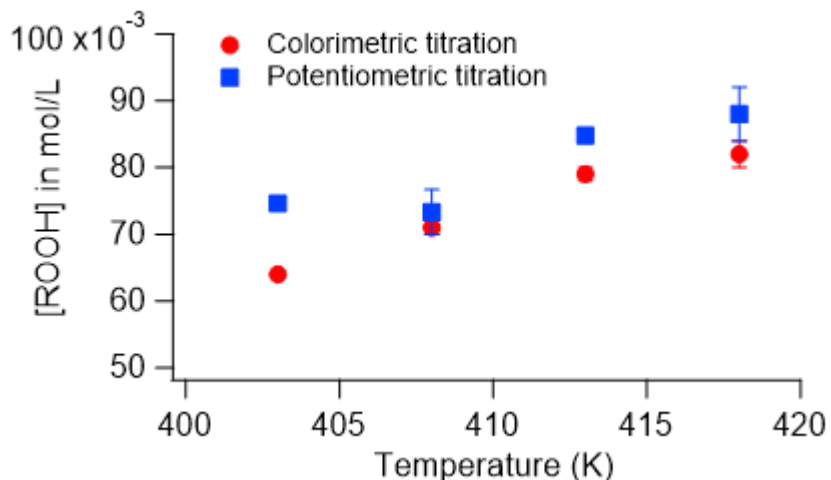
417 Figure 6 presents the measured induction periods of *n*-decane as a function of the inverse of the  
418 temperature. The IP of *n*-decane measured in this work are consistent with the data reported by  
419 Chatelain et al. [20].



420  
421 *Figure 6. Induction periods of n-decane measured in a PetroOxy at 7 bar initial of oxygen and comparison with data reported by*  
422 *Chatelain et al. [20].*

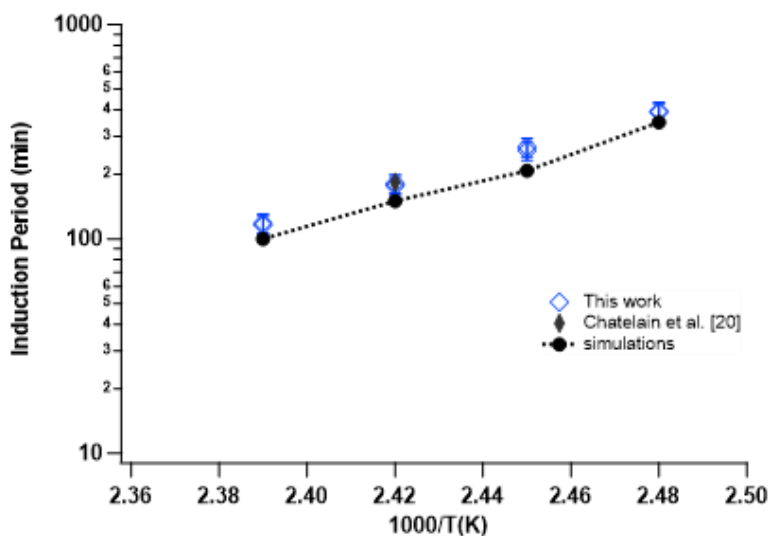
423 Total hydroperoxides content in aged *n*-decane was quantified by iodometry, using colorimetric and  
424 potentiometric titrations. The measured hydroperoxide (ROOH) concentrations at the IP time are

425 presented as a function of the PetroOxy cell temperature in Figure 7. IP and [ROOH] data are given in  
426 Table S4 and S5.



427  
428 *Figure 7.* Total hydroperoxides content in *n*-decane, at IP (experiments at 7 bar initial of O<sub>2</sub>), measured by colorimetric and  
429 potentiometric titrations. Error bars are the repeatability standard deviations.  
430 Both endpoint detection methods indicate that the ROOH concentration increases with temperature.  
431 The ROOH concentrations obtained from potentiometry are generally higher than those measured by  
432 colorimetry by a about  $5 \times 10^{-3} \text{ mol l}^{-1}$ . Our uncertainty calculations showed that potentiometric titration  
433 is more accurate than colorimetric titration since an electronic signal is used in the former method (see  
434 Table S2). Consequently, the potentiometric total ROOH concentrations were used as the criterion to  
435 determine the IP time in the simulation: the simulated IP is reached when the simulated total  
436 concentration of ROOH matches the experimental one.  
437 Figure 8 presents the simulation of measured IP of *n*-decane in this work using the liquid-phase kinetic  
438 model developed.



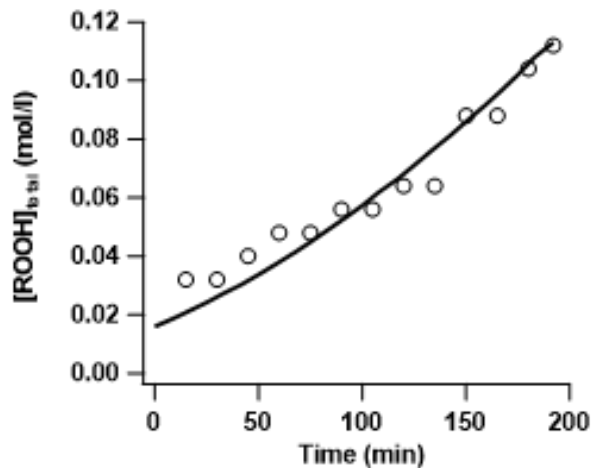


439

440 *Figure 8.* Comparison between simulated and experimental induction periods of *n*-decane in a PetroOxy device, at 7 bar of  
 441 oxygen. Criteria for simulated IP: simulated  $[\text{ROOH}]_{\text{total}} = [\text{ROOH}]_{\text{total}}$  measured at IP.

442 Under the investigated conditions, the measured IP of *n*-decane presented in logarithmic scale varies  
 443 nearly linearly with the inverse of reactor temperatures. The simulation reproduces experimental results  
 444 with a mean relative deviation of 16% over the temperature range studied. Further validations of the  
 445 kinetic model were performed using oxidation products profiles.

446 For one condition of oxidation stability test, at 413 K and 7 bar of oxygen, the total concentration of  
 447 ROOH as a function of time was measured. To do so, PetroOxy tests were stopped every  $t = t(\text{previous}$   
 448  $\text{test}) + 15$  min until the IP time was reached (Figure 9). The total [ROOH] content was measured by  
 449 potentiometric titration. The titration of fresh, unaged, *n*-decane revealed that the liquid already  
 450 contained hydroperoxides at a concentration of 0.016 mol/L. This initial hydroperoxides content was also  
 451 employed as inputs in all simulations of *n*-decane autoxidation.



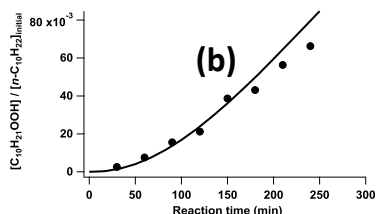
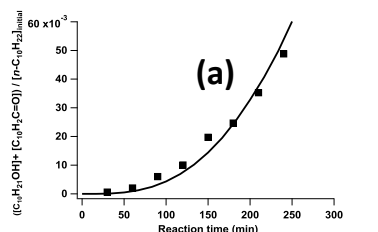
452

453 *Figure 9.* Simulated and measured concentrations of total hydroperoxides formed during a PetroOxy test of *n*-decane at 413 K  
 454 and 7 bar initial of oxygen. Experimental data are given in Table S6.

455 The experiments show that the concentration of hydroperoxides increases with time as *n*-decane  
 456 oxidation progresses. For these conditions, and within the IP time range, no extremum is observed in the  
 457 [ROOH] curve as a function of time. The simulations agree with the ROOH profile measured in the  
 458 PetroOxy rig. Simulations show that the formed ROOH are solely C<sub>10</sub>H<sub>21</sub>OOH. Under these conditions, the  
 459 conversion of *n*-decane at the end of the test (190 minutes) reaches 3.6% and the product branching  
 460 ratios are 0.76, 0.18 and 0.06 for C<sub>10</sub>H<sub>21</sub>OOH, C<sub>10</sub>H<sub>21</sub>OH and C<sub>10</sub>H<sub>20</sub>(C=O), respectively (C<sub>10</sub>H<sub>20</sub>(C=O) are  
 461 lumped decanones and decanals and C<sub>10</sub>H<sub>21</sub>OH are lumped decanols). Figure S1 presents these product  
 462 profiles as a function of time. The flux analysis shows that almost all C<sub>10</sub> alcohols come from H-  
 463 abstractions from *n*-decane by C<sub>10</sub> alkoxy radicals, which are produced in the unimolecular  
 464 decomposition of the C<sub>10</sub>H<sub>21</sub>OOH.

465 Our new kinetic model of autoxidation of *n*-decane was also compared with experimental data of the  
 466 literature. Cullis et al. [17] investigated *n*-decane autoxidation in a semi-open reactor in which a flux of  
 467 oxygen was passed through the liquid fuel, at a constant temperature of 423 K. Major products of *n*-  
 468 decane autoxidation includes C<sub>10</sub>-hydroperoxides, C<sub>10</sub>-alcohols, and C<sub>10</sub> carbonyls that were quantified as  
 469 a function of time. Figure 10.a presents the formation of C<sub>10</sub> hydroperoxides per initial mole of *n*-decane

470 and figure 10.b illustrates the formation of sum of C<sub>10</sub>-decanols and C<sub>10</sub>-decanones/decanal per initial  
471 mole of *n*-decane.



472

473 *Figure 10.* Simulation of products formed during the autoxidation of *n*-decane and comparison with experiments from Cullis et  
474 al. [17] at 423 K,  $P_{ini, O_2} = 700$  kPa,  $V_{ini, liquid} = 5$  ml. Symbols: experiments, lines: simulations. (a): formation of C<sub>10</sub>-  
475 hydroperoxides, (b): formation of C<sub>10</sub>-ketones/decanal and C<sub>10</sub> alcohols.

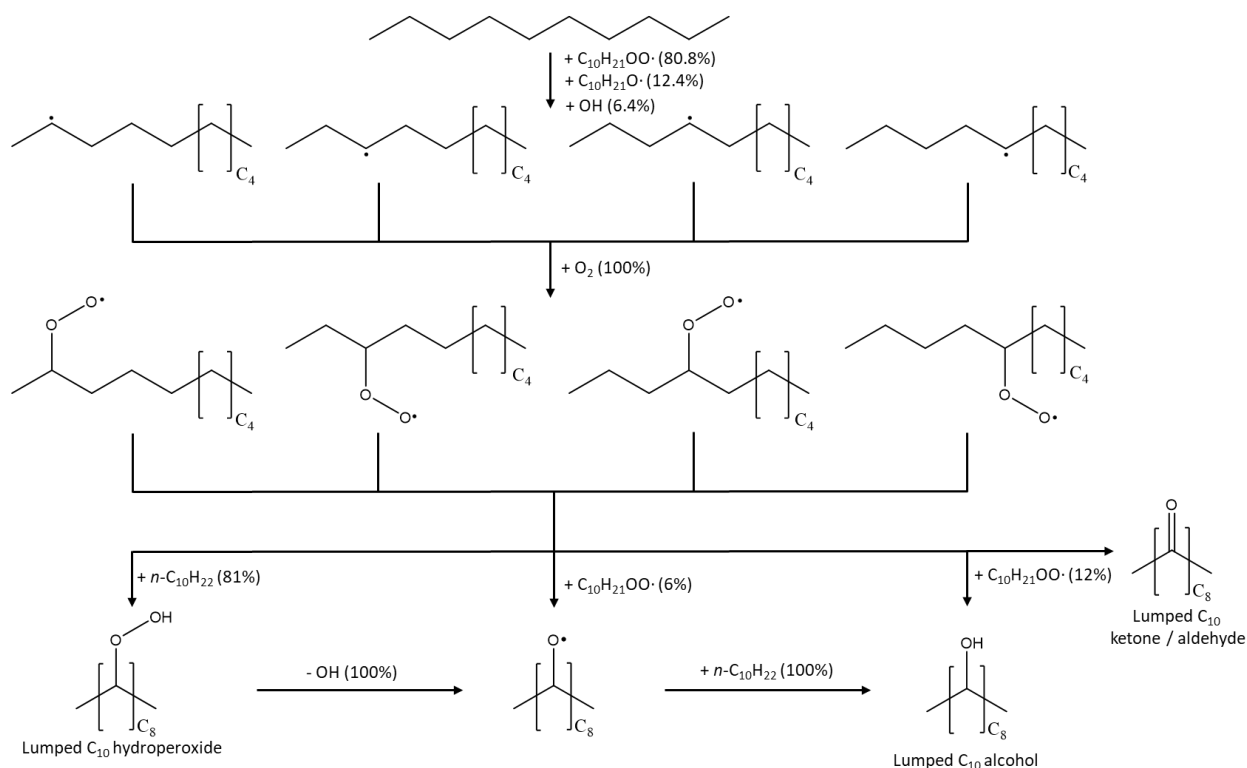
476 The simulation agrees with experimental results. The ratio  $[C_{10} \text{ alcohol}] / [C_{10} \text{ carbonyls}]$  is constant over  
477 the reaction time and is equal to 3. At a reaction time of 117 min, 3.6% of conversion is reached and the  
478 same branching ratios as those found in the simulation plotted in Figure 9 are found for C<sub>10</sub>H<sub>21</sub>OOH,  
479 C<sub>10</sub>H<sub>21</sub>OH and C<sub>10</sub>H<sub>20</sub>(C=O) (0.76, 0.18 and 0.06). At 250 min, *n*-decane conversion is 16% and the  
480 branching ratios of C<sub>10</sub>H<sub>21</sub>OOH, C<sub>10</sub>H<sub>21</sub>OH and C<sub>10</sub>H<sub>20</sub>(C=O) are 0.58, 0.31 and 0.10, respectively. It can be  
481 noted that water is also a major product of *n*-decane autoxidation but is not included in the latter

482 branching ratios because it does not contain carbon atoms. The concentration of H<sub>2</sub>O is always similar to  
 483 that of C<sub>10</sub>H<sub>20</sub>(C=O) in the simulations of PetroOxy experiments and of the data of Cullis et al. [17]. For  
 484 example, simulated [H<sub>2</sub>O] is equal to 6.7 10<sup>-2</sup> mol l<sup>-1</sup> at the end of Cullis et al. experiments vs 6.67 10<sup>-2</sup>  
 485 mol l<sup>-1</sup> for C<sub>10</sub>H<sub>20</sub>(C=O).

## 486 4.2. Kinetic model analysis

### 487 4.2.1. Reaction pathways of *n*-decane autoxidation

488 Rate of production (ROP) analyses were carried at 413 K, P<sub>ini,O<sub>2</sub></sub> = 700 kPa, V<sub>ini,liq</sub> = 5 mL for a conversion of  
 489 *n*-decane of about 4%. Figure 11 presents the main reaction pathways of *n*-decane liquid-phase oxidation  
 490 at the examined condition.



491  
 492 *Figure 11. Reaction pathways of n-decane in the liquid phase at 413 K. ≈ 4% conversion of n-decane (190 min residence time).*

493  
 494 The reaction scheme of *n*-decane is found to be very similar to the one of *n*-butane [26]. The main  
 495 consumption flux of *n*-decane is H-atom abstractions by *n*-decyl peroxy radicals (C<sub>10</sub>H<sub>21</sub>OO•) (80.8%), C<sub>10</sub>  
 496 alkoxy radicals (C<sub>10</sub>H<sub>21</sub>O•) (12.4%), and OH (6.4%) radicals, yielding five isomers of decyl radicals. The

497 latter radicals entirely yield decyl peroxy radicals ( $C_{10}H_{21}-OO\cdot$ ) through addition on  $O_2$ . The majority of  
498 decyl peroxy radicals (81%) leads to the formation of decyl hydroperoxide through H-atom abstractions  
499 from *n*-decane. The remaining part of  $C_{10}H_{21}-OO\cdot$  reacts in the self-termination reactions to produce  
500 decanol ( $C_{10}H_{21}-OH$ ),  $C_{10}$  decanone/decanal ( $C_{10}H_{20}-OK$ ), and  $C_{10}$  alkoxy radicals ( $C_{10}H_{21}-O\cdot$ ). Decyl  
501 hydroperoxide decomposes into two fragments,  $C_{10}$  alkoxy radicals, and OH radicals. This reaction is the  
502 most important reactions governing the liquid-phase reactivity of *n*-decane as it transforms a neutral  
503 molecule into two reactive radicals. Sensitivity analyses presented in Figure 12 confirm the central  
504 kinetic role of this reaction.  $C_{10}$  alcohols are produced by both self-termination reactions of decyl  
505 peroxide radicals and by H-abstraction by  $C_{10}H_{21}-O\cdot$  from *n*-decane. The major part of decanols is  
506 produced in the latter process. Once formed,  $C_{10}$  alcohols are principally consumed by reactions with  $C_{10}$   
507 peroxy radicals (97.7%), through H-abstractions producing  $C_{10}$  alcohols radicals ( $\cdot C_{10}H_{20}-OH$ ). The latter  
508 radical is then oxidized into  $C_{10}$  carbonyl compounds by successive processes: addition of  $O_2$ , and  
509 elimination of  $HO_2$ .

#### 510 **4.2.2. Sensitivity analysis of the autoxidation kinetic model of *n*-decane**

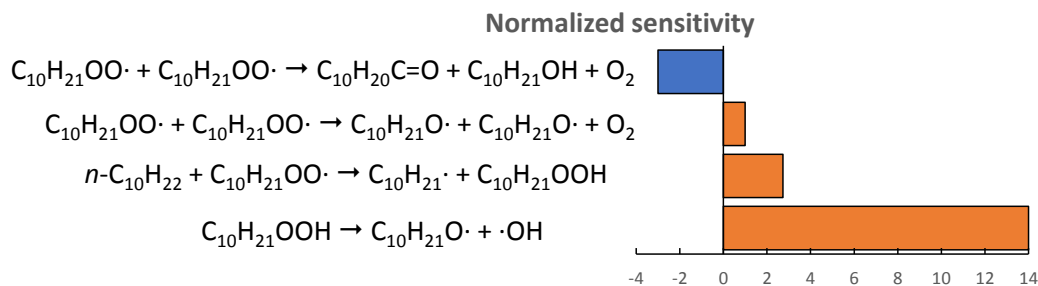
511 Sensitivity analyses have been performed to determine the most sensible reactions in an oxidation  
512 mechanism of fuel [54]. These analyses were conducted on the conversion of *n*-decane at 413 K and 7  
513 bar initial of oxygen. Sensitivity analyses were initiated by the modification of the A-factor of the rate  
514 constant of each reaction, which was multiplied by a factor of ten. For each modification, a simulation  
515 was performed to determine the modified conversion ( $X_i$ ) of *n*-decane. The sensitivity coefficient ( $\tau_i$ ) of  
516 each reaction was then calculated as follows:

$$\tau_i = \frac{X_i - X_0}{X_0} \times 100 \%$$

517  $X_0$  corresponds to the simulated conversion of *n*-decane with the original unmodified model. A positive  
518 sensitivity coefficient represents a promoting effect of the considered reaction on the conversion of *n*-

519 decane. Conversely, a negative coefficient shows an inhibiting effect of the considered reaction on the  
 520 reactivity of *n*-decane. Figure 12 summarizes the results of the sensitivity analyses.

521



522

523 *Figure 12.* Sensitivity analyses on the conversion of *n*-decane during its autoxidation at 413 K

524 The reactions that promote the conversion of *n*-decane are H-atom abstractions from *n*-decane (*n*-  
 525  $C_{10}H_{22}$ ) by  $C_{10}$  peroxy radicals ( $C_{10}H_{21}OO\cdot$ ), the disproportionations of  $C_{10}$  peroxy radical producing  $C_{10}$   
 526 alkoxy radicals ( $C_{10}H_{21}O\cdot$ ) and the decompositions of  $C_{10}$  hydroperoxide ( $C_{10}H_{21}OOH$ ). The latter reaction  
 527 has the highest promoting effect on *n*-decane conversion. The termination reactions of  $C_{10}$  peroxy radical  
 528 producing  $C_{10}$  alcohols ( $C_{10}H_{21}OH$ ) and  $C_{10}$  carbonyl compounds ( $C_{10}H_{20}C=O$ ) is the most inhibiting  
 529 reaction of the mechanism. The branching ratios for the reaction products of the self-termination  
 530  $C_{10}H_{21}OO\cdot + C_{10}H_{21}OO\cdot$  is sensitive for the conversion of *n*-decane. In this study, the ratio of the channel  
 531 ' $C_{10}H_{21}O\cdot + C_{10}H_{21}O\cdot + O_2$ ' over the channel ' $C_{10}H_{22}C=O + C_{10}H_{21}OH + O_2$ ' was fixed to a factor of 2. Further  
 532 work is deserved to refine the determination of this ratio in the autoxidation of *n*-decane and other  
 533 alkanes.

## 534 5. Conclusion

535 Experiments and modeling works were conducted to investigate the autoxidation of *n*-decane. The  
 536 induction periods of *n*-decane were measured in a PetroOxy and the total hydroperoxydes content in  
 537 oxidized *n*-decane was systematically quantified using colorimetric and potentiometric titrations.

538 Modeling works were performed to examine, in depth, the liquid-phase reactivity of *n*-decane. For the  
 539 first time, a physical model was proposed to estimate liquid-phase composition at the beginning of a

540 petroOxy experiment. Indeed, the knowledge of the liquid-phase composition is essential to rigorously  
541 simulate the autoxidation of fuels in PetroOxy experiments. A detailed kinetic model for *n*-decane  
542 oxidation in the liquid phase was developed using a state-of-the-art methodology which was developed  
543 based on solvent-adapted corrections for thermodynamic data (with an equation of state) and for the  
544 most sensitive kinetic data. Kinetic modeling shows a good agreement with experiments. The developed  
545 kinetic model is able to reproduce reliably the measured IP of *n*-decane, at different temperatures, with  
546 a mean relative deviation of 16%. The model was also able to satisfactorily simulate our new  
547 experimental profiles of hydroperoxides measured during PetroOxy tests. In addition, the kinetic model  
548 was validated against literature data, which reported experimental concentration profiles of C<sub>10</sub>-  
549 hydroperoxides, C<sub>10</sub>-ketones and C<sub>10</sub>-alcohols during *n*-decane autoxidation.

550 Kinetic analyses indicate that *n*-decane autoxidation follows a classical chain mechanism applied for the  
551 liquid-phase oxidation. The main consumption pathway of *n*-decane is the H-abstraction by C<sub>10</sub> peroxy  
552 radicals leading to the formation of C<sub>10</sub> hydroperoxides as major products. Similar to *n*-butane  
553 autoxidation modeling, the self-reactions of peroxides radicals (ROO·) and its exit channels branching  
554 ratios play an important role in the reaction fluxes. The uncertainty of the kinetic parameters of this type  
555 of reactions remains high and deserves more studies. The proposed kinetic model is validated for limited  
556 conversions (up to about 15%) of *n*-decane. In order to extend its validity for higher conversions, the  
557 secondary mechanism needs to be further detailed.

558 This work contributes to the systematic understanding of the oxidation stability of *n*-decane and the  
559 validated kinetic model is a first step towards the development of a detailed kinetic model for the  
560 autoxidation of a more complex jet fuel surrogate.

561 **Supplemental material**

562 Simulations of products formation in a Petroxy test, measured IPs, pressure profiles in the PetroOxy,  
563 [ROOH] concentrations, calculations of uncertainties in [ROOH] and the simulation of product profiles as  
564 a function of time for the autoxidation of *n*-decane at 413K are given in supplemental material.

565

566

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