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# Pyrolysis of *n*-Octane at Very Low Concentration and Low Temperature

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G. Scacchi <sup>a</sup>, P.M. Marquaire <sup>a</sup>

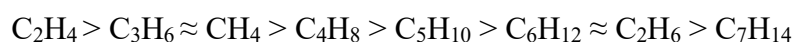
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## **Abstract**

Hydrocarbon pyrolysis concerns many different fields (petroleum geochemistry, refinery, fuel thermal stability, pyrocarbon deposition, etc.). It is therefore studied in a wide variety of temperature-pressure experimental conditions, which strongly affect the chemistry of hydrocarbons cracking.

An experimental study of the pyrolysis of *n*-octane has been performed at very low reactant concentration (1 mbar diluted in inert gas - total pressure 1500 mbar - molar fraction 0.07%) in a closed reactor, at temperatures ranging between 350°C and 450°C, and reaction time from 1 h to 70 h. The major products of the reaction are 1-alkenes (C<sub>2</sub>H<sub>4</sub> to C<sub>7</sub>H<sub>14</sub>), methane and ethane; other alkanes (C<sub>3</sub>H<sub>8</sub> to C<sub>6</sub>H<sub>14</sub>) are minor products. At 450°C and 4 h, the conversion is close to 9% and we observe, in terms of molar fractions:



These experimental results are very different from those of the thermal decomposition of *n*-alkanes at the same low temperature but at high pressure. In particular, the cracking stoichiometric equations (for example: C<sub>8</sub>H<sub>18</sub> = C<sub>6</sub>H<sub>14</sub> + C<sub>2</sub>H<sub>4</sub>) are not observed since alkanes

28 (except methane and ethane) are in very low quantities. This can be explained by the very low  
29 concentration of reactant which limits the bimolecular reactions. In our conditions, the radicals  
30 decompose several times by beta-scissions of C-C bonds when it is possible (unimolecular  
31 reaction), rather than react by H-transfers (metathesis) with the reactant (bimolecular reaction)  
32 which produce alkanes. A detailed free radical mechanism (184 reactions, 16 molecules and 18  
33 radicals – mechanism available as Supplementary Material) allows modelling the experimental  
34 results.

35

### 36 **Keywords**

37 Pyrolysis, *n*-Octane, Thermal decomposition, High dilution of reactant, Kinetic modelling.

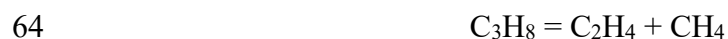
38

### 39 **1. Introduction**

40 Thermal chemistry of hydrocarbons during pyrolysis is important in many research fields as  
41 petroleum geochemistry [1-3], refining of crude oils, cracking of hydrocarbons to produce light  
42 olefins [4-7], thermal decomposition of endothermic jet fuels [8-10], conversion of coal and  
43 biomass to liquid fuels [11-14], depolymerization and recycling of synthetic polymers [15-17],  
44 pyrocarbon deposition for the elaboration of C/C composite materials [18-20], etc. The reaction  
45 conditions considered cover a very wide range of time and temperature, from 150°C during  
46 several millions of years in geochemistry studies, to 900°C for a few milliseconds or seconds  
47 during ethane/propane steam-cracking for instance. The pressure (and consequently the  
48 concentration of hydrocarbons) can also vary in a very large domain, from some millibars to  
49 1000 bar. This diversity of pyrolysis conditions is illustrated in different reviews (e.g. [21, 22]).  
50 Free-radical reaction pathways are considered as the dominant mechanisms for pyrolysis  
51 reactions of organic materials (e.g. [22-24]). The pyrolysis chemistry of the same reactant (and  
52 the main products formed) can largely be modified according to the conditions of the reaction  
53 (temperature, pressure and time). The knowledge of the thermal reaction mechanism and the rate

54 of the different pathways provide means to better understand hydrocarbon pyrolysis as well as  
55 valuable information for kinetic modelling.

56 The study of the pyrolysis of *n*-alkanes is simpler than that of other hydrocarbons or organic  
57 components. It is rather well known because it has been widely studied for a long time (e.g. [24-  
58 34]). Except for methane, the pyrolysis of alkanes consists of free-radical chain reactions. The  
59 chemistry is similar whatever the size of the alkane, yet the number of products formed (and the  
60 size of the reaction mechanism) increases with the number of carbon atoms of the molecule. At  
61 low and usual pressure (0.1-10 bar), the pyrolysis of an alkane produces 1-alkenes and smaller  
62 alkanes or hydrogen by cracking reaction. For example, the pyrolysis of propane leads to two  
63 main stoichiometric equations:



66 This reaction is used for olefin production by steam-cracking for instance.

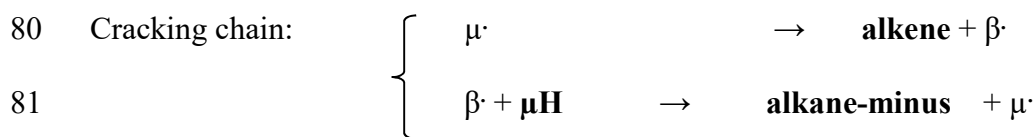
67 In petroleum geochemistry, at high pressure ( $P > 100\text{bar}$ ) and low temperature ( $200 < T < 500^\circ\text{C}$ ),  
68 several alkanes were chosen as model molecules of the alkane family in oils. For instance, *n*-  
69 hexane was chosen [28-29], as well as *n*-pentacosane [35], *n*-hexadecane [36-38] and *n*-octane  
70 [39]. In HP-LT (High Pressure-Low Temperature) conditions, the pyrolysis of alkanes is a long  
71 chain radical-reaction with two major types of propagation chains: a cracking chain and an  
72 alkylation one.

73 In HP-LT conditions, the detailed kinetic model of alkane pyrolysis was already investigated by  
74 several authors (e.g. [24, 29, 40-42]). Therefore, only the major aspects will be recalled here.

75 The pyrolysis of an alkane (here called «  $\mu\text{H}$  » [40]) can be schematized by the following free-  
76 radical cracking mechanism where  $\mu\cdot$  and  $\beta\cdot$  are free radicals.

77 Each cracking propagation chain includes two steps: a decomposition reaction by  $\beta$ -scission and  
78 an H-transfer reaction:

79



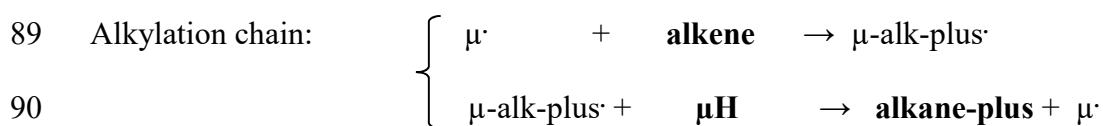
82 The corresponding cracking stoichiometric equation (I) is:



84 where  $\beta\cdot$  is a radical lighter than  $\mu\cdot$ , and « alkane-minus » is an alkane lighter than the reactant  
85  $\mu\mathbf{H}$ .

86 The alkylation propagation chains include two types of free radical reactions: additions of  $\mu\cdot$   
87 radicals to alkenes and H-transfers:

88



91

92 It leads to the alkylation stoichiometric equation (II):



94 where  $\mu\text{-alk-plus}\cdot$  is a radical heavier than  $\mu\cdot$ , and « alkane-plus » is the corresponding alkane  
95 which is heavier than the reactant  $\mu\mathbf{H}$ .

96 At low temperature, the addition reactions are fast and the alkylation chains become important,  
97 because the activation energy of the additions is particularly low (about 25-34 kJ/mol). So the  
98 alkenes become minor products and the global (I + II) stoichiometric equation is:



100 Isomerization reactions also play an important role in product distribution. They can be  
101 unimolecular (1,4 and 1,5 H shift isomerization) and bimolecular by H-transfers between the  
102 reactant  $\mu\mathbf{H}$  and one of its associated radicals  $\mu_i\cdot$  leading to another isomer radical  $\mu_j\cdot$ :



105

106 We already studied and modelled the pyrolysis at high pressure (700 bar) and low temperature  
107 (300-400°C) of *n*-octane [39] and hexadecane [36-38]. The mechanisms described above lead to  
108 modelling results consistent with the experimental ones and they are therefore considered as  
109 sufficiently complete (meaning that no major reaction was missing).

110 For *n*-octane pyrolysis, there are 4 radicals  $\mu_i$  ( $i = 1$  to 4, Figure 1) and 6 stoichiometric  
111 equations. The major products are:

112 - 6 “alkane-minus”:  $\text{CH}_4$  to  $\text{C}_6\text{H}_{14}$

113 - 6 “alkane-plus”:  $\text{C}_{10}\text{H}_{22}$  to  $\text{C}_{15}\text{H}_{32}$

114 and the alkenes are minor products :  $\text{C}_2\text{H}_4$  to  $\text{C}_7\text{H}_{14}$

115 The objective of this work is to provide background information on the radical reactions  
116 occurring during the pyrolysis of *n*-octane at very low reactant concentration (1 mbar diluted in  
117 inert gas - total pressure 1500 mbar - molar fraction 0.07%). It is to be noted that the pressure  
118 dependence of rate constant (“fall-off”) [e.g. 23] is not studied here, because the total pressure is  
119 always above 1 bar. These results are used for constructing a kinetic model. Conditions of low  
120 reactant concentration ( $\leq 10$  mbar of partial pressure) can be found in various processes or  
121 natural conditions: unburned gas and pollutants in fumes [43, 44], low pressure plasmas,  
122 chemical vapor deposition (CVD) [45-48], very low pressure pyrolysis (VLPP) studies [25-28],  
123 atmospheric chemistry (earth or other planets) [49, 50], etc.

124

## 125 **2. Experimental technique**

126 The experimental pyrolysis study of *n*-octane has been performed in gas phase at very low  
127 reactant pressure (1 mbar) in a closed reactor (1 L) made of Pyrex. The *n*-octane is diluted in  
128 argon and the total pressure is close to 1500 mbar. Special care was taken to avoid oxygen traces.

129 The temperatures range between 350°C and 450°C and the reaction time from 1 h to 70 h. The  
130 analysis was performed by two on-line gas chromatographs. Figure 2 shows the flow sheet of the  
131 experimental apparatus.

132 The experimental setup is connected to a vacuum pump ( $< 10^{-3}$  mbar). The gases are introduced  
133 in the reactor via a round-bottomed flask (2 L) which allows the mixing of the reactant and the  
134 inert gas (argon). The liquid reactant (*n*-octane) is introduced by a syringe through a double  
135 septum, protected from the air by a flow of argon. The amount of reactant is very small (10-50  
136  $\mu\text{L}$ ), as to ensure that it is totally vaporized in the mixer which is under vacuum ( $<10^{-3}$  mbar).  
137 Inert gas is introduced by a central injector equipped with 4 nozzles in order to homogenize the  
138 mixture. The total pressure in the mixer reaches 2-3 bar, which allows the expansion of the gas  
139 toward the reactor in a second step.

140 The main three steps of an experiment are:

- 141 - pumping of all experimental setup and heating of the empty reactor,
- 142 - mixing of the reactant-argon mixture in the mixer and waiting for the homogenization  
143 during 10 min,
- 144 - expansion of the gases toward the reactor and beginning of the thermal reaction.

145 During the same experiment, an aliquot fraction is removed at different reaction times from the  
146 reactor by expansion toward the heated analysis line. The amount of the aliquot fraction is very  
147 small and controlled by the pressure in the reactor (maximum drop of pressure = 20 mbar). The  
148 pressure drops are small in regards to the total pressure in the reactor (1500 mbar). Therefore,  
149 several aliquot fractions can be removed from the reactor without disturbing the reaction.

150 The analysis of the reactant and the products is performed by two online Gas Chromatographs.  
151 The chromatograph HEWLETT-PACKARD HP 6850 is equipped with a FID and a semi-  
152 capillary column (GS-Alumina, length 30 m, diameter 0.53 mm). The temperature program of  
153 the oven is as follows: the initial temperature is set at 40°C during 10 min, then a heating rate of  
154 10 °C/min is applied up to 190°C, and the final temperature is kept at 190°C during 20 min. This  
155 allows the analysis of the light alkanes and alkenes (from C<sub>1</sub> to C<sub>8</sub>). In this setup, hydrogen  
156 cannot be measured.

157 The chromatograph SHIMADZU GC 17 is equipped with a FID and a packed column (Alltech,

158 length 3.6 m, stationary phase: 35% BCEF – 10% OV 101), which works isothermally at 50°C.  
159 It is particularly well adapted to the analysis of the heavy alkanes from C<sub>9</sub> to C<sub>15</sub>, but none of  
160 them was detected in the entire study. The GC calibrations were performed by using several  
161 standard mixtures.

162 All data presented in this paper were generally verified by three or four sets of GC data. The  
163 repeatability for the molar fractions is usually less than 5% for the major products. The carbon  
164 balance is typically 1±0.05 and the C/H ratio remains quite constant (between 0.40 and 0.44 at  
165 400°C and between 0.44 and 0.47 at 450°C).

### 166 3. Experimental results

167 The major products obtained are methane, ethane and 1-alkenes (C<sub>2</sub>H<sub>4</sub> to C<sub>7</sub>H<sub>14</sub>). Figures 3 show  
168 the evolution of conversion versus reaction time at different temperatures.

169 At 450°C and 4 h, the *n*-octane conversion is greater than 8% and the three main reaction  
170 products are ethylene, propene and methane, with molar fractions ranging in the following order:



172 followed by higher alkenes and ethane:



174 The minor products observed are alkanes from C<sub>3</sub>H<sub>8</sub> to C<sub>7</sub>H<sub>16</sub>.

175 The evolution of products versus reaction time will be detailed beneath in section 5 dedicated to  
176 the modeling. Figure 4 represents the global evolution of alkanes-minus and alkenes that are the  
177 two families of products.

178 It should be noted that these experimental results are very different from the thermal  
179 decomposition of *n*-alkanes at the same low temperature but at high pressure [39]. In particular,  
180 the cracking stoichiometric equations (for example: C<sub>8</sub>H<sub>18</sub> = C<sub>2</sub>H<sub>4</sub> + C<sub>6</sub>H<sub>14</sub>) are not observed  
181 since C<sub>3</sub><sup>+</sup> alkanes are in very low quantities and the alkylation stoichiometric equation (for  
182 example: C<sub>8</sub>H<sub>18</sub> + C<sub>2</sub>H<sub>4</sub> = C<sub>10</sub>H<sub>22</sub>) are negligible: alkenes are important and alkanes-plus (C<sub>8</sub><sup>+</sup>) are



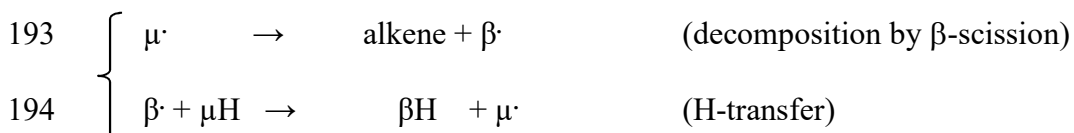
183 not detected. The experimental results at 450°C are given in Table 1 and the details as  
184 Supplementary Materials.

185

#### 186 4. Discussion: kinetic mechanism of *n*-octane pyrolysis at very low concentration

187 In comparison with the study of the pyrolysis of *n*-octane at 700 bar [39], the range of  
188 temperature is the same (350-450°C), but the reactant partial pressure (1 mbar) is very different,  
189 the initial concentration of reactant being lower by more than a factor of 10<sup>5</sup>. The very low  
190 concentration of reactant (called μH) minimizes the importance of the bimolecular reactions in  
191 the mechanism, in particular the H-transfer in the cracking propagation chain:

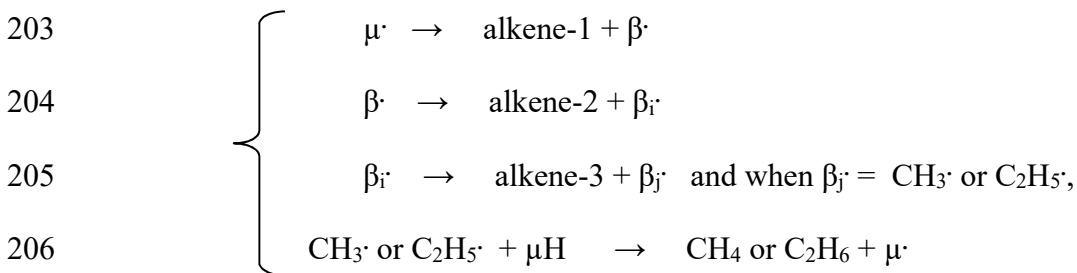
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195

196 In our low concentration conditions, the radicals are decomposed by β-scission of C-C bonds as  
197 much as possible (unimolecular reaction), rather than reacting by H-transfer with the reactant  
198 (bimolecular reaction, which produces an alkane). The methyl and ethyl radicals cannot be  
199 decomposed by β-scission of C-C bonds, so they react by H-transfer with the reactant and  
200 produce methane or ethane and μ· which is the chain carrier radical. At low temperature and low  
201 pressure, the cracking propagation chain becomes:

202

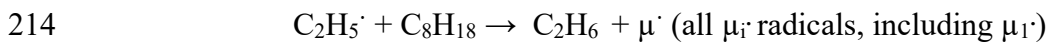
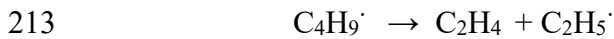
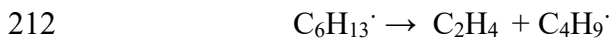
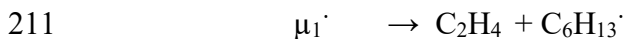


207

208 For the *n*-octane pyrolysis, there are 4 μ<sub>*i*</sub>· radicals (Figure 1), which lead to 4 cracking

209 propagation chains and 4 stoichiometric equations.

210 From  $\mu_1\cdot$  radical, the low pressure propagation chain is:



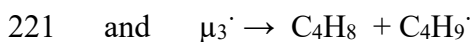
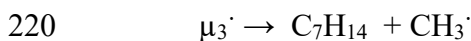
215 The corresponding cracking stoichiometric equation is:



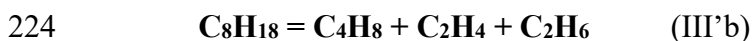
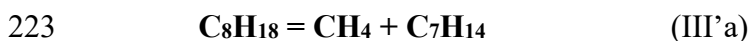
217 From  $\mu_2\cdot$  radical, an equivalent propagation chain leads to the stoichiometric equation:



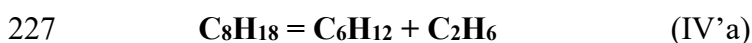
219 In the case of  $\mu_3\cdot$ , there are two possibilities of C-C bond scission:



222 These chain reactions lead to the following stoichiometric equations:



225 In the  $\mu_4\cdot$  radical, there are also two possibilities of C-C bond scission and the stoichiometric  
226 equations are:

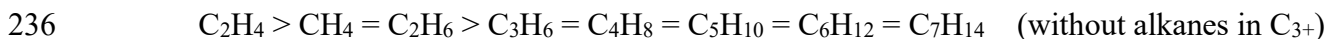


229 So, the stoichiometric equations lead to the formation of two alkanes,  $CH_4$  and  $C_2H_6$ , and all  
230 alkenes from  $C_2$  to  $C_7$ . This well agrees with the main products observed when the pyrolysis of  
231 *n*-octane is performed at very low reactant concentration.

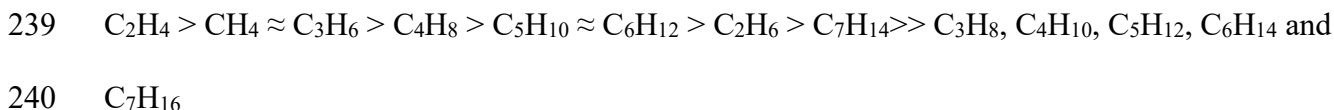
232 If we suppose, in a first approximation, that all the cracking stoichiometric equations have the  
233 same rate, the global stoichiometric equation is:



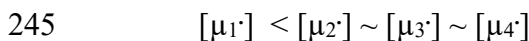
235 That leads to the following classification:



237 The classification has to be compared with our experimental results at 450°C and 4 h (Figures 5  
238 and 6):

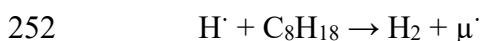


241 The little quantitative differences between the experimental classification and the classification  
242 obtained by the stoichiometric equations could be explained by three approximations. First, the  
243 concentrations of the  $\mu_i\cdot$  are not equal, because  $\mu_1\cdot$  is a primary radical which is less stable than a  
244 secondary one:

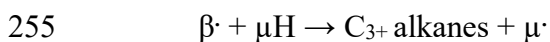


246 Consequently, the stoichiometric equation I' (leading to  $C_2H_6$ ) is overestimated in the argument  
247 which only considers the stoichiometric equations.

248 Another correction is that the decompositions by  $\beta$ -scission of C-H bonds are not completely  
249 negligible at 450°C. They lead to the conversion of ethane into ethylene, which is the major  
250 product:



253 Finally, the formation of  $C_3^+$  alkanes in very low quantities indicates that the H transfer reactions  
254 of  $\beta\cdot$  radicals ( $C_3$ - $C_6$  radicals) are not totally negligible and produce  $C_3^+$  alkanes:



256 This brief kinetic interpretation well explains the chemistry observed for the *n*-octane pyrolysis  
257 at low reactant concentration and low temperature, and the differences in the product distribution  
258 obtained at high concentration and pressure (competition: unimolecular versus bimolecular  
259 reactions).

260

## 261 **5. Modeling of *n*-octane thermal decomposition at very low reactant concentration.**

262 On the basis of these free-radical reactions, a systematic approach is used to build a detailed  
263 mechanism of *n*-octane pyrolysis at low reactant concentration and low temperature. Using  
264 EXGAS software [40, 51], the mechanism (primary and partial secondary) is made of 184  
265 reactions involving 34 species (16 molecules and 18 radicals). The kinetic data originate from  
266 NIST Database [52] or literature and are summarized in [40]. The simulations are performed  
267 using Chemkin II software [53], in a closed isochoric and isothermal reactor (Senkin).

268 The comparison between the experimental results and simulation ones led to the adjustment of  
269 some rate constants by a minor factor (less or equal to 10) in order to better account for main  
270 pyrolysis products. Figures 5, 6 and 7 present the comparison between the experimental data and  
271 the simulation results of the molar fractions (*n*-octane and reaction products) versus time (1 to  
272 240 minutes) at 450°C and 1 mbar of *n*-octane partial pressure (total pressure 1500 mbar - molar  
273 fraction 0.07%).

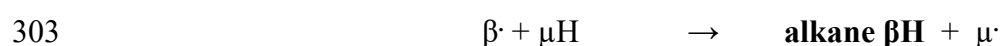
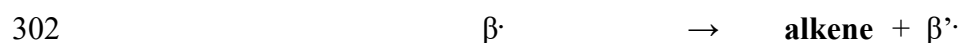
274 The detailed kinetic model accounts for the nature of the products observed as well as for their  
275 amounts, at least semi-quantitatively. The evolution of alkenes, *n*-octane and propane is well  
276 simulated by the kinetic model, although ethene is very slightly over-estimated, and pentene and  
277 hexene are under-estimated, but they are minor products. The overestimation of ethene can be  
278 due to additions of some radicals to alkenes, which are secondary reactions not taken into  
279 account by the model. Methane and ethane are also very slightly overestimated by the model,  
280 probably for the same reason, because methyl and ethyl radicals are the predominant radicals. In  
281 the case of ethane, this may also be due to the decomposition of C-H bonds, which is not  
282 completely negligible at 450°C and leads to the conversion of ethane into ethylene. Nevertheless  
283 we can therefore conclude that the kinetic model is globally validated as well as the kinetic  
284 scheme proposed to explain the chemistry observed at very low concentration.

285 By simulation of the kinetic model, the chain length can be estimated by the ratio of the global  
286 propagation rate to the initiation rate. The main H-transfers with *n*-octane are those implying the

287 methyl and ethyl radicals. The chain length is equal to 120 at 450°C and low *n*-octane  
288 concentration (molar fraction 0.07%). The chain length increases when the temperature  
289 decreases and in our conditions, the chain length is always very high.

290 When a reaction follows a first order kinetic law, the plot of log (1-conversion) versus time must  
291 give a linear relationship and the slope corresponds to the rate constant. Assuming a first order  
292 kinetics, we can estimate the apparent activation energy of *n*-octane pyrolysis: it is close to 218  
293 kJ/mol and the frequency factor is about  $3.63 \times 10^{10}$  (s<sup>-1</sup>), in the range 350°C – 450°C and 1 mbar  
294 of *n*-octane partial pressure. This apparent activation energy is lower than that of alkane  
295 pyrolysis at the same temperatures but at high pressure (100-700 bar), which is close to 284-289  
296 kJ/mol [35, 39, 42, 54].

297 This difference can be explained by the concentration of reactant that is totally different in our  
298 case in comparison to those applied in [35, 39, 42]. The elementary reactions that are important,  
299 are also different, depending on the reaction conditions. Indeed, in the chain propagation, the H-  
300 transfers of radicals with reactant, which produce smaller alkanes than the reactant, are in  
301 competition with the decomposition of this radical by  $\beta$ -scission which produce smaller alkenes:



304 At very low reactant concentration, unimolecular decomposition reactions are greatly favored  
305 over bimolecular reactions, and that leads to very different apparent activation energies.

306

## 307 **6. Conclusion**

308 An experimental study of the pyrolysis of *n*-octane has been performed at very low reactant  
309 concentration (1 mbar diluted in inert gas - total pressure 1500 mbar - molar fraction 0.07%) in a  
310 closed reactor, at temperatures between 350°C and 450°C and reaction time from 1 h to 70 h.

311 The major products of the reaction are 1-alkenes (C<sub>2</sub>H<sub>4</sub> to C<sub>7</sub>H<sub>14</sub>), methane and ethane. These  
312 experimental results are different from the thermal decomposition of *n*-octane at the same low

313 temperature but at high pressure (the major products are only alkanes at 700 bar).  
314 Indeed, at very low reactant concentration, unimolecular decomposition reactions are greatly  
315 favored over bimolecular reactions. In our low concentration conditions, radicals decompose  
316 several times by  $\beta$ -scission of C-C bonds as much as possible (unimolecular reaction), rather  
317 than react by H-transfer with the reactant (bimolecular reaction) which produces an alkane. The  
318 methyl and ethyl radicals cannot decompose by C-C  $\beta$ -scission, and so they react by H-transfer  
319 with the reactant and produce methane or ethane and  $\mu\cdot$ , which is the chain carrier radical.

320  
321 On the basis of these free-radical reactions, a detailed kinetic model (184 reactions, 16 molecules  
322 and 18 radicals) is proposed, which allows a satisfying description of the experimental results:

- 323 - the nature of the principal reaction products is correct,
- 324 -  $C_2H_4$  is the most important product,
- 325 -  $CH_4$  and  $C_2H_6$  are the only two important alkanes,
- 326 - the alkenes from  $C_3$  to  $C_7$  are formed in rather close quantities,
- 327 - the  $C_3^+$  alkanes are very minor products.

328 These results of *n*-octane pyrolysis obtained at very low reactant concentration underline the  
329 crucial role of concentration and partial pressure in the reaction pathways and products of the  
330 alkane pyrolysis. They clearly demonstrate that results obtained at low partial pressure cannot be  
331 extrapolated at high pressure and vice versa.

332

333

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474 TABLE CAPTION

475

476 **Table 1:** Product distribution in mol. % - Octane pyrolysis at 450°C-initial pressure of octane =

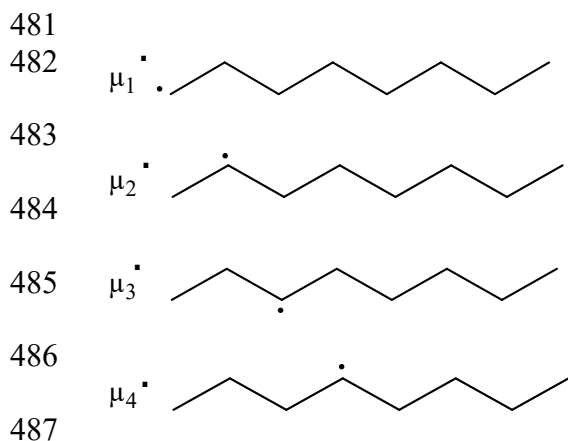
477 1 mbar - total pressure = 1500mbar

478

<b>CH<sub>4</sub></b>	-	$9.40 \times 10^{-4}$	$1.39 \times 10^{-3}$	$1.87 \times 10^{-3}$	$2.25 \times 10^{-3}$
<b>C<sub>2</sub>H<sub>6</sub></b>	-	$2.40 \times 10^{-4}$	$3.21 \times 10^{-4}$	$4.06 \times 10^{-4}$	$5.32 \times 10^{-4}$
<b>C<sub>3</sub>H<sub>8</sub></b>	-	$8.07 \times 10^{-6}$	$1.01 \times 10^{-5}$	$9.46 \times 10^{-6}$	$1.31 \times 10^{-5}$
<b>C<sub>4</sub>H<sub>10</sub></b>	-	$3.23 \times 10^{-6}$	$4.90 \times 10^{-6}$	$4.71 \times 10^{-6}$	$5.27 \times 10^{-6}$
<b>C<sub>2</sub>H<sub>4</sub></b>	-	$3.28 \times 10^{-3}$	$4.79 \times 10^{-3}$	$6.31 \times 10^{-3}$	$7.56 \times 10^{-3}$
<b>C<sub>3</sub>H<sub>6</sub></b>	-	$1.32 \times 10^{-3}$	$1.94 \times 10^{-3}$	$2.65 \times 10^{-3}$	$3.22 \times 10^{-3}$
<b>C<sub>4</sub>H<sub>8</sub></b>	-	$6.56 \times 10^{-4}$	$8.85 \times 10^{-4}$	$1.16 \times 10^{-3}$	$1.40 \times 10^{-3}$
<b>C<sub>5</sub>H<sub>10</sub></b>	-	$5.18 \times 10^{-4}$	$7.50 \times 10^{-4}$	$8.74 \times 10^{-4}$	$9.61 \times 10^{-4}$
<b>C<sub>6</sub>H<sub>12</sub></b>	-	$4.94 \times 10^{-4}$	$6.43 \times 10^{-4}$	$7.50 \times 10^{-4}$	$8.60 \times 10^{-4}$
<b>C<sub>7</sub>H<sub>14</sub></b>	-	$1.02 \times 10^{-4}$	$1.43 \times 10^{-4}$	$2.16 \times 10^{-4}$	$2.02 \times 10^{-4}$
<b>C<sub>8</sub>H<sub>18</sub></b>	$6.65 \times 10^{-2}$	$6.49 \times 10^{-2}$	$6.31 \times 10^{-2}$	$6.21 \times 10^{-2}$	$6.11 \times 10^{-2}$

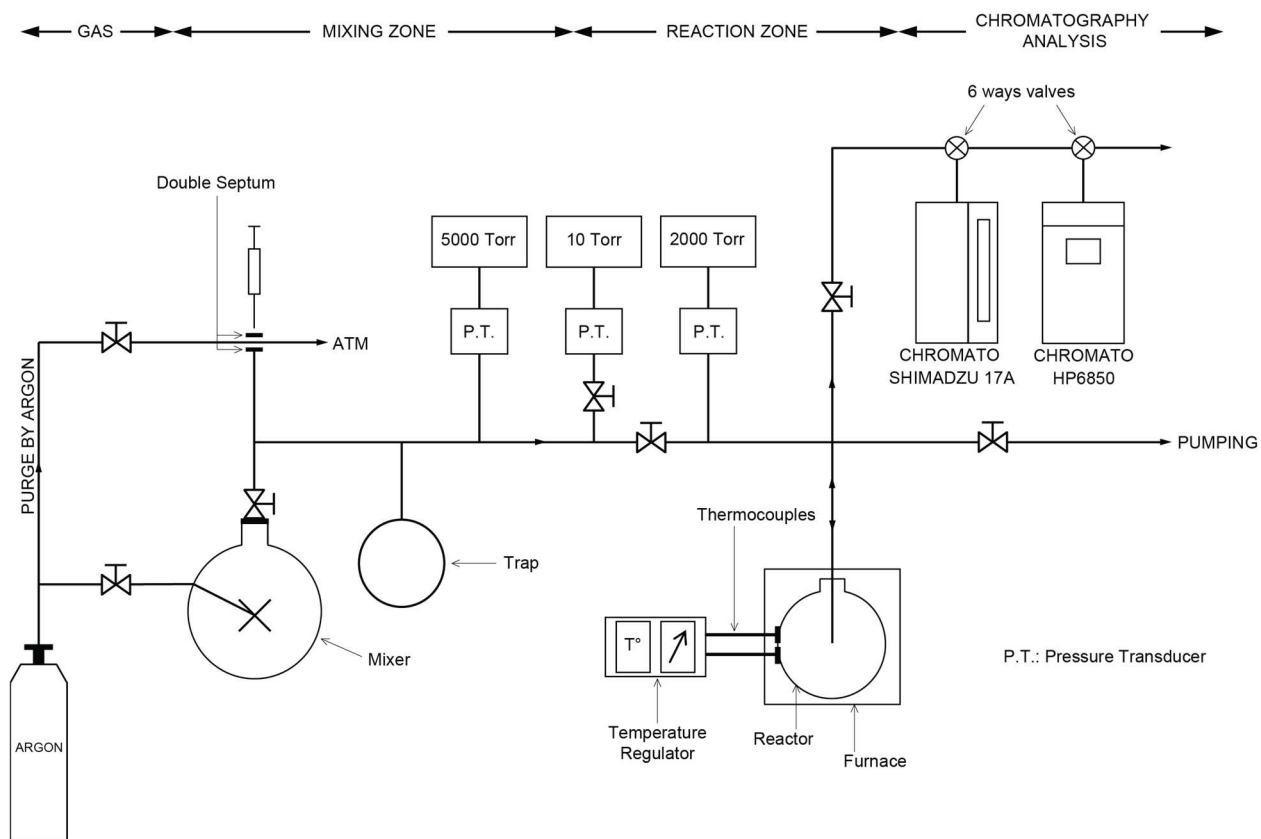
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480 FIGURE CAPTIONS



488 **Figure 1.** The  $\mu_i$  radicals of *n*-octane. Names used in the equations of reactions.

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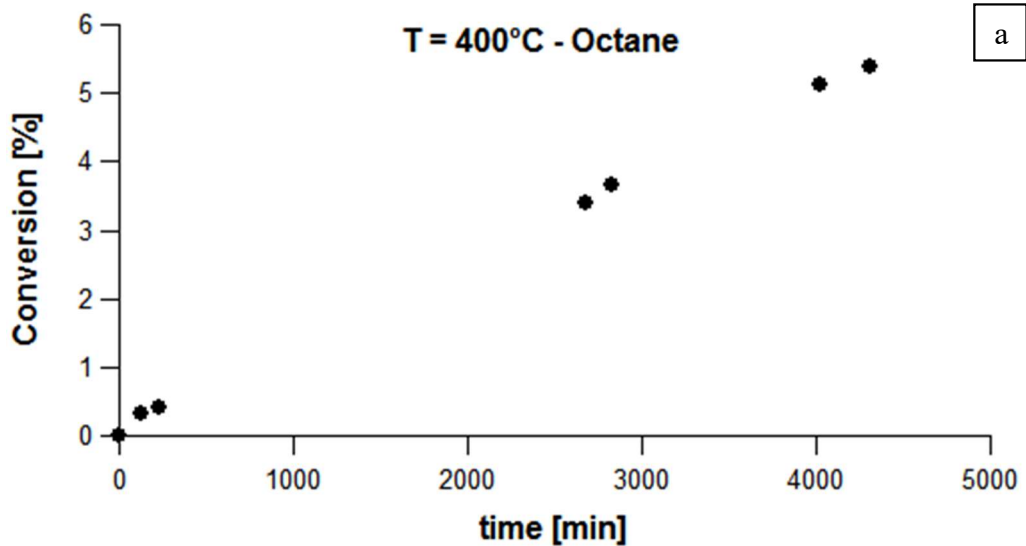
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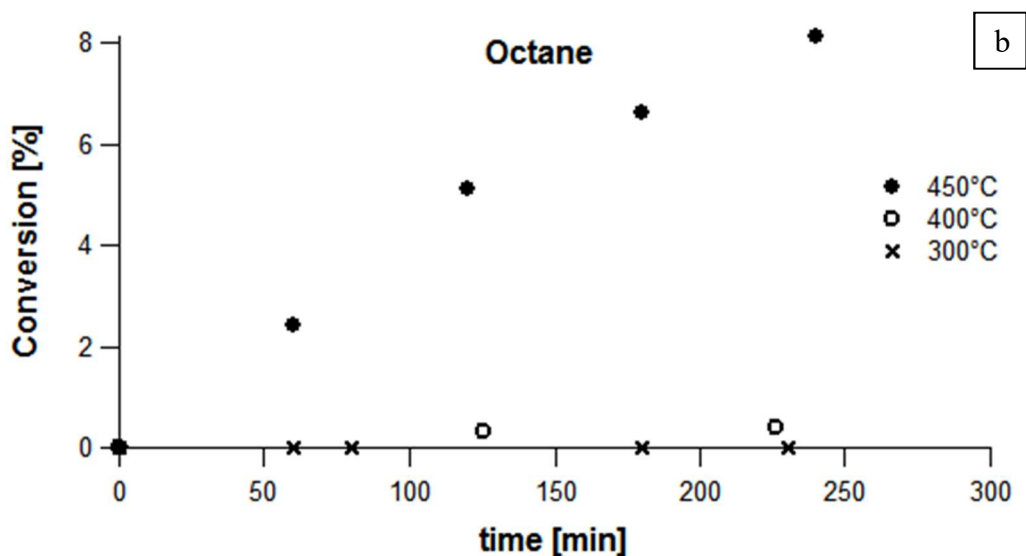
494 **Figure 2.** Flow sheet of the experimental setup.

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501 **Figures 3.** Evolution of *n*-octane conversion as a function of time, a) at 400°C, up to 4300 min,

502 and b) at 350, 400, 450°C, up to 240 min (1mbar initial *n*-octane pressure).

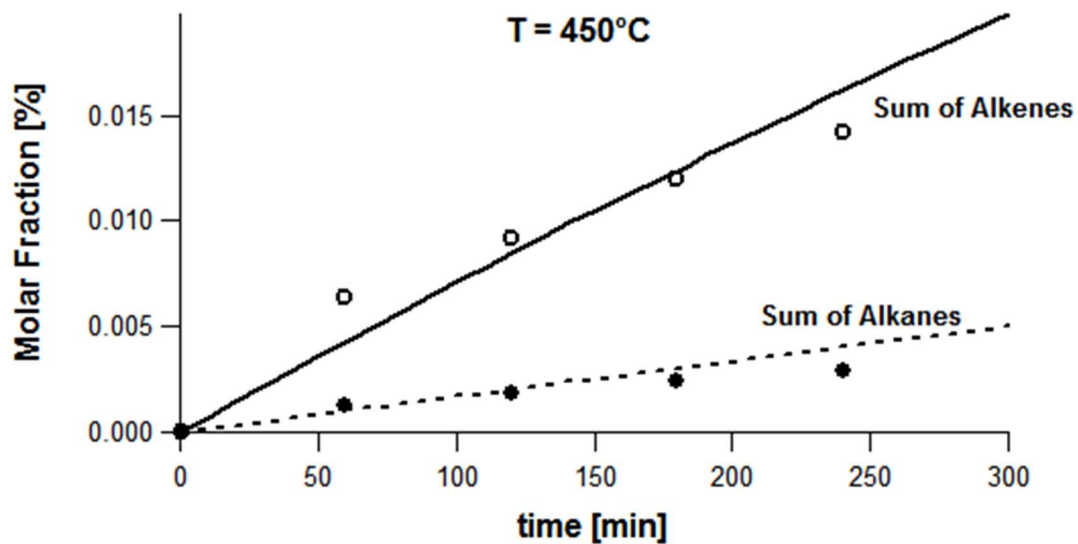
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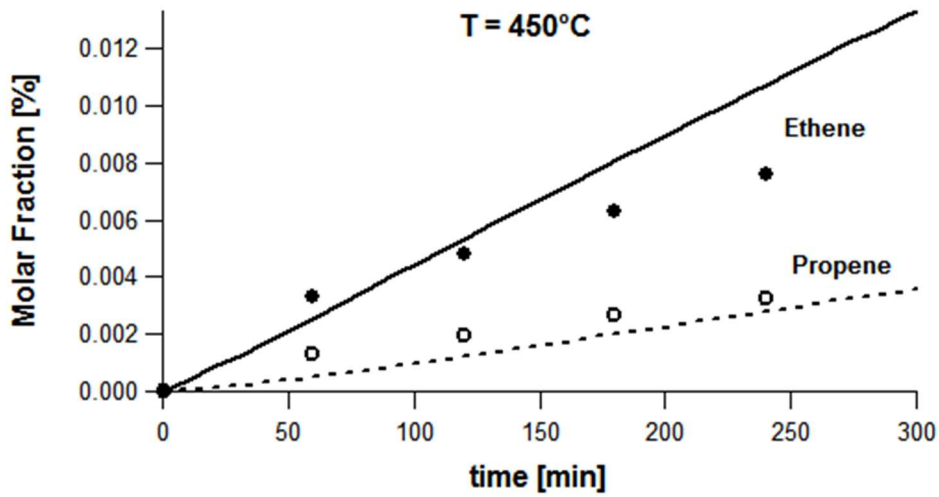


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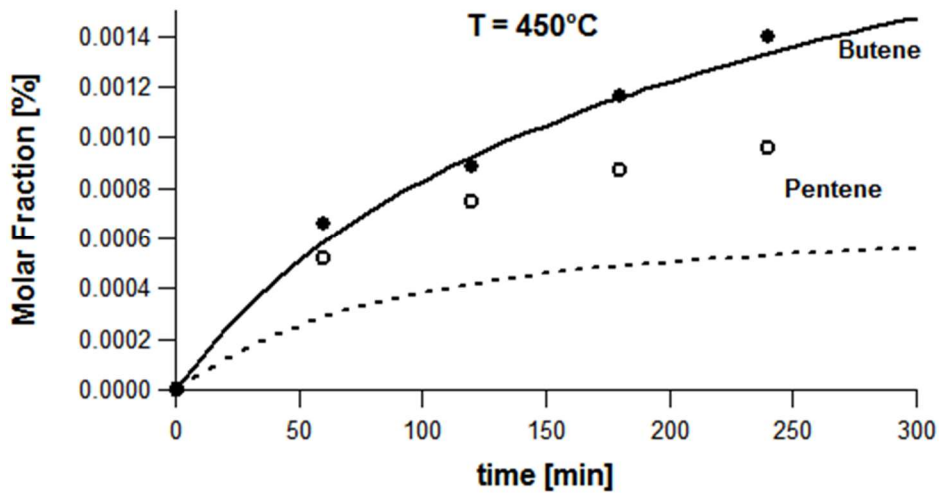
510 **Figure 4.** Comparison between experimental (dots) and simulation (solid lines) molar fractions  
511 of the alkanes-minus and alkenes, as a function of time, at 450°C and 1mbar initial *n*-octane  
512 pressure.

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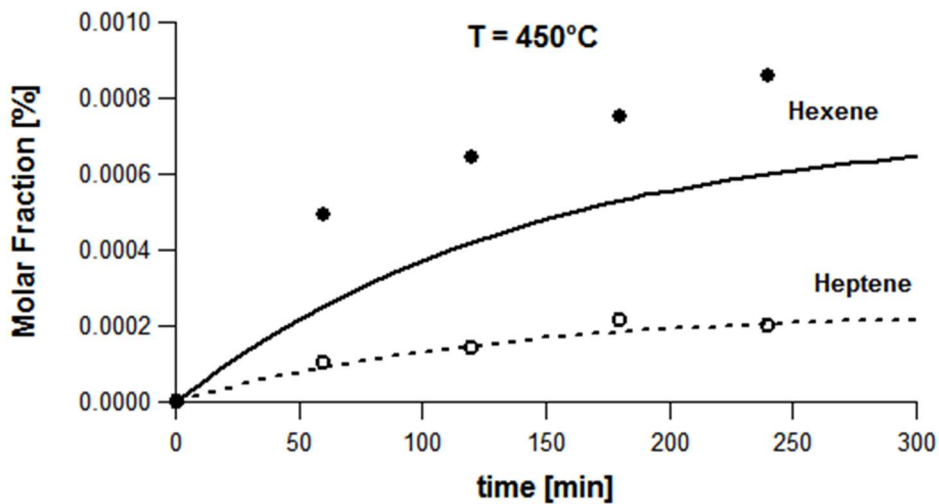




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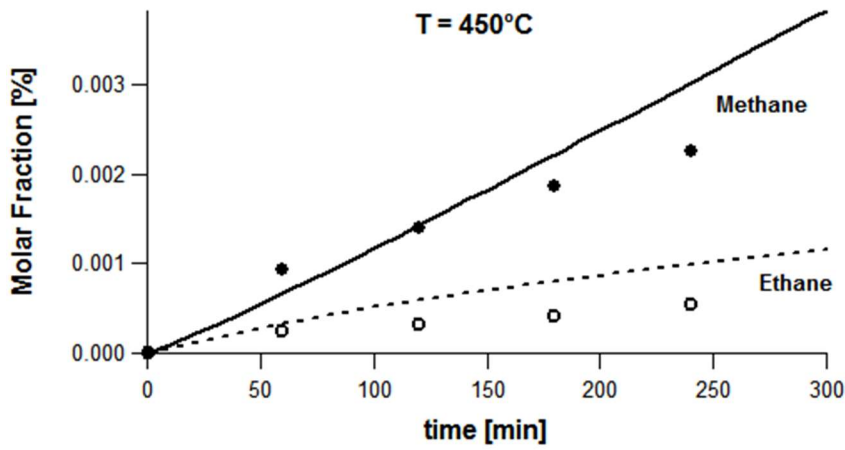
519 **Figures 5.** Comparison between experimental (dots) and simulation (solid lines) molar fractions

520 of the alkenes (from ethylene to heptene), as a function of time, at 450°C and 1mbar initial *n*-

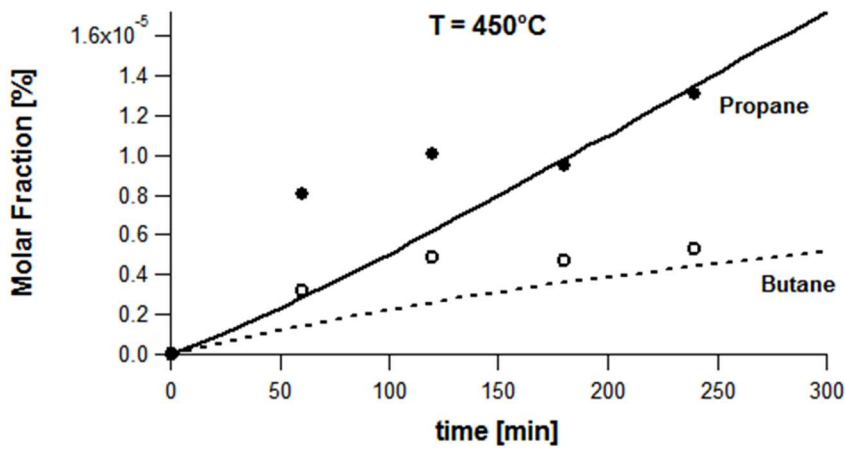
521 octane pressure.

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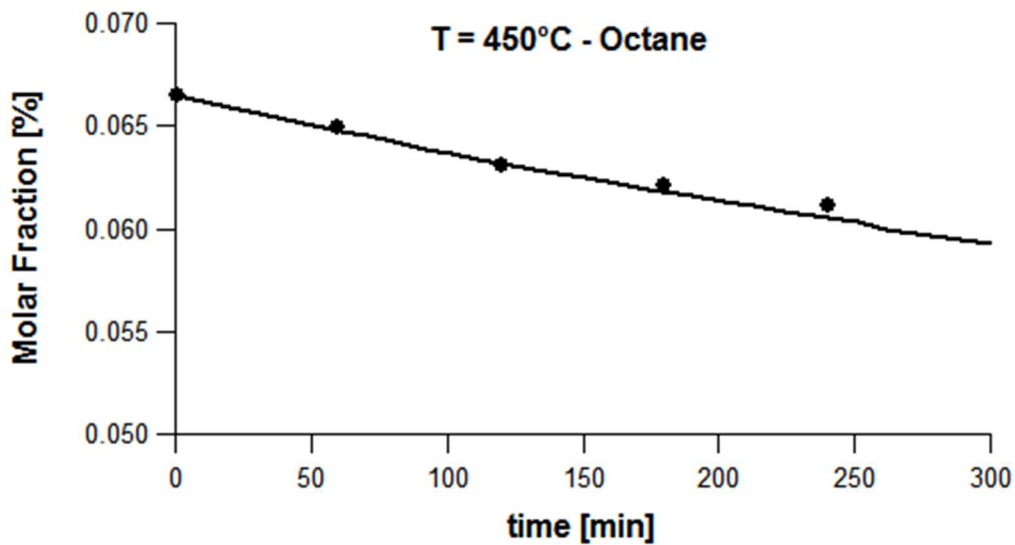
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527 **Figures 6.** Comparison between experimental (dots) and simulation (solid lines) molar fractions  
528 of the alkanes (from methane to butane), as a function of time, at 450°C and 1mbar initial *n*-  
529 octane pressure.



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534 **Figure 7.** Comparison between experimental and simulation molar fraction of *n*-octane, as a  
535 function of time, at 450°C and 1mbar initial *n*-octane pressure.

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