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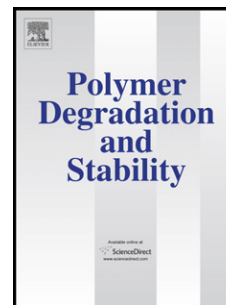
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Kinetic Modelling of High Density PolyEthylene Pyrolysis:

Part 1. Comparison of existing models.

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High Density Poly-Ethylene (HDPE) is one of the possible solid fuels to be used in hybrid rocket propulsion, despite its low ability of rapidly producing combustible gas. This drawback may be balanced by the auto-ignition delay of the pyrolysis products, which would conduct to the increase of the heat release rate in the engine and thus to the one of the regression rate. Six single and multi steps HDPE pyrolysis mechanisms from the literature are compared in this paper to determine their ability to predict the production of by-products and the consumption of HDPE. Transient pyrolysis is observed from 650 K to 823 K at atmospheric pressure and discrepancies up to a factor 7 are found between these mechanisms, despite they are all derived from experimental data. One mechanism is finally selected to conduct a parametric study in more realistic operating conditions for hybrid rocket, up to 1700 K and 100 bar. Identifying and quantifying pyrolysis products are necessary to study their combustion with another detailed mechanism.

Keywords: Polyethylene; pyrolysis; kinetic mechanism; hybrid propulsion.

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19 1. Introduction

20 Nowadays, the interest in polymeric material pyrolysis is increasing. Two principal application fields are found:
21 innovative polymer recycling techniques [1],[2],[3] and solid fuel for aerospace applications [4]. In the first one,
22 detailed chemistry allows controlling the final recycling products through the regulation of the pyrolysis
23 temperature. In the second one, it allows estimating the time constant of involved driving phenomena (multi-
24 component diffusion, auto-ignition delay) as a function of operating conditions. **The study developed in this paper**
25 **specifically focuses on the last field but it is intimately linked to the first one since no kinetic chemistry work**
26 **is available** on HDPE -to the authors' knowledge- **for propulsion need**. It is thus required to take advantage of
27 studies developed in other fields of research despite the operating conditions are not the same.

28 1.1. Need of chemistry in hybrid propulsion

29 During polymer's recycling, the applied temperature and the way to heat-up polymeric material both determine
30 which final products are obtained. The degradation of plastics in a variety of different reactor types has been
31 investigated at various processing scales [5]. Polyethylene and polypropylene are the major components of plastic
32 wastes from domestic refuse. Until now, plastic wastes have been mainly disposed of by landfill or incineration,
33 which are inefficient and highly contaminating techniques [6]. These processes are not acceptable under policies
34 which focus on efficient recovery of raw material and energy. Pyrolysis and gasification processes are promising
35 routes for optimal material recycling. Moreover, pyrolysis of plastics at different temperatures allows the treatment
36 of polymers with simultaneous decomposition and separation. Combustible, gases and energy can be obtained at the
37 same time with only one recycling process. Logically, the first step for a suitable design of any pyrolysis reactor
38 intended to plastic recycling is a high knowledge and a control of the involved kinetics.

39 Hybrid engines are generally composed of an oxidizer tank connected by a valve to the solid fuel tank, which
40 ensures the function of the combustion chamber [4]. One to several channels are drilled in the solid fuel to achieve
41 the combustion with injected gaseous oxidiser [4]. The combustible gas is produced by the pyrolysis of the solid fuel
42 thanks to the heat release due to the combustion. The decomposition products react with the oxidizer depending on
43 their nature, increasing the flame temperature, and favouring pyrolysis process. This brief description could be
44 extended due to the complexity of hybrid engine (injection mode and technologies, multi-ports grain, thermal and

45 mechanical effects in the solid fuel [4]). Numerous fuels have been investigated since the 1970's and polyethylene is
46 one of them because of safety, cost and environment-friendliness reasons, despite its so-called regression rate
47 (related to the conversion rate) remains low, particularly when estimated with low heating rate systems [7]. It can be
48 noted that High Density PolyEthylene is preferred to standard polyethylene for specific weight reason.

49 The most important particularity of the hybrid combustion behaviour is the axial dependency of the combustion.
50 The equivalence ratio varies along the length of the fuel grain, so the temperature and the regression rate fluctuate.
51 There is also a time dependency because the cross-section of the gas flow increases due to the solid regression. The
52 dynamics of the chemical, thermal and hydraulic phenomena changes during the functioning. To understand the
53 physics of the process and the fuel-oxidiser interaction, a transient and reactive numerical simulation is required.
54 Such a Computational Fluid Dynamics code (CFD) should consider the chemistry with a particular interest since it is
55 the driving process of the system (heat release and combustible generation) [7]. For this reason, this work is
56 intended to determine if existing detailed kinetic models from open literature can be used for this purpose. Their
57 validity for hybrid application must be verified and their compatibility with later combustion study is mandatory.

58 1.2. Available kinetic mechanisms for HDPE pyrolysis

59 As it was pointed out by Mastral *et al.* [8], only few kinetic data are available in open literature on HDPE
60 pyrolysis. Moreover, Poutsma [9] clearly showed the inconsistency of numerous experimental results from the
61 literature. Concerning the pyrolysis modelling, several authors worked for a recycling purpose [1],[2],[5],[6].
62 Because of different aims, the range of validity (in terms of operating conditions) differs from one mechanism to an
63 other one. The set of considered species vary and their consumption is rarely taken into account. Since they can be
64 complementary, they all are useful to better understand the phenomena. Nevertheless, it is not possible for
65 consistency reason to use them all in a CFD code and, as a consequence, it is necessary to determine the most
66 relevant under hybrid rocket engine conditions. The available mechanisms are either analytical single step Arrhenius
67 laws or detailed kinetic mechanisms with primary and secondary reaction sets. The polymer pyrolysis usually
68 involves three general reaction pathways, depending on the polymer nature [10]:

- 69 - **Unzipping (UZ)**: successive enchain β -scission reactions, which yield monomer from the polymer chain.
- 70 - **Backbiting (BB)**: specific intramolecular hydrogen transfer reactions followed by mid-chain β -scission to
71 yield a series of specific low molecular weight products (LMWPs).

72 - **Random scission (RS):** involves intermolecular hydrogen transfer followed by mid-chain β -scission to yield
73 a diverse set of LMWP.

74 Depending on the predominant chemical bond in polymeric material, there will be a dominance of one of the
75 three degradation modes. Polyethylene is especially susceptible to both BB and RS pathways because every mid-
76 chain hydrogen yields an equally stable secondary carbon radical. Understanding the competition between RS and
77 BB is important for fully understanding the polyethylene pyrolysis mechanism [1]. In addition, the particular role of
78 free radicals in the pyrolysis process should be addressed since the elaboration of kinetic scheme clearly depends on
79 these compounds [11].

80 The kinetic mechanism of Németh *et al.* [12] considers most of these possible reaction pathways. The polymer
81 thermal degradation is accounted by 7541 reactions and 1014 species. To develop their mechanism, the authors took
82 most of the possible reactions into account before removing the less important ones. This mechanism can be
83 integrated with a stiff differential solver in order to have a numerical simulation of the physical process. A strong
84 domination of alkenes production is verified [12]. The authors compared numerical data to experimental product
85 distribution obtained in a micropyrolyzer reactor at 500 °C and 20 s of reaction time. The model fairly predicts the
86 degradation of polymer at low conversion rate despite 13% of uncertainty is found for propane and up to a factor 6
87 for butane for example. Further researches are needed to improve the accuracy of this mechanism at higher
88 conversion rate. A second detailed mechanism has been found [1]. Levine and Broadbelt elaborated a kinetic
89 scheme with 11000 reactions and 151 species on the basis of previous experiments [13]. They used a population
90 balance based lumping technique to limit the number of polymeric species, which is of strong interest for CFD
91 application. Indeed, the number of species plays a role in the computing cost. Limiting it is favourable for future
92 numerical simulations. The way the lumping of heavy species could be achieved will be discussed in a companion
93 paper, where the major role of alkenes will be detailed [14]. An excellent agreement between numerical results and
94 experimental data was obtained by Levine and Broadbelt and the mechanism is considered to be validated for the
95 temperature range 693 K – 773 K. They demonstrated dominance of RS reactions for thermal degradation of HDPE.
96 Unfortunately, the present authors faced a major difficulty to test the mechanism of Levine and Broadbelt since it is
97 not freely available, even on demand (no ASCII file compatible with CHEMKIN like programs). Thus, it has not
98 been possible to test it in the present work. In addition, the final aim of the present study is to implement a kinetic
99 mechanism in a CFD code. As a result, considering available mechanism is the first requirement.

100 Reduced mechanisms are also available. Al-Salem and Lettieri [2] proposed a simple model, where kinetic
101 parameters are obtained from experimental data under isothermal conditions. With only 7 basics reactions and 5
102 groups of species, this mechanism can be easily integrated in a CFD code. Nevertheless, it is not suitable for hybrid
103 rocket application. The main reason is that they considered a gas entity without taking its chemical composition into
104 account. To perform combustion studies, the gas composition is of first importance because the auto-ignition delay
105 will vary depending on the species (a large difference exists between acetylene and methane for example). Elordi *et*
106 *al.* [15] proposed a similar size mechanism, which has been validated for a larger temperature range (723 K to
107 988 K) than the one of Salem *et al.* (773 K – 873 K). It is based on the Westerhout's kinetic mechanism [3] but it fits
108 experimental data with better accuracy. Nevertheless, with 6 basics reactions and 6 groups of species, Elordi's
109 mechanism is again too much simplified. It does not allow considering the variation of gas products composition as
110 a function of the operating conditions. The same drawback is observed for the work of Johannes *et al.* [16]. They
111 developed a simple kinetic model with 4 groups of species and 8 basics reactions, which takes into account the non-
112 linear effect of temperature increase during material pyrolysis. Similarly, Mastral *et al.* [8] studied HDPE pyrolysis
113 up to 973 K in fluidised bed reactor for residence time lower than 2.6 s. They focused on the aromatic formation and
114 they aimed at proposing a small size mechanism (seven groups of compounds are defined). Finally, some global
115 Arrhenius laws can be found to represent the HDPE pyrolysis. They are specifically oriented for hybrid rocket
116 engine but they are based on the regression measures of the solid surface under given operating conditions [4]. As a
117 consequence, they do not allow considering multi-species formation and consumption. The work of Paik and Kar
118 [17] can also be mentioned. They estimated the one step Arrhenius parameters of HDPE pyrolysis as a function of
119 the size of the samples with Thermogravimetric (TG) apparatus. Discrepancies up to 12 % were found.

120
121 To the authors' knowledge, no detailed kinetic mechanism considering chemical composition of by-products
122 with limited size suitable for CFD applications (less than 2000 reactions) does exist in open literature. For this
123 reason, the only mechanism to allow computing the pyrolysis products distribution, despite its size, is the one of
124 Németh *et al.*. It is used in the following section to test its validity in comparison with all other available
125 mechanisms and experimental data.

126 2. Computations of HDPE pyrolysis

127 2.1. Comparison of existing mechanisms from literature

128 The work referring to Németh *et al.* in this section means that it has been achieved by the present authors with
129 the Németh *et al.*'s mechanism of HDPE pyrolysis (validated by the Németh *et al.* at 773 K). No modification of the
130 kinetic scheme has been done. It is purely apply in the operating conditions of other existing data to enable a
131 comparison of the validity of all the HDPE pyrolysis studies available in open literature.

132 2.1.1. Comparison with Al-Salem and Lettieri experimental data

133 Al-Salem and Lettieri conducted experiments with TG balance in which 15 mg samples were heated under
134 undetermined heating rate. Their results are related to solid species, not only HDPE. To make the comparison with
135 Németh *et al.*'s mechanism data, species products with more than 18 carbon atoms are considered to be in solid
136 phase (Figure 1a). An overall fair agreement is found over the time duration of 600 s for both temperatures (773 K
137 and 823 K). The final solid conversion degree changes from 85 wt.% at 773 K to 100 % at 823 K. The fact that a
138 better agreement is found for both mechanisms under long residence time shows that the initial reaction steps
139 probably differ. In addition, numerical computations allow considering instantaneous heating while it is not possible
140 experimentally. This impacts the initial transient behaviour of the data. The timescale to be considered in hybrid
141 propulsion is typically less than 1 s at elevated temperature, over 1000 K. For this reason, the initial instants are of
142 high importance to represent the dynamics of the phenomena. The disagreement in terms of time, for a given level of
143 solid conversion, will be analysed in section 2.1.6 to be summarized with other data.

144 ***Figure 1 should be placed here.***

145 2.1.2. Comparison with Johannes *et al.*' mechanism

146 Johannes *et al.* [16] studied 4 g HDPE samples pyrolysis in autoclave from 723 K to 813 K under steady-state
147 conditions with successive runs at different residence time. These conditions are closer to the numerical simulation
148 assumptions (instantaneous heating) because no heating slope is considered. This is also closer to hybrid rocket
149 conditions. Johannes *et al.* proposed variable Arrhenius parameters, depending on the temperature, because of the
150 material heating-up process. This correction of kinetic coefficients slows down the pyrolysis process. Their data
151 have been reproduced in the present work with fixed values within an in-house code. The comparison with Németh

152 *et al.*'s data (Figure 1b) shows discrepancies which are stronger with variable coefficients than with fixed ones,
153 particularly for the initial time. The earliest steps of conversion shows a better agreement between Németh *et al.*'s
154 data and those obtained with fixed coefficient values of Johannes *et al.*. After a time of 2 s, the discrepancies
155 strongly increase. It can be noticed that it is not clear in the Johannes *et al.*' paper if the autoclave apparatus allows
156 the gas products to go out or if the system is closed. This is important because it impacts the pressure of the system.
157 As a consequence, this may contribute to understand the discrepancies found on Figure 1b.

158 2.1.3. Comparison with Budrugaec's experimental data

159 The TG experimental data of Budrugaec [18] have been considered despite low heating rates from 2.99 K.min^{-1}
160 to 12.36 K.min^{-1} were used, which do not correspond to hybrid engine (10^3 to 10^6 K.s^{-1}). Time delays of almost two
161 hours are found for temperatures between 673 K and 708 K, before the polymer's pyrolysis starts [18]. The material
162 is not instantaneously heated contrary to numerical simulation. To eliminate this inconsistency, an offset is
163 introduced in all Budrugaec's experimental curves (data are shifted to the left), neglecting the heating-up process
164 (Figure 1c). The kinetics of HDPE pyrolysis is faster at higher temperature. For this reason, the agreement between
165 numerical and experimental results is better at 708 K than at 673 K. This comparison underlines the difficulty to find
166 appropriate validation data. To the author's knowledge, the only available data on HDPE pyrolysis obtained with
167 flash pyrolysis apparatus are those of Németh *et al.* while other authors mainly use TG balance. To confirm this
168 point, additional computations have been made by programming numerically the temperature as a function of time
169 (Figure 2). A much better agreement is found compared to isothermal conditions. The transient behaviour from
170 100 min to 300 min for the 673 K test case (Figure 2a) still differs while at 708 K (Figure 2b), the dynamics of
171 pyrolysis is better, which is satisfying for high temperature application of the Németh *et al.*'s mechanism. The errors
172 will be computed and presented in section 2.1.6.

173 ***Figure 2 should be placed here.***

174 2.1.4. Comparison with Broadbelt and co-workers' experimental results

175 De Witt and Broadbelt [13] carried out low pressure HDPE pyrolysis experiments at 693 K with different
176 reactant loadings. The species quantification, expressed in molar yield, is given in Table 1. Molar yield is defined by
177 the authors as the number of moles of product divided by the moles of initial reactant charge, which is determined
178 thanks to the molecular weight of HDPE ($125000 \text{ g.mol}^{-1}$). Levine and Broadbelt [1], on the basis of De Witt and

179 Broadbelt experimental data, proposed a very detailed kinetic mechanism (11000 reactions and 151 species). A
180 conversion of the experimental data, furnished by Broadbelt and co-workers, has been achieved by the present
181 authors to enable comparing them with numerical results (Table 1). A graphical comparison of alkenes (Figure 3a)
182 and alkanes (Figure 3b) distribution shows stronger deviation for low molecular weight species than for heavier
183 ones. The discrepancies are generally lower for alkenes (Figure 3c). For alkenes, the minimal deviation is found for
184 medium molecular weight species. For alkanes distribution, errors are less important for very low molecular weight
185 species, like methane, or for species with more than 20 carbon atoms. It is interesting to observe the ethylene
186 formation because this is one of the major compounds to be produced by HDPE pyrolysis. The experiments of
187 Broadbelt and co-workers show a molar fraction of 7 mol.% for ethylene after 150 minutes (Figure 3b), while for
188 Németh *et al.*' mechanism, a stationary phase was already reached after 16.7 min, corresponding to an ethylene
189 content over 20 mol.%. The deviation between these results remains high. This may be attributed to the dynamics of
190 heating. De Witt and Broadbelt placed a Pyrex ampoule containing HDPE in an isothermal sand bath. The time
191 constants of the system are not given.

192 Another comparison is proposed for the pyrolysis time at which Németh *et al.*' kinetic mechanism gives the same
193 ethylene quantity as De Witt and Broadbelt experimental results. The aim is to clarify whether the source of error is
194 related to a time shift or to a chemical reactions set problem. For a time of 433 s, a comparison of alkanes and
195 alkenes distribution is done (see Supplementary materials: Figure 9). Strong discrepancies are still visible and the
196 errors should be compared for the two selected time (after stabilisation at 150 min and for the same ethylene content
197 at 433 s). For alkanes distribution (see Supplementary materials: Figure 9c), the errors are practically the same, and
198 still too high to consider the results as satisfactory. For alkenes distribution (see Supplementary materials: Figure
199 9d), the deviations between the experimental and numerical results are decreasing for the species with more than 16
200 atoms of carbon. However, they are much higher for low molecular weight species. A large difference can be found
201 for the 1-pentadecene, for example. Again, these results underline the need for appropriate experimental data,
202 particularly for hybrid rocket application.

203 ***Figure 3 should be placed here.***

204 ***Table 1 should be placed here.***

205 2.1.5. Comparison with single step Arrhenius law

206 Finally, a comparison with the results obtained with one step Arrhenius law is given in Figure 4. The values for
207 the activation energy and the pre-exponential factor from [4] have been obtained at 650 K with TG measurements
208 ($E_c = 251040 \text{ J.mol}^{-1}$, $A_c = 2 \cdot 10^{16} \text{ s}^{-1}$, $n=1$). The overall agreement is average. Discrepancies from 30 % and up to
209 several orders of magnitude are found. It is not possible to determine which set of data is correct but, at least, these
210 calculations demonstrate the strong differences which can be obtained between simple Arrhenius laws (which are
211 generally used in hybrid rocket applications) and highly detailed mechanisms. Again, the heating rate may be
212 responsible of these differences. It can be noted that this Arrhenius law has been used at 950 K by the authors [4]
213 and compared to other experimental data with discrepancies over 50 %. In addition, no product formation is
214 proposed with this one step law, which explains why no validation on other species, such as C_2H_4 , can be proposed.

215 ***Figure 4 should be placed here.***

216 2.1.6. Estimation of time discrepancies during transient pyrolysis

217 The discrepancies between Németh' *et al.*s data and the other ones from literature have been expressed in terms
218 of HDPE or pyrolysis products content. Nevertheless, this is not sufficient since a time shift of two identical curves
219 would not be seen and such case would present disagreement on the chemical composition. Thus, the time for which
220 80 mol.% of conversion rate is obtained is determined for all the cases presented above. The relative time error is
221 computed by dividing the time shift between Németh *et al.* data and the other ones by the highest value of the two
222 (Table 2). A strong disagreement is generally observed. The smallest difference under isothermal conditions is
223 observed with Al-Salem and Lettieri data at 773 K. Due to the wide diversity of experimental conditions and
224 probably of initial HDPE nature, composition and purity (presence of additives), the comparisons of results turn to
225 be highly complicated. For example at 673 K, a time of 19500 s is found for Budrugaec and 2400 s for the one step
226 law, based on experiments. The results obtained with Németh *et al.*' mechanism are in this range (5700 s). This
227 behaviour is due to the heating rate. Indeed, a minimum error is obtained for Budrugaec comparison with time-
228 function programming of the temperature. When the experimental conditions are thus better reproduced numerically,
229 the Németh *et al.*'s mechanism is found to be of fair agreement with experimental results. This tends to confirm the
230 validity of Németh *et al.*' mechanism despite additional validation should be done with appropriate experimental
231 data in order to guarantee the mechanism's validity and its suitability for the range to be considered in hybrid rocket.

232 ***Table 2 should be placed here.***

233 2.2. Further analysis of the Németh *et al.* mechanism

234 In order to conduct combustion study to determine auto-ignition delays, it is required to have a pyrolysis scheme
235 which is able to fairly predict the consumption of HDPE and the production of the main gas products (ethylene,
236 methane, ethane,...). In addition, this mechanism should be compatible with CFD applications. The one of Dagaut
237 and Cathonnet [19] is expected to be used in the CFD code (size of 1592 reactions and 207 species). The Németh *et*
238 *al.*'s mechanism is the only available mechanism to answer to the first criterion. It may answer the second one if 1-D
239 simulations are conducted but it needs to be reduced for 2-D computations. The reduction of detailed kinetic
240 mechanism is a complex work and before doing it, it must be verified that the initial mechanism is well suited for
241 the application. For this reason, the above section 2.1 aimed at investigating the validity of the scheme, without
242 clearly demonstrating it due to the lack of suitable validation data in open literature. Thus, it is decided to conduct an
243 additional work on the behaviour of the mechanism in operating conditions close to those expected for hybrid
244 propulsion. This work is presented in the present section 2.2.

245 A brief parametric study on pressure and temperature effects is achieved to observe the results on HDPE
246 consumption and on ethylene production. For each thermal plateau (700 K, 1200 K and 1700 K), the pressure is
247 varied from 1 bar to 100 bar (under isobaric conditions). The time for which 80 mol.% of conversion rate is obtained
248 is determined. An intrinsic limit of the homogeneous kinetic scheme is finally presented.

249 2.2.1. Parametric study

250 The transient variations of molar fraction under different pressure and temperature conditions are shown in
251 Figure 5 at 700 K (see Supplementary materials Figure 10 for 1200 K). At 700 K (Figure 5), the pressure slows the
252 pyrolysis process and it reduces the amount of ethylene content (from 32 mol.% at 1 bar to 10 mol.% at 100 bar). It
253 has a lighter effect on HDPE consumption. The pyrolysis times are very high, over 15 min, and they are not
254 compatible with the conditions to be encountered on hybrid rocket engine (residence time of oxidiser flow less than
255 1 s [4]). At 1200 K (see Supplementary materials: Figure 10), the pyrolysis time is strongly reduced to the order of
256 millisecond. This time is in conformity with the dynamics of phenomena involved in hybrid rocket [7].
257 Nevertheless, this temperature is outside the range of experimental validation proposed by Németh *et al.* [12]. The
258 kinetic mechanism accuracy is not guaranteed. Increasing the pressure at 1200 K slows down the ethylene
259 production but in a very slight way (from 45 mol.% to 40 mol.% at 1 bar and 100 bar respectively). Additional

260 computations at 1700K have shown characteristic pyrolysis time of the order of the nanosecond, which is
261 questionable. This behaviour is due to the exponential form of Arrhenius law which is enhanced by the temperature.
262 The Németh *et al.*' mechanism probably reaches its limit of validity over 1200 K.

263 ***Figure 5 should be placed here.***

264 The pressure effect which is clear at 700 K (Figure 5), tends to get negligible at 1200 K in the range 1 bar –
265 34 bar and it could be omitted as a first approximation (Figure 6a). This is mainly acceptable for stabilised
266 conditions (after 2 ms) but for transient state (from initial time to 2 ms), the pressure has a greater impact. The
267 coupled effect of temperature and pressure can be observed for ethylene which formation is important in terms of
268 combustion. For a fixed pressure value between two temperatures (Figure 6b) the higher the pressure, the more
269 important the curve's slope. That means that the effect of temperature increase is stronger for high pressure. The
270 pyrolysis times related to a HDPE conversion rate of 80 mol.% are summarized in Table 3. The temperature rise
271 accelerates the pyrolysis phenomenon. For fixed temperature, high pressures favour HDPE consumption except for
272 some conditions, like 700 K and over 10 bar for example. This is clearly visible on Figure 7a where low temperature
273 conditions present a minimum of pyrolysis time versus the pressure. This minimum depends on the pressure and the
274 corresponding pressure can be plotted as a function of the temperature (Figure 7b). The exponential trend highlights
275 the difficulty to find a pressure at temperature over 900 K, for which the pyrolysis time would be minimum. This
276 specific behaviour is further detailed in next section since the pressure effect is more complex than only impacting
277 the concentration of gas species and thus enhancing the molecular collisions.

278 ***Figure 6 should be placed here.***

279 ***Table 3 should be placed here.***

280 ***Figure 7 should be placed here.***

281 2.2.2. *Limit of the mechanism used in a 0-D closed vessel*

282 The pyrolysis calculations are achieved in this study under 0-D configuration. The perfect gases law is used to
283 determine the density, which is of importance in energy equation and in the calculation of species concentrations. If
284 the chemical products are not produced in gas phase, the resulting error is not negligible. For example, the HDPE
285 density is 950 kg.m^{-3} but at 700 K and 1 bar, the value of 9.673 kg.m^{-3} is computed. This is not realistic and it can be

286 corrected by choosing an artificially high pressure (approximately 100 times more), as it is done by Nemeth *et al.*
287 **The drawback of such method is that it would also impact the gas phase.** Then, the pressure effect would not
288 properly be taken into account. As a consequence, it must be determined when the solid content is higher than the
289 gas content. If the first is higher than the second, an artificial pressure should be considered. To the opposite, no
290 artificial pressure should be considered if the gaseous compounds are the major products. This would allow suitably
291 addressing the chemistry in gas phase.

292 For two different pressures and for temperatures from 700 K to 1700 K, the yields of solid and of gaseous
293 compounds have been computed to determine which method should be considered (Figure 8a). For temperatures
294 under 850 K at 1 bar and under 1000 K at 34 bar, the solid species content is higher than the gas one. Consequently,
295 for these cases, the pressure should be increased strongly to simulate the right polymer density (Figure 8b). The
296 error which is due to the pressure setting can be observed by comparing Figure 5a and Figure 5d since the
297 temperature is lower than 850 K. A factor 3 is found on the ethylene formation and a strong time delay is also
298 remarkable. This highlights the difficulty of considering single phase computations. Nevertheless, this will be
299 corrected in future work because this mechanism will be implemented in a 2-D geometry considering both solid and
300 gas phases with appropriate description.

301 *Figure 8 should be placed here.*

302 By fixing the pressure at 112 bar and the temperature at 773 K, the polymer density is 950 kg.m^{-3} . The
303 comparison of these results with those from Németh *et al.*' experiments, for the same temperature and residence
304 time, gives fortunately a very good agreement (see Supplementary materials: Figure 11).

305 3. Conclusion

306 A strong lack of chemical kinetic mechanisms and of experimental data has been found in actual bibliography
307 for polyethylene pyrolysis. The rare data must be carefully considered before applying them to propulsion
308 application since they are generally obtained for polymer's recycling purpose. The temperature and pressure levels
309 and the heating rate differ up to several orders of magnitude. As a consequence, a comparative work has been
310 achieved in this paper to determine the consistency of existing works. Only six studies with single step or multi-step
311 mechanisms have been found. They have been compared with the most detailed mechanism to determine their
312 respective efficiency. Up to 85 % of time shift has been found. A factor 7 is even found between two experimentally

313 based works. This is due to the test conditions, to the heating rate and to the apparatus which differ between these
314 studies. Due to the wide diversity of experimental conditions and initial HDPE nature, comparing these mechanisms
315 turns to be highly complicated. The conclusion of this comparative work is that further experiments in conditions of
316 use are necessary to get reliable data for correcting existing mechanisms. A parametric study has been achieved on
317 temperature, time and pressure effect with the most detailed kinetic scheme to observe its strength and weak points,
318 particularly for hybrid rocket application. The high temperature range (over 1200 K) is probably not appropriate.

319 Nevertheless, the most detailed mechanism is the only one to quantify the gas products by identifying the
320 different species instead of using a global approach with a single gas compound. This fine description is compulsory
321 for a later step to conduct a combustion study aiming at determining the auto-ignition delays of the pyrolysis
322 products. A two dimensions numerical code is under development to combine both pyrolysis and combustion studies
323 in a hybrid combustor. The existing detailed kinetic mechanism must now be reduced to an acceptable size for
324 Computational Fluid Dynamics simulation (less than 2000 reactions and 300 species instead of 7541 reactions and
325 1014 species presently). This work is presented in a companion paper [14]. Only later, experimental work will be
326 achieved to get reliable data and to correct the reduced mechanism, which should be easier to handle than the
327 original one.

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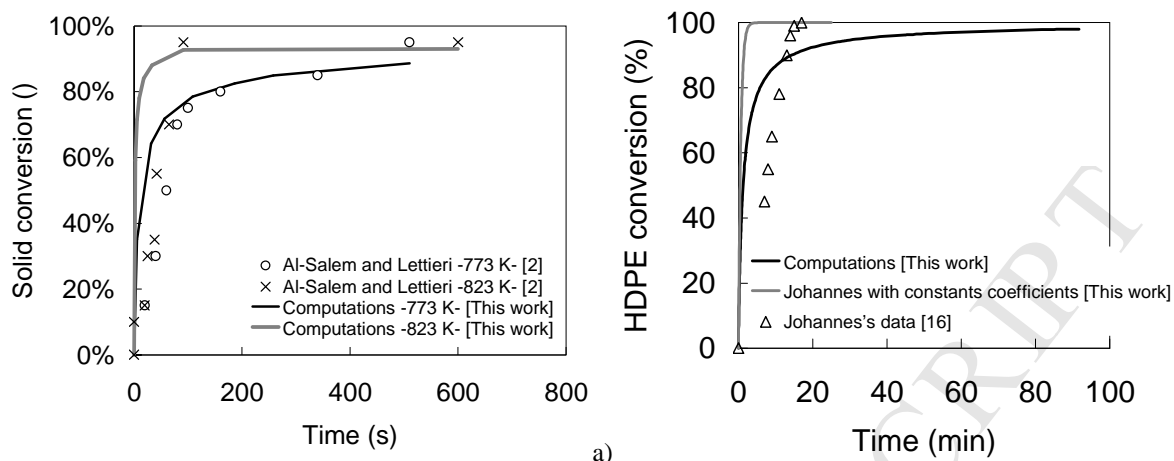
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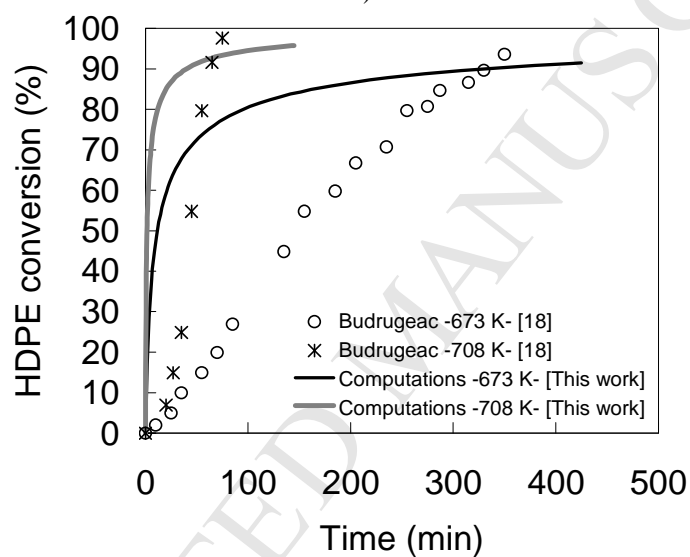
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- 374 Figure 1. Comparison of computations with Németh *et al.* mechanism with experiments of Al-Salem and Lettieri (a),
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- 376 Figure 2 Comparison between Budrugaec's experimental results at 673 K (a) and 708 K (b) with time-function
377 results obtained with Németh *et al.*'s mechanism.
- 378 Figure 3 Comparison of computations with Broadbelt and coworkers' experimental results [13] after 150 minutes of
379 pyrolysis at 693 K for alkanes (a) and alkenes distribution (b) and corresponding error distributions (c).
- 380 Figure 4 Comparison of detailed kinetic mechanism numerical results (—) with one step Arrhenius law (****) at
381 650 K (a) and 673 K (b).
- 382 Figure 5. HDPE consumption and C₂H₄ production at 700 K and 1bar (a), 10 bar (b), 34 bar (c), 100 bar (d)
- 383 Figure 6 Pressure influence (1 bar, 10 bar, 34 bar) on HDPE consumption and C₂H₄ production for different
384 temperature values: 1200 K (a) and Influence of temperature in C₂H₄ production for different pressure values (b)
- 385 Figure 7 Evolution of pyrolysis time with pressure and temperature increase (a) and temperature-pressure
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- 387 Figure 8 Gas and solid content during HDPE pyrolysis (a) and domain of applicability of the Németh *et al.*
388 mechanism (b).
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- 391 Table 1. Identification and quantification of HDPE thermal degradation products [13] at low pressure and 693 K
392 after 150 minutes of pyrolysis. Comparison with numerical results of Németh *et al.*' mechanism.
- 393 Table 2. Relative errors found when comparing data with those from Németh *et al.*' mechanism.
- 394 Table 3 Pyrolysis time for different operating conditions.
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- 398 SUPPLEMENTARY MATERIAL
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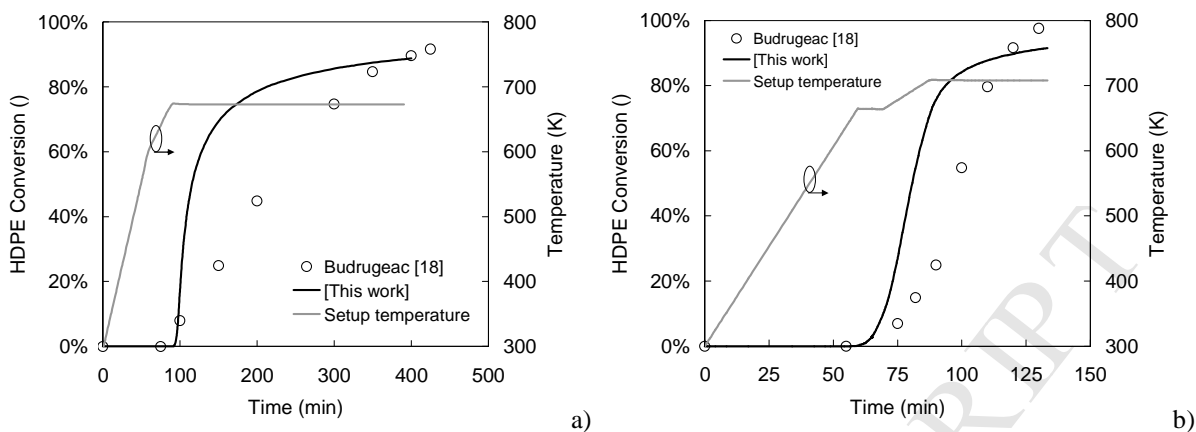


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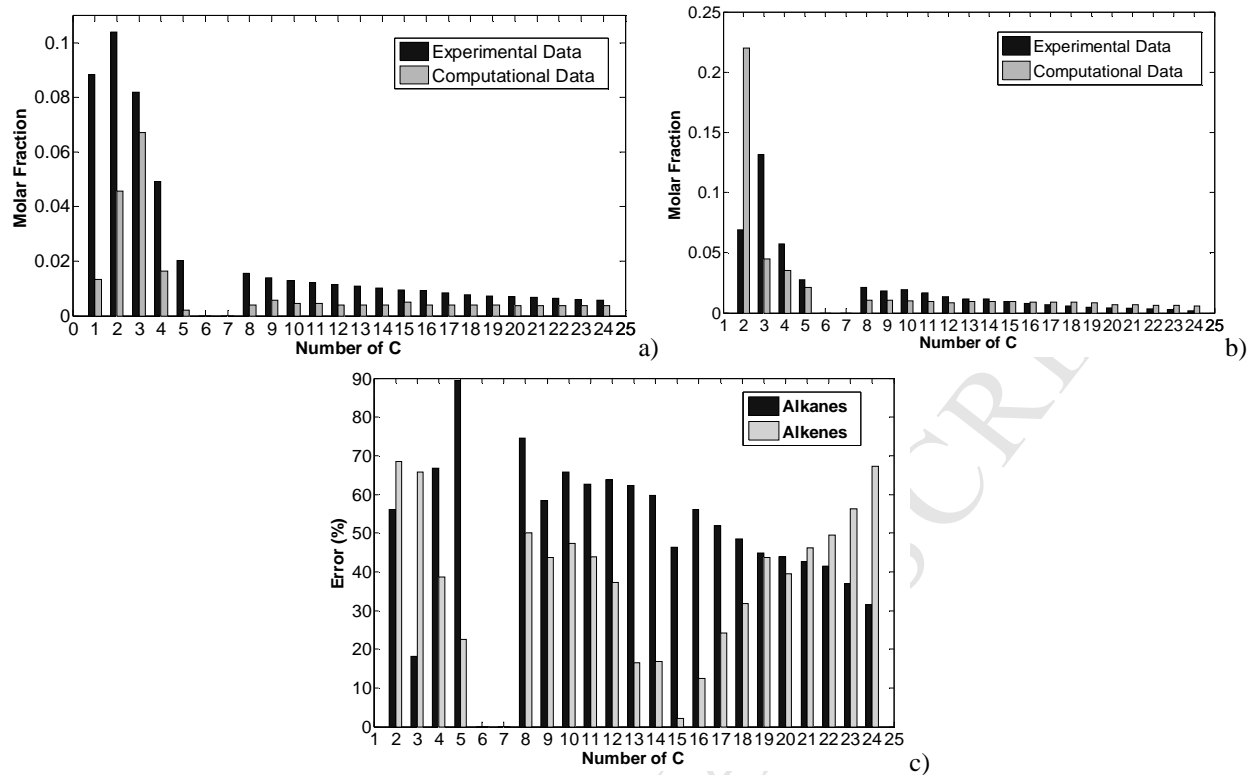


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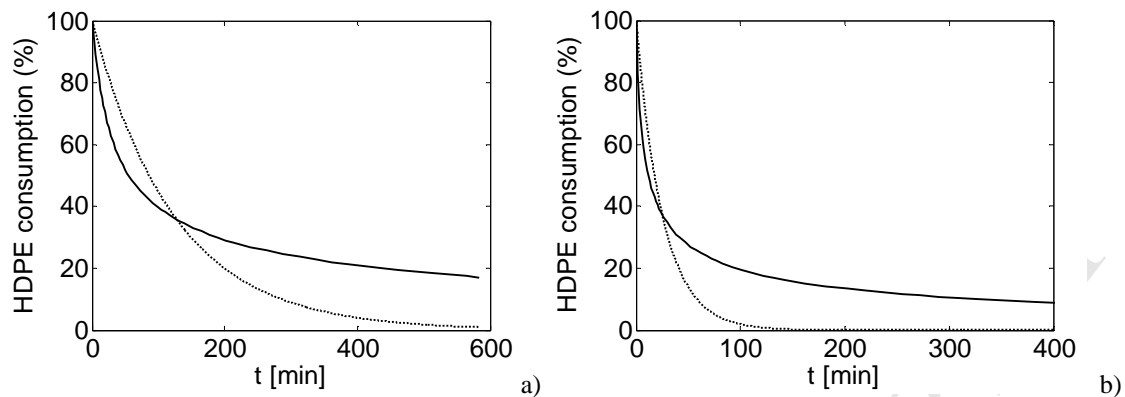
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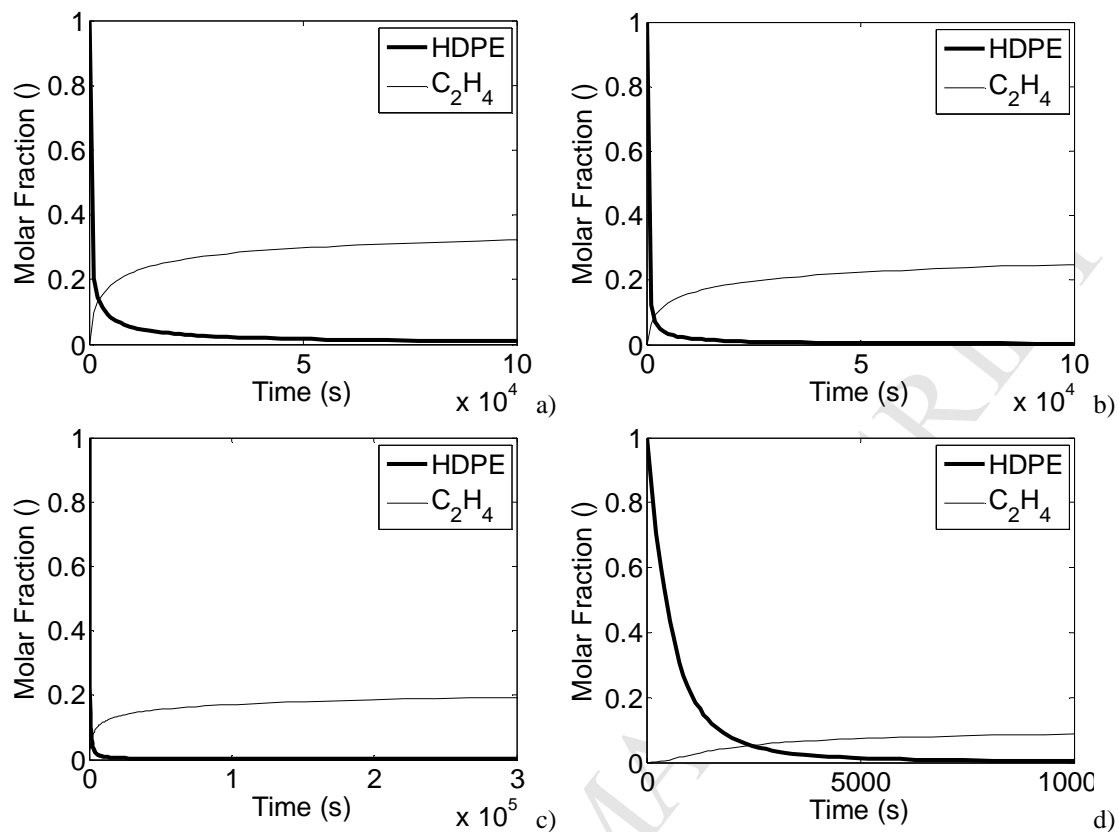
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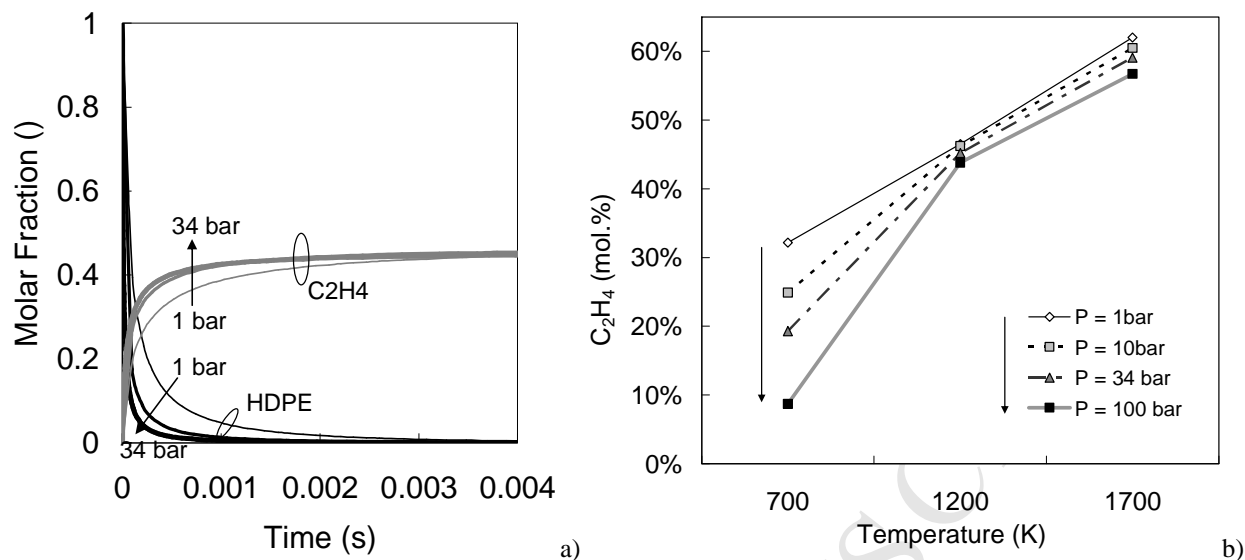
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 421 **distributions (c).**



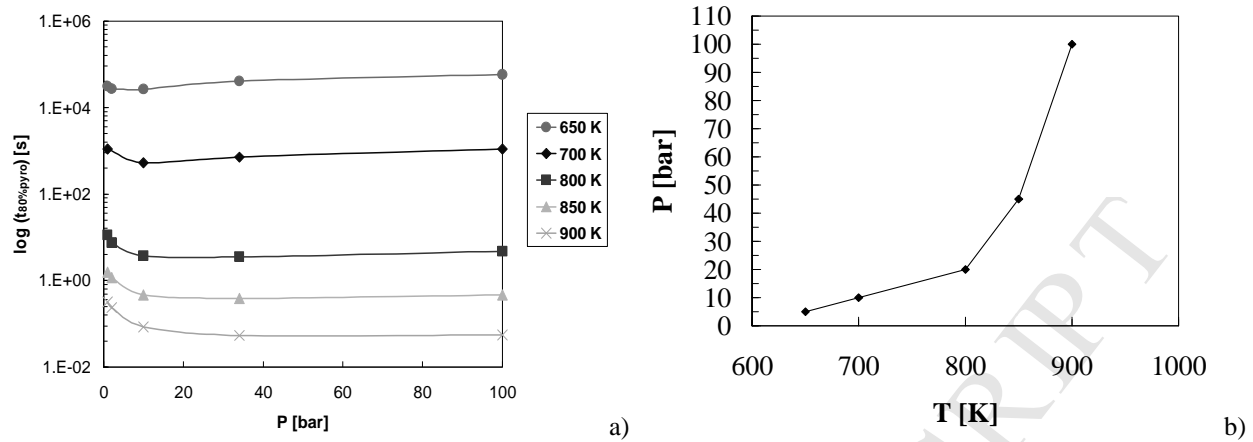
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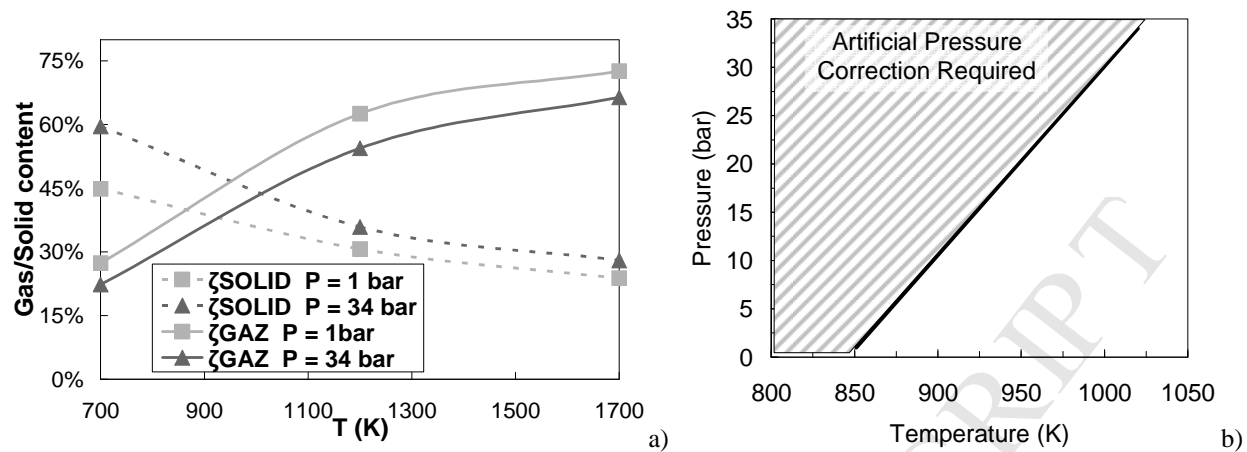
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 431 **temperature values: 1200 K (a) and Influence of temperature in C₂H₄ production for different pressure values**
 432 **(b)**
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435 **Figure 7 Evolution of pyrolysis time with pressure and temperature increase (a) and temperature-pressure**
436 **coordinates of the minimum of pyrolysis time (b)**

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440 **mechanism (b).**
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442

443 **Table 1. Identification and quantification of HDPE thermal degradation products [13] at low pressure and**
 444 **693 K after 150 minutes of pyrolysis. Comparison with numerical results of Németh *et al.*' mechanism.**

	Normalized Yield [25]	Corresponding Molar Fraction	Computed Molar Fraction with Nemeth's mech.
methane	35.46	0.088	0.013
ethylene	27.83	0.069	0.220
ethane	41.71	0.104	0.046
propylene	52.72	0.132	0.045
propane	32.86	0.082	0.067
1-butene	23.09	0.058	0.035
n-butane	19.75	0.049	0.016
1-pentene	11.08	0.028	0.021
n-pentane	8.15	0.020	0.002
1-octene	8.51	0.021	0.011
n-octane	6.24	0.016	0.004
1-nonene	7.41	0.018	0.010
n-nonane	5.55	0.014	0.006
1-decene	7.77	0.019	0.010
n-decane	5.24	0.013	0.004
1-undecene	6.64	0.017	0.009
n-undecane	4.94	0.012	0.005
1-dodecene	5.53	0.014	0.009
n-dodecane	4.62	0.012	0.004
1-tridecene	4.68	0.012	0.010
n-tridecane	4.4	0.011	0.004
1-tetradecene	4.62	0.012	0.010
n-tetradecane	4.09	0.010	0.004
1-pentadecene	3.85	0.010	0.009
n-pentadecane	3.85	0.010	0.005
1-hexadecene	3.23	0.008	0.009
n-hexadecane	3.73	0.009	0.004
1-heptadecene	2.76	0.007	0.009
n-heptadecane	3.39	0.008	0.004
1-octadecene	2.41	0.006	0.009
n-octadecane	3.15	0.008	0.004
1-nonadecene	1.95	0.005	0.009
n-nonadecane	2.9	0.007	0.004
1-eicosene	1.73	0.004	0.007
n-eicosane	2.8	0.007	0.004
1-heneicosene	1.49	0.004	0.007
n-heneicosane	2.72	0.007	0.004
1-docosene	1.34	0.003	0.007
n-docosane	2.65	0.007	0.004
1-tricosene	1.11	0.003	0.006
n-tricosane	2.47	0.006	0.004
1-tetracosene	0.8	0.002	0.006
n-tetracosane	2.28	0.006	0.004

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Table 2. Relative errors found when comparing data with those from Németh *et al.*' mechanism.

	Temperature	$t_{80\%}$ Németh (s)	$t_{80\%}$ other (s)	Relative Time Error	
Al-Salem and Lettieri*	773 K	83	160	48.25 %	
	823 K	8	82	89.95 %	
Budrugaec	Isothermal	673 K	5700	19500	70.76 %
		708 K	720	6616	89.12 %
	Time-function	673 K	22971	19500	15.11 %
		708 K	5645	6616	14.68 %
Johannes <i>et al.</i>	773 K	348	60 (k_i cte)	-82.18 %	
			675 (k_i var)	-48.44 %	
One step Arrhenius law	650 K	25800	12000	53.48 %	
	673 K	5700	2400	57.90 %	

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* Pyrolysis time for conversion of all solid species, not only HDPE consumption

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Table 3 Pyrolysis time for different operating conditions.

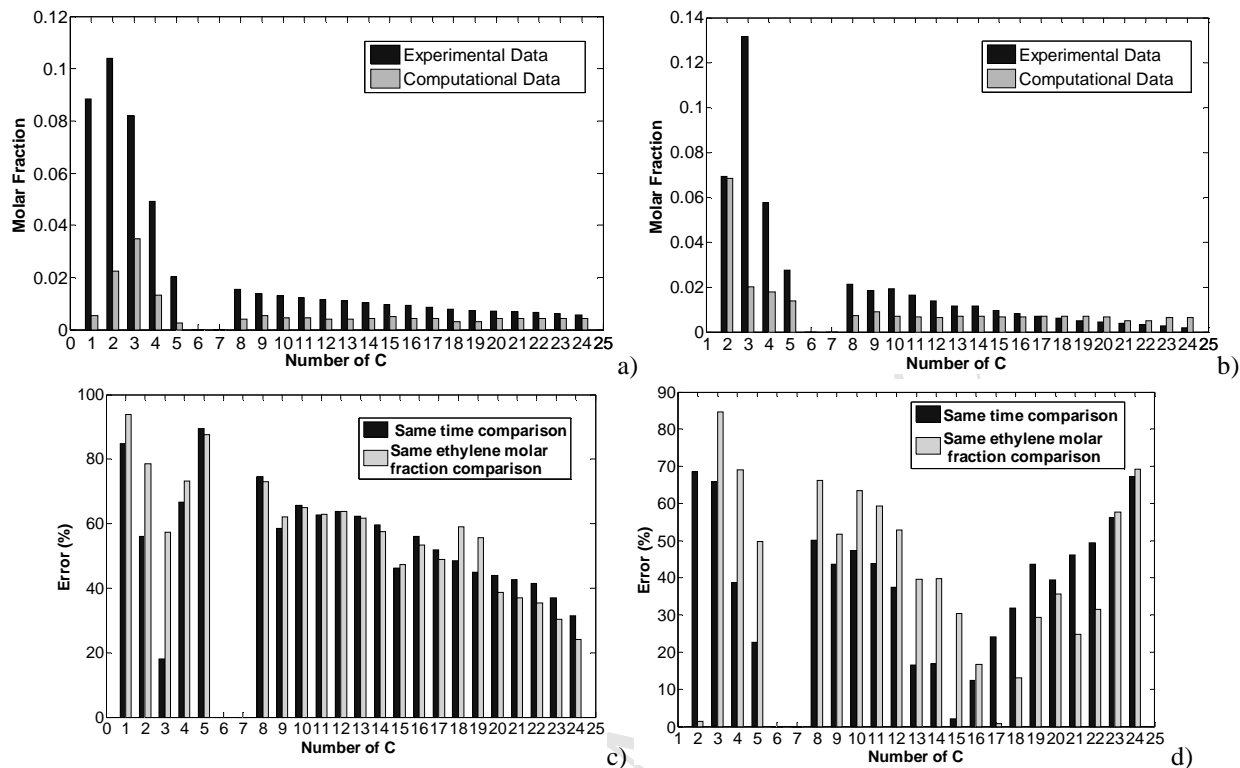
	650 K	700 K	800 K	850 K	900 K	1200 K	1700 K
1 bar	$3,12 \cdot 10^4$ s	1090 s	11,1 s	1,57 s	$3,19 \cdot 10^{-1}$ s	$2,46 \cdot 10^{-4}$ s	$8,16 \cdot 10^{-8}$ s
2 bar	$2,68 \cdot 10^4$ s	---	7,33 s	1,15 s	$2,35 \cdot 10^{-1}$ s	---	---
10 bar	$2,59 \cdot 10^4$ s	523 s	3,72 s	$4,65 \cdot 10^{-1}$ s	$8,42 \cdot 10^{-2}$ s	$8,54 \cdot 10^{-5}$ s	$6,5 \cdot 10^{-8}$ s
34 bar	$4,05 \cdot 10^4$ s	716 s	3,49 s	$3,77 \cdot 10^{-1}$ s	$5,31 \cdot 10^{-2}$ s	$3,9 \cdot 10^{-5}$ s	$4,94 \cdot 10^{-8}$ s
100 bar	$5,73 \cdot 10^4$ s	1090 s	4,70 s	$4,65 \cdot 10^{-1}$ s	$5,44 \cdot 10^{-2}$ s	$1,96 \cdot 10^{-5}$ s	$3,41 \cdot 10^{-8}$ s

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SUPPLEMENTARY MATERIALS

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455 **Figure 9 Comparison between computations after 493 s of pyrolysis and Broadbelt and coworkers'**
 456 **experimental results [13] after 150 minutes of pyrolysis for the same ethylene production during HDPE**
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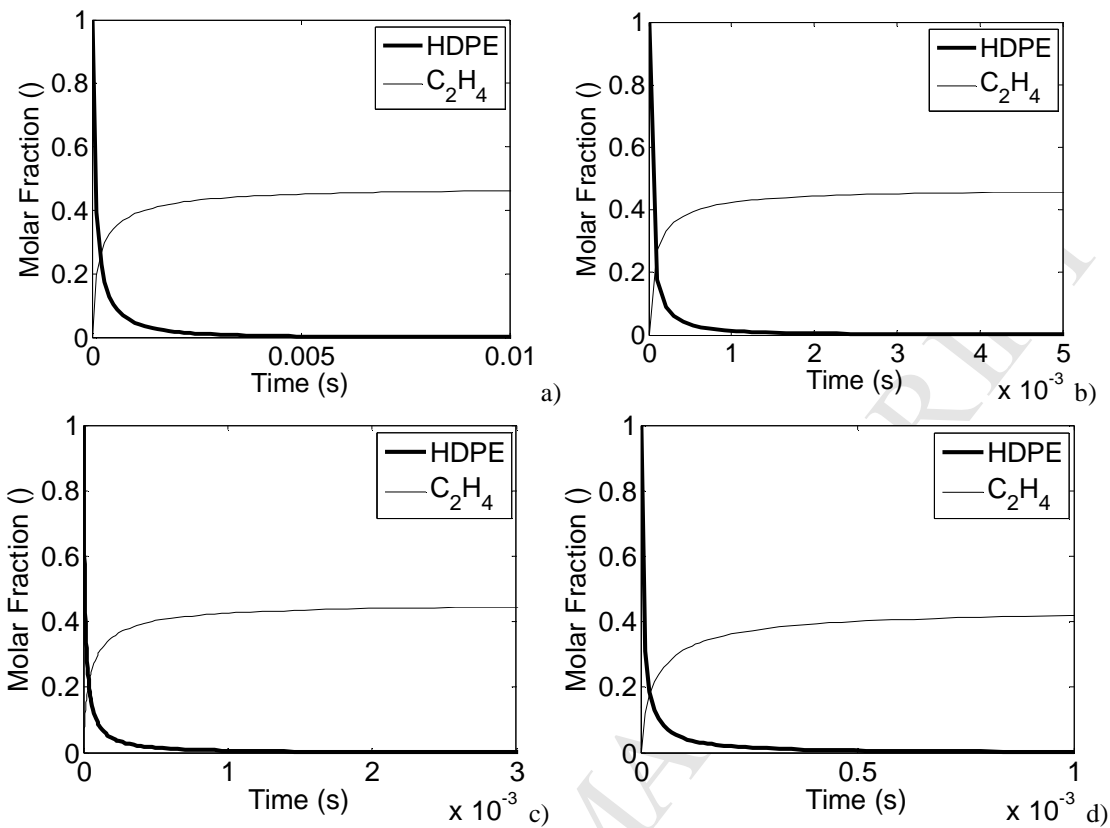
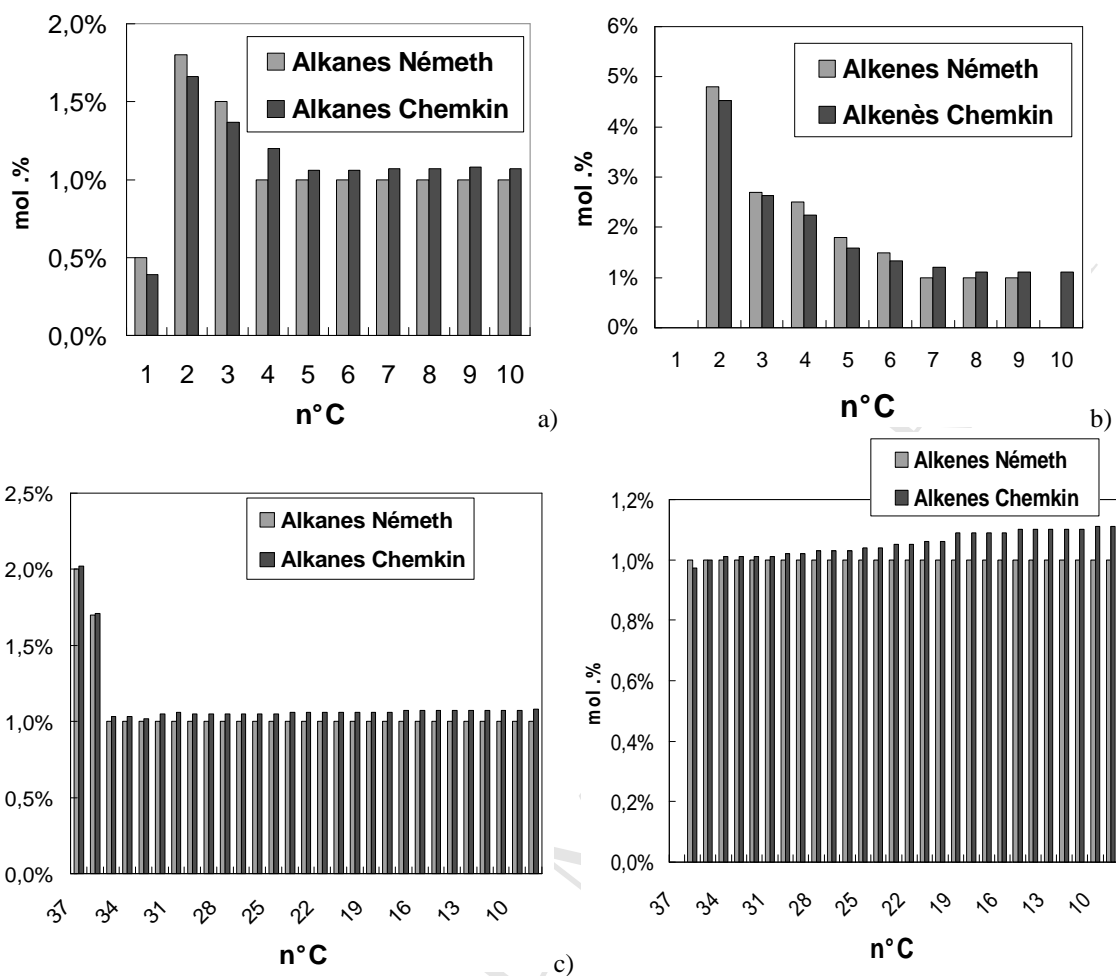


Figure 10. HDPE consumption and C_2H_4 production at 1200 K and 1bar (a), 10 bar (b), 34 bar (c), 100 bar (d)



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