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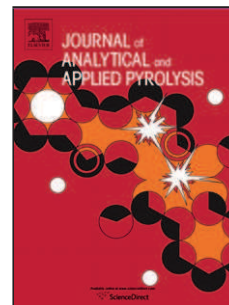
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1 **Fuel Pyrolysis through Porous Media:**
2 **Coke Formation and Coupled effect on Permeability**

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10 **ABSTRACT**

11 The development of hypersonic vehicles (up to Mach 10) leads to an important
12 heating of the whole structure. The fuel is thus used as a coolant. It presents an endothermic
13 decomposition with possible coke formation. Its additional permeation through the porous
14 structure involves internal convection. This implies very complex phenomena (heat and mass
15 transfers with chemistry). In this paper, the n-dodecane pyrolysis is studied through stainless
16 steel porous medium up to 820 K and 35 bar (supercritical state). The longitudinal profiles of
17 chemical compositions inside the porous medium are given thanks to a specific sampling
18 technique with off-line Gas Chromatograph and Mass Spectrometer analysis. By comparison
19 with previous experiments under plug flow reactor, the conversion of dodecane is higher for
20 the present experimental configuration. The pyrolysis produces preferentially light gaseous
21 species, which results in a higher gasification rate for a similar pyrolysis rate. The effects of
22 the residence time and of the contact surface area are demonstrated. The transient changes of
23 Darcy's permeability are related to the coke formation thanks to previous experimental
24 relationship with methane production. A time shift is observed between coke chemistry and

25 permeability change. This work is quite unique to the author's knowledge because of the
 26 complex chemistry of heavy hydrocarbon fuels pyrolysis, particularly in porous medium.

27 **Keywords:** Permeation, pyrolysis, porous medium, coke, active cooling, catalytic effect.

28

29

Nomenclature

A_{CH_4} = area of methane FTIR signal	Greek Symbols
C_1 = numerical constant (2096.3)	μ = dynamic viscosity (Pa.s ⁻¹)
C_2 = numerical constant (2193.7)	ρ = density (kg.m ⁻³)
\dot{C} = coking rate (g.m ⁻² .s ⁻¹)	τ = gasification rate (wt. %)
g = Earth's gravity (m ² .s ⁻¹)	\emptyset = diameter (m)
K_D = Darcy's permeability (m ²)	
K_F = Forchheimer's permeability (m)	Subscripts
L = sample thickness (m)	fluid = subscript for considered fluid
\dot{m} = mass flow rate (g.s ⁻¹)	in = subscript for inlet conditions
P = pressure (Pa)	int. = subscript for internal
ΔP = pressure loss (Pa)	out = subscript for outlet conditions
Q = volumetric flow rate (m ³ .s ⁻¹)	
S = characteristic cross section (m ²)	Superscripts
t_r = residence time (s)	liquid = superscript for liquid phase
v = volume of the flow line (m ³)	solid = superscript for solid phase
V = fluid velocity (m.s ⁻¹)	total = superscript for all phases
Y_i = i specie mass fraction (wt. %)	

30

I. Introduction

High speed vehicles are facing large thermal load because of the high velocity and because of the accumulated combustion heat. To challenge this problem, several cooling systems have been developed. Two major axis have been particularly studied: the material withstanding against high pressures and high temperatures on the one hand and a reliable cooling of the combustion chamber on the other hand [1-3]. The European ATLLAS project (Aerodynamic and Thermal Load interactions with Lightweight Advanced materials for high Speed) supported by the European Space Agency is investigating this topic, notably the transpiration through Ceramic Matrix Composite (CMC) structures. This cooling technique presents difficulties, which needs to be investigated. The coolant can react with the material (catalytic effect) and the coke formation can modify the structure's permeability [4]. As a result, the coupling of heat and mass transfer is directly impacted by the chemistry and such phenomenon need to be more understood. For this reason, the present work presents experiments in order to investigate the fuel pyrolysis through porous media and the associated phenomena (permeation, catalysis and coke production).

I . 1. Permeation through porous media

The permeation process is a complex phenomenon widely studied in various research areas such as nuclear power [5] or geology [6]. This particular phenomenon is treated experimentally [7,8], numerically [9,10] or mathematically [11]. A first approach to understand this specific phenomenon is to express the well-known Darcy's law:

$$Q = KS \frac{\Delta P}{\rho \cdot g \cdot L} \quad (1)$$

This law is a linear part (only available for laminar flow) and should be completed by an additional one (for so-called turbulent flow). Thus, the next equation follows [12]:

54
$$\frac{\Delta P}{L} = \mu \cdot \frac{V}{K_D} + \rho \cdot \frac{V^2}{K_F} \quad (2)$$

55 This law (known as the Brinkman's equation) can be derived and expressed with a large
56 panel of relationships according to the application fields. Additional terms, like the Stokes
57 term [13], can be added and the pressure loss can be written in several ways [14]. Depending
58 on the selected expression, the fluid properties are given either by inlet or mean conditions.
59 The permeation mainly depends on the material structure which can be considered at different
60 scales (macro, micro and also meso scale) [15]. Due to the complexity of composite materials,
61 it is chosen in this paper to consider metallic samples which are homogeneously made of
62 stainless steel agglomerated particles.

63 **I . 2. Pyrolysis of hydrocarbons and hypersonic conditions**

64 The general scheme of pyrolysis is composed of the following successive and simultaneous
65 reactions: random scission (the chain scission produces the free radicals), H-abstraction and
66 beta scission (production of unsaturated compounds with one or two terminal double bond)
67 [16]. These reactions appear in primary and secondary mechanisms. The degree of
68 decomposition is highly dependent on the operating conditions (temperature, pressure, type of
69 flow, nature of reactor) [17-21]. Thermal cracking of hydrocarbons have been widely studied
70 in petrochemical industry [18,22-26]. It appears than the bigger the molecule, the higher the
71 number of reactions which occur. Considering dodecane pyrolysis, the number of reactions
72 largely overpasses 1000. Light hydrocarbons like methane, acetylene or ethylene are produced
73 such as heavy compounds (benzene) and even more complex ones (notably Polycyclic
74 Aromatics Hydrocarbons –PAH – such as naphthalene and pyrene) which are precursors of
75 solid carbon formation [27]. This coke may interfere with the permeation process by lowering
76 the porosity and reducing the contact surface between coolant and solid surface. Thus, the
77 comprehension of the reaction pathway is one of the key to monitor and control such a

78 phenomenon. Last element to consider is that in real conditions, the fuel temperature can
79 reach 1500 K and the pressure can be higher than 30 bar. This leads the fuel to be at
80 supercritical state. To the authors' knowledge, no study does exist on fuel pyrolysis under
81 permeation configuration. The challenge of the present work is thus to achieve supercritical
82 fuel pyrolysis in porous media and to monitor the longitudinal chemical composition profile
83 inside the structure thanks to appropriate sampling technique.

84 **I . 3. Surface catalytic effect and coke formation**

85 Some interactions between the molecules constituting the wall and the fluid may happen
86 (surface reactions). This could modify strongly the reaction pathway and it can lead to a
87 potential higher production of coke (which justifies considering specifically this point) [28-
88 30]. Considering this element, the treatment of the inner wall could have a critical impact on
89 the fuel degradation. It was shown that an oxygen treatment generally enhances the catalytic
90 activity (considering a metallic reactor) and leads to a higher production of coke [28,31]. The
91 treatment by hydrogen sulphide permits to inhibit this phenomenon and to act as passivation.
92 A recent study also showed that coating the inner wall with zeolites or with a ceramic-like
93 binder both limit the coke production, enhance the fuel decomposition and, consequently,
94 increase the heat sink capacity of the material [32]. Hence, the choice of the wall material is a
95 critical point and has to be considered with respect to the surface catalytic effect. In the
96 present work, some investigations will be proposed in order to estimate its impact on the
97 distribution of pyrolysis products.

98 Finally, the present study aims at investigating fuel pyrolysis in porous media to determine
99 the intrinsic effect of the permeable material compared to existing data on fuel pyrolysis in
100 open tubular reactor. The effects of the contact surface, of the residence time, of the catalytic
101 effect and of heat and mass transfers are of interest. This work is even more important since it
102 is the first frontier work, to the author's knowledge, between pyrolysis, catalysis and filtration.

103 The final aim is to be able predicting the coke formation and its effect on permeability in
104 order to ensure the cooling efficiency of regenerative cooling technique. Scientifically, major
105 progresses are waited on the understanding of coupled heat and mass transfer with chemistry
106 by experimentally observing the heterogeneous profiles of permeation and of pyrolysis inside
107 the porous medium.

108 **II. Material and method**

109 **II . 1. Experimental bench**

110 A high pressure and high temperature experimental bench (1200 K, 60 bar) is used with a
111 novel sampling technique to investigate the pyrolysis products distribution as a function of
112 operating conditions. The setup is derived from the one of the COMPARER project (CONtroll
113 and Measure of PArAmeters in a REacting stReam) conducted by the University of Orléans
114 and MBDA-France [29]. The liquid fuel is injected by a pump (80 bar, $0.5 \text{ g}\cdot\text{s}^{-1}$) inside a
115 chemical reactor, which is placed in a furnace. This reactor is made of a preheated stainless
116 steel tubular reactor ($\text{Ø}_{\text{int.}} = 3.45 \text{ mm}$, length = 550 mm) and of a dedicated cell
117 ($\text{Ø}_{\text{int}} = 30 \text{ mm}$, length = 100 mm) in which the porous medium is inserted (filtration diameter
118 of 16 mm only). A cooling reactor ($\text{Ø}_{\text{int.}} = 3.45 \text{ mm}$, length = 300 mm) is placed at the cell
119 outlet to conduct the fluid out of the furnace before being analyzed transiently by Infra Red
120 spectrometry (FTIR) for the gas phase and before being sampled. These samples under liquid
121 and gas phases at ambient conditions are a posteriori analyzed separately by both Gas
122 Chromatograph (GC) and Mass Spectrometer (MS). Further details on the bench description
123 can be found in previous work [33,34].

124 An improvement of the described bench consists on a novel technique of sampling
125 (Figure 1). This allows obtaining the longitudinal distribution of pyrolysis mixture
126 composition inside the permeable medium. First, sampling tubes have been placed as close to

127 the medium as possible. The porous sample is drilled to get samples in its middle. A good
128 contact is ensured to get reliable samples. A complex system of small size cylinders, valves
129 and pump has been designed to ensure the smallest possible residence time between the
130 sampling point and the cylinder, a fast filling of these cylinders, a sufficient sample quantity
131 for the GC/MS analysis, a good synchronization of the sampling during the test and finally the
132 good representativeness of the samples compared to the real process itself. The dynamics of
133 this system is of importance to have a "non intrusive" device. The following sampling
134 locations are noted for this work: upstream (point A, Figure 1), inside (point B, Figure 1) and
135 downstream (point C, Figure 1). The distance between each point is equal, around 1.5 mm.
136 Considering the test cell itself, further information can be found in previous work [33].

137 *Figure 1 should be placed here*

138 **II . 2. Test methodology**

139 N-dodecane (VWR, Rectapur 99% of purity) is used for these experiments because it is
140 known as a good kerosene surrogate. It has been extensively studied by the authors in
141 numerous pyrolysis configurations [4,29,30]. Thus, comparison with existent experimental
142 data can be easily made. A stainless steel sample ($\varnothing = 30$ mm, filtration diameter = 16 mm
143 thickness of 3 mm) is preferred as a porous medium compared to composite material because
144 it is well characterized. Its implication in coke enhancing was notably demonstrated by
145 PRISME team in tubular reactor configuration [30]. Nevertheless, no data are available for
146 permeation configuration so that these works will provide new information on stainless steel
147 surface effect and be compared with precedent results. Its class of porosity number 3 (the so-
148 called SS₃, Figure 2) presents an overall porosity of 30 %, pores diameter of 4.1 μm and grain
149 diameter of 14.1 μm [33]. SEM (Scanning Electron Microscope) images with EDS (Energy
150 Dispersive Spectroscopy) analysis are conducted after the tests on the porous sample to
151 determine the nature of the deposited carbon. Initial composition is given in Figure 2.

152

Figure 2 should be placed here

153 The tests are conducted with successive stationary thermal plateaus. For a given mass flow
154 rate ($65 \text{ mg}\cdot\text{s}^{-1}$), the setup furnace temperature is increased from ambient to 750 K and then by
155 50 K steps after thermal stabilization (about 45 minutes for each plateau). The outlet pressure
156 is regulated (35 bar) and the inlet pressure is measured. The samples are realized for the three
157 locations during 10 s at the end of each thermal plateau. Three setup furnace temperatures are
158 studied (750 K, 800 K and 850 K), which corresponds respectively to maximum fluid
159 temperatures of 725 K, 765 K and 820 K. The gasification rate (quantity of produced gas
160 divided by the injected fuel quantity) and the pyrolysis rate (also noted the conversion rate,
161 i.e. the quantity of decomposed dodecane divided by the initial dodecane quantity) are
162 determined by mass balance for each thermal plateau. The gas and liquid phases are analyzed
163 separately for each sample. Some species can be found under both phase due to saturated
164 vapour pressure. Grouping liquid and gas phase analysis, the mass fraction of each species are
165 expressed by Eq. 3 where Y_i^{liquid} denotes the mass fraction of the specie in the liquid phase
166 and Y_i^{gas} the mass fraction in the gas phase.

$$167 \quad Y_i = Y_i^{\text{liquid}} \times (1 - \tau) + Y_i^{\text{gas}} \times \tau \quad (3)$$

168 The permeabilities of Darcy and Forchheimer are computed thanks to the pressure drop
169 and to the flow rate monitored as a function of time, using the Eq. 2. Eq. 2 is rewritten in
170 conformity with the international norm ISO 4022 (Eq. 4) and the fluid properties are the mean
171 one between the inlet and outlet conditions.

$$172 \quad \frac{\Delta P}{L \cdot \mu \cdot V} = \frac{1}{K_D} + \frac{\rho \cdot V}{\mu \cdot K_F} \quad (4)$$

173 A linear relationship (Eq. 5) derived from previous experiments with stainless steel tubular
174 reactors [4] has been used in this work to determine the coke formation as a function of time
175 on the basis of methane production which is monitored by FTIR spectrometer at the process

176 outlet. This law will be used later in the paper to analyze and to explain the variations of
177 Darcy's permeability of the material during the coking activity.

$$178 \quad m_c = \frac{A_{\text{CH}_4} - C_1}{C_2} \quad (5)$$

179 **III. Results and discussion**

180 **III . 1. Distribution of pyrolysis product yields**

181 The pyrolysis tests are conducted under the stationary thermal conditions described
182 previously. The samplings are done for fluid temperatures of 725 K, 765 K and 820 K. For
183 points A and B (upstream and inside the porous media), the samplings were only made for the
184 two last temperatures because negligible pyrolysis was observed for the first temperature.

185 Table 1 presents the mass composition of the pyrolysis mixtures. The authors precise that
186 the precision is voluntary set at one hundredth in order to avoid the suppression of species
187 which were detected in very low quantity. Nevertheless, the quantity lower than 0.1 wt.%
188 should be considered for illustrative purpose mainly. First, it can be noted that the
189 decomposition of dodecane varies not only with temperature but also as a function of the
190 location in the porous medium (points A to C). The conversion rate increases along the flow.
191 This result is in qualitative agreement to that obtained under plug flow reactor on
192 COMPARER project [29-30]. This is directly related to the residence time distribution and to
193 the convective heat transfer. Considering the pyrolysis products (Table 1), n-dodecane is
194 preferentially decomposed into light species at the entrance of the cell and at the process
195 outlet (respective predominant species: butane / ethane at 765 K and ethane / propylene at
196 820 K). Alkanes are found in majority compared to alkenes, contrary to what was observed
197 generally in plug flow reactor during previous experiments [29-30]. This is due to the heat
198 transfers, which are enhanced in the porous material due to the high contact surface. The flow
199 behaviour in porous medium is closer to the one in perfectly stirred reactor (homogeneous

200 flow) than to the plug flow reactor (spatial heterogeneity). The H over C atoms mass ratio
201 tends to one sixth for all the alkenes; it is one twelfth for benzene and it starts from one third
202 for methane to around 0.181 for dodecane. It was found in previous work [29] that the H over
203 C ratio increases (higher than 0.18) when the heat transfers increase, which indicates a higher
204 alkanes production. The present results (Table 1) thus confirm this observation. Indeed, a
205 higher proportion of ethane than ethylene or propane than propylene are found whatever the
206 temperature or the axial position, with a H over C ration always higher than 0.18. Additional
207 comments will be provided on this point at the end of this section with Figure 3.

208 *Table 1 should be placed here*

209 A different repartition is found (Table 1) inside the porous medium (preponderant mid-
210 weigh species: hept-1-ene 765 K and hex-1-ene and butane at 820 K). Several assumptions
211 can be made to explain these facts.

212 First, the light compounds are sampled preferentially due to a bad sampling technique and
213 the absence of heavy species at the inlet is the consequence. Nevertheless, this is not the most
214 possible reason because heavy compounds are found for the samples related to point B with
215 the same sampling technique. It is thus supposed that the sampling technique provides reliable
216 samples, which are representative of the test conditions. It must be noted that samples at the
217 outlet are satisfactory because they are obtained with a validated methodology which is used
218 since 2005 (6 years of intensive pyrolysis work).

219 Second, this could be attributed to the chemical diffusion of the species in the porous
220 media. The lack of light species at point B is due to their higher filtration speed. Nevertheless,
221 under steady-state conditions, this effect should be low. Some numerical computations have
222 been done for another project and only small discrepancies in similar conditions have been
223 found between simulations with and without chemical diffusion.

224 Third, the radial heterogeneity of the thermal, hydraulic and chemical parameters implies
225 that the samples are mostly representatives of the specific locations where they are made and
226 not of the corresponding longitudinal coordinate. This is a possibility which can not be easily
227 investigated by experimental test. For this reason, numerical simulation should be conducted
228 in a near future.

229 Finally, the differences can be related to the coking activity which modifies the surface
230 effect (heterogeneous reactions) and the heat and mass transfers. In case of deactivation of the
231 surface or of the saturation of the sites, a limitation of the surface catalytic effect could be
232 encountered. Such dynamic was already found considering other fuel [28]. Thus, this
233 assumption must be correlated with coke analysis and to the formation and consumption of
234 some species (acetylene, ethylene, benzene). The benzene, toluene and p-xylene formation
235 increases for a temperature of 765 K at point B, and then decreases at 820 K (Table 1). This
236 can sign the coke formation (in a first time, production of coke precursors, and then an
237 aggregation of those ones to form solid carbon). The heat transfers are reduced and the
238 pyrolysis is slowed down (less formation of light compounds). On the contrary, it can also be
239 assumed that the light species, precursors of coke, begin to react and form the secondary
240 species involved in the formation of carbon deposit (decrease also shown at point B, Table 1).
241 As a consequence, this analysis remains difficult on the basis of these first results and, again,
242 numerical simulation would be of great interest. However, the amplitudes of the variations are
243 quite small and the accuracy of the measures could be responsible for these changes regarding
244 benzene, toluene and p-xylene for example.

245 The chemical spatial profiles of group species can be further discussed. It is clear that the part,
246 where chemical reactions are the most intense, is the second half of the porous medium.
247 Significant fall of light species mass fractions (C_1 to C_3) can be seen at the point B for the two
248 temperature plateaus. Regarding mid-weight species (C_4 - C_6) the production is quite similar

249 even if the drop between A and B is less important. The profile of heavy precursors of coke is
250 comparable for a temperature of 820 K but is clearly different for the 765 K thermal stage.
251 Due to the very low mass fractions, the interpretation of such results remains very difficult.
252 Nevertheless it could be assumed that this profile is due to the chemical induction delay which
253 depends on the fluid temperature. But, this can not fully explain such an activity. Spatially,
254 point A and B are very close so that the fluid temperature is identical. The presence of the
255 porous medium may increase the residence time and, consequently, the decomposition rate.
256 The high difference between the profiles may also be linked to a catalytic activity of the
257 porous medium. To investigate the intrinsic effect of the porous media, a comparison can be
258 made with previous COMPARER data obtained under open tubular reactor configurations
259 [30]. The comparison is conducted for the samples issued from the point C. For the plug flow
260 reactor (pressure = 10 - 60 bar, residence time = 50 - 100 s and mass flow rate = 50 -
261 100 mg.s⁻¹), the dodecane decomposition rate is lower than 10 wt.% for a furnace
262 temperature close to 850 K instead of about 48 wt.% for the porous sample (Table 2). Indeed,
263 even by considering a lower pressure (10 bar), a lower mass flow rate (50 mg.s⁻¹) and
264 consequently a theoretical higher decomposition, the pyrolysis rate is more than five times
265 lower for plug flow experiment.

266 *Table 2 should be placed here.*

267 To reach a comparable decomposition, the considered temperature must be far higher (over
268 1250 K, Table 3). The species repartition is quite different: more light and mid-weighted
269 species are found for plug flow reactor experiments while heavy species and, in particular,
270 coke precursors are more present in the permeation configuration (Table 3). So, the increase
271 of the dodecane decomposition and its different profile compared with plug flow reactor may
272 be explained by the presence of the porous medium (i.e. increase of the residence time, of the
273 contact surface and of the catalytic effect).

274

Table 3 should be placed here.

275 Finally, the gasification and pyrolysis rate have been plotted for the three temperatures and
276 three sampling locations (points A to C) (Figure 3). A qualitative parabolic trend
277 corresponding to the plug flow reactor is given from the COMPARER project results (full
278 black curve, Figure 3). The experimental data points obtained for the porous flow are close to
279 the line. This line (from [0%;0%] to [100%;100%]) means that 100 % of the pyrolysis
280 products are found under gas phase at ambient conditions. This clearly highlights the
281 difference between the two types of flow. The strong gas formation, in case of porous flow, is
282 mainly due to the higher contact surface between the fluid and the overall reactor because of
283 the presence of the porous medium. The residence time also explains the differences but it is
284 not possible to estimate the one in porous media for compressible reactive fluid without
285 numerical simulation support.

286 Additional computations were done for the same operating conditions than the experiments
287 but using a perfectly stirred reactor configuration with the n-dodecane pyrolysis mechanism
288 furnished by Dahm [35]. The results show strong similarities between PSR and porous flow
289 compositions while PSR computations are not able to represent the multiphysic coupled
290 phenomena involved in open tubular reactor [29]. Consequently, the permeation through
291 porous media seems to present more similarities with PSR like conditions than with plug flow
292 ones.

293

Figure 3 should be placed here

294 **III . 2. Coking activity**

295 At the end of the pyrolysis tests, the central zone on the porous sample -which corresponds
296 to the fluid flow cross-section- is clearly covered on the side of point A by a black layer of
297 about 0.3 mm (Figure 4a). No carbon deposit is found on the opposite side (point C). This
298 coke formation has been observed by SEM and an accumulation of solid micrometric particles

299 is found. and which mean diameter is of the order of 1 μm (Figure 4b). After surface cleaning,
300 another SEM images clearly shows a clogging of the pores by similar particles with much
301 smaller diameter (of the order of 0.1 μm or less) (Figure 4c). The particles of the permeable
302 sample which are visible on the Figure 4c are covered by a carbon layer which composition is
303 not so different from the one of the solid coke particles. Indeed, the coke particles at the
304 surface are almost constituted of pure carbon (96 wt.% with 4 wt.% of O atoms, Figure 4)
305 while the stainless steel particles reveal a higher carbon content (about 20 wt.% instead of
306 7 wt.% initially, Figure 2). These 20 wt.% are found with an increase of about 1 wt.% of O
307 atoms (2.34 wt.% instead of 1.31 wt.% initially). The C/O ratio is thus about 24 for the solid
308 coke particles and around 20 for the coke at the stainless steel particles surface (if this 1 wt.%
309 is strictly attributed to the coke formation, which is questionable). This slight difference may
310 be related to the origin of formation of the coke (catalytic, i.e. inside the porous medium, and
311 pyrolytic, i.e. at the surface) as it has been studied in previous work [4]. Nevertheless, the
312 differences are too small to be quantitatively interpreted and these results should be completed
313 in a future work to determine quantitatively the effect of stainless steel and of the contact
314 surface area in the process. It can only be mentioned that the presence of carbon layer on the
315 particles of stainless steel demonstrates the implication of the solid material in heterogeneous
316 reactions.

317 *Figure 4 should be placed here*

318 In addition to this macroscopic quantification, the mass of carbon deposit can be
319 approximated as a function of time thanks to a previous experimental relationship as
320 described in section II.B. The methane formation has been monitored by FTIR measures
321 during the test and the estimated coke mass is given with and without its normalisation to the
322 final mass measured at the end of the test (Figure 5). Indeed, directly using the relationship as
323 mentioned in section II.B gives a total amount of coke of 3 g at the end of the experiment

324 while only 0.46 g are detected. This over-prediction can be related to the contact surface area
325 differences between the porous flow and the plug flow reactor. As a consequence, it is
326 preferred to normalise the coke mass evolution to the maximum measured one, that is to say
327 0.46 g. This carbon deposit formation is also given as a function of temperature (Figure 6).
328 Both parameters are roughly related except when the temperature reaches a thermal plateau
329 (725 K, 765 K and 820 K). The mass of coke increases during these plateaus because of the
330 time of experiment.

331 *Figure 5 should be placed here.*

332 *Figure 6 should be placed here.*

333 **III . 3. Clogging effect of the coke formation**

334 The formation of coke deposit inside the pores of the permeable material and on its surface
335 modifies the filtration of the fluid. During the initial heating of the system from ambient to
336 700 K, before the n-dodecane starts to pyrolyse, a constant value of $1.96 \cdot 10^{-13} \text{ m}^2$ is found
337 for the Darcy's permeability. This is in complete agreement with the value found at ambient
338 condition with a nitrogen flow [33]. Then, the transient darcian value computed during the
339 experiment is given in Figure 7. The vertical straight lines represent the sampling times at the
340 point A. Some decreases are found up to 2 to 3 orders of magnitude, which signify strong
341 clogging of the porous medium. In addition, several sudden increases are observed at the
342 locations marked by the vertical lines. On the basis of Figure 7, it is assumed that making a
343 sampling upstream the porous medium impacts the flow. When opening the sampling line to
344 the cylinder, the inlet pressure briefly becomes lower than the outlet one so that the flow is
345 reversed (because of a lower pressure in the cylinders than in the process). The porous
346 medium is temporarily cleaned and solid particles are removed. As a result, the Darcy's
347 permeability increases.

348 The effect of the coke formation on the Darcy's permeability is mainly due to the
349 accumulation of carbon particles inside the pores of the stainless steel sample because the
350 permeability of the coke deposit on a surface (as observed on point A) has been determined
351 previously to be about 10^{-8} m² [36]. Thus, this high value (in comparison to the original
352 permeability of the medium) should not impact the measure of the K_D . This conclusion is
353 reinforced by the determination of mass of carbon deposit which is detected at the surface
354 (8.66 mg) compared to the one inside the sample (460 mg). The coke quantity is 50 times
355 more important in the medium than at its surface. Considering the density of solid carbon, this
356 corresponds to a volume of about 0.230 cm³, which can be compared to the volume of pore in
357 case of a porosity of 30 %. (about 0.645 cm³). Thus, the coke limits this volume by about
358 30 % which may have an important impact on the filtration (Figure 7).

359 *Figure 7 should be placed here*

360 The surface weight information can also be used to determine the coking rate. To provide a
361 relationship between permeability variations and chemical phenomena, the coke formation is
362 a good witness of the process (Figure 8). The coking rate is calculated using the following
363 equation:

$$364 \quad \dot{C} = \frac{m_c}{S \times t_r} \quad (6)$$

365 Where the residence time is varying during the experiment and it is estimated by:

$$366 \quad t_r = \frac{\rho \times v}{\dot{m}_{\text{fluid}}} \quad (7)$$

367 Two qualitative similar behaviors are found for the coking rate and for the rate of change
368 in Darcian permeability (Figure 8). The production of coke limits directly the filtration
369 surface. This has an impact on heat and mass transfer because the residence time decreases
370 and it should lead to a lower decomposition. Nevertheless, such comportment is not clearly
371 understood and further work is requirement to confirm these preliminary results. This

372 relationship between coke formation and its modification of the permeability is of great
373 interest in case of active cooling in order to predict the modification of cooling efficiency. In
374 addition, a time delay may appear between both curves because the arrows are not all vertical
375 and their slope is decreasing, which means that the clogging process slows down but the
376 cleaning effect of the sampling at point A modifies the dynamics of the system and this
377 conclusion remains questionable.

378 *Figure 8 should be placed here*

379 **IV. Conclusion**

380 Regenerative cooling by fuel permeation through porous material are some of the available
381 efficient methods to face the thermal issue of hypersonic vehicles. Instead of using inert flow,
382 as it is often seen in open literature for simplification reason, n-dodecane pyrolysis has been
383 achieved in the present work through stainless steel porous sample under supercritical state
384 (820 K and 35 bar). A specific sampling technique has been developed to analyze the
385 chemical composition distribution of the pyrolyzed fuel through the longitudinal coordinate of
386 the permeable medium. The monitoring of chemical species enables to understand that the
387 major part of the pyrolysis is observed in the second half of the medium. A coke formation is
388 principally observed at the inlet surface of the solid and also inside the pores. An analysis (C
389 and O atoms content) proves the dual origin of this coke deposit (catalytic and pyrolysis
390 effects). The relationship between the solid carbon formation and the changes of Darcy's
391 permeability is investigated. A time shift between both of them is proposed. This is of interest
392 to characterize the dynamics of coupled phenomena. In terms of pyrolysis, the effect of
393 porous medium is clear since the products which were found are in majority gaseous at
394 ambient conditions. This is different from the results obtained under plug-flow reactor for
395 which the gasification rate was lower than the present one for the same pyrolysis rate and with
396 similar conditions. The pyrolysis in porous sample can be modeled by perfectly stirred reactor

397 because of the residence time and large contact surface between the solid and the fluid. This
398 work will now be extended to investigate in more details the catalytic effect by using
399 composite media and other materials in same operating conditions. In addition, numerical
400 simulation will be achieved to furnish further results on the spatial heterogeneity of the
401 thermal, hydraulic and chemical parameters.

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509 Table 1. Pyrolysis products distribution and parameters (in wt.%) at locations A (upstream),
510 B (inside) and C (downstream) analyzed by GC/MS as a function of the maximum fluid
511 temperature.

512 Table 2. Comparison of pyrolysis parameters (in wt.%) with or without porous medium
513 considering similar conditions

514 Table 3. Comparison of pyrolysis products (in wt.%) with or without porous medium
515 considering similar decomposition rates

516

517

518 Figure 1. Schematic of the apparatus to be inserted in the furnace with representation of the
519 sensors.

520 Figure 2. a) Stainless steel porous medium: Fe (62 wt.%), Cr (18 wt.%), Ni (11 wt.%)
521 C (7 wt.%), O (1 wt.%) and Si 1 wt.%. b) Visualization by SEM (4000 times magnification).

522 Figure 3. Type flow effect on the relationship between gasification and pyrolysis rate.

523 Figure 4. a) Coked porous medium. b) Visualization by SEM (5000 times magnification) and
524 EDS analysis: C (96 wt.%), O (3.5 wt.%) and Fe (0.5 wt.%). c) After surface cleaning:
525 Fe (52 wt.%), C (20 wt.%), Cr (14.5 wt.%), Ni (9.5 wt.%), O (2.5 wt.%) and Si (1.5 wt.%).

526 Figure 5. Time evolution of the mass of coke deposit with the one of methane production and
527 the fuel temperature.

528 Figure 6. Relationship between coke formation and fluid temperature.

529 Figure 7. Variation of the Darcian term and estimated mass of coke.

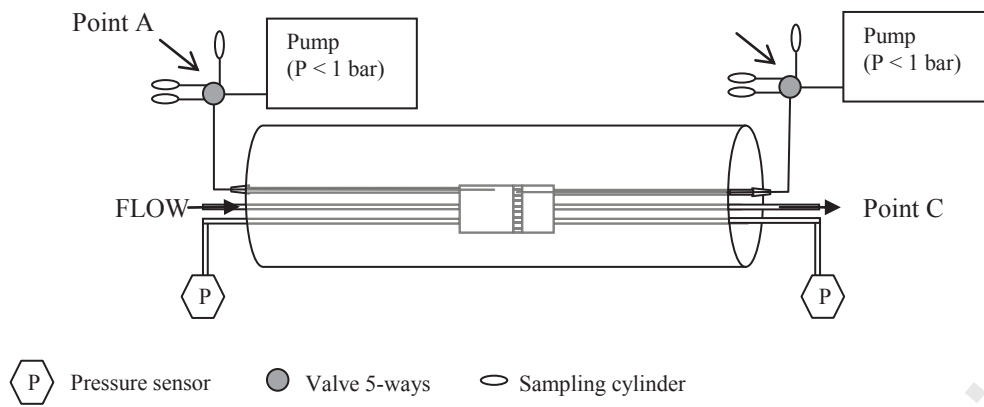
530 Figure 8. Relationship between coking activity and Darcian permeability.

Product	725 K			765 K			820 K		
	A	B	C	A	B	C	A	B	C
Hydrogen	~	~	0,00	0,01	0,00	0,04	0,03	0,00	0,04
Methane	~	~	1,28	0,38	0,10	1,33	1,16	0,33	2,16
Ethylene	~	~	1,49	0,49	0,15	2,52	1,16	0,56	3,84
Ethane	~	~	3,27	1,18	0,38	5,09	2,30	1,24	6,70
Propylene	~	~	2,06	1,04	0,47	5,30	1,83	1,72	7,84
Propane	~	~	2,42	1,26	0,68	5,99	1,88	2,31	7,17
But-1-ene	~	~	1,00	0,48	0,42	2,46	0,77	1,21	4,45
Butane	~	~	1,89	1,80	1,70	2,18	1,07	2,50	3,72
(E)-Pent-2-ene	~	~	0,44	0,25	0,87	0,68	0,69	1,40	2,05
Pentane	~	~	0,20	0,40	1,13	0,50	0,94	1,50	1,80
Cyclopentane	~	~	0,00	0,00	0,00	0,00	0,00	0,00	0,01
Hex-1-ene	~	~	0,50	0,64	2,01	0,67	1,10	2,27	1,95
Hexane	~	~	0,17	0,33	1,00	0,19	0,44	1,04	0,58
Benzene	~	~	0,00	0,01	0,03	0,00	0,08	0,01	0,08
Cyclohexene	~	~	0,00	0,01	0,01	0,00	0,03	0,01	0,06
Hept-1-ene	~	~	0,15	0,31	2,44	0,35	0,73	1,53	1,29
Heptane	~	~	0,51	0,10	1,12	0,22	0,15	0,63	0,54
Toluene	~	~	0,00	0,03	0,09	0,01	0,15	0,03	0,18
Oct-1-ene	~	~	0,12	0,23	0,15	0,26	0,27	0,16	1,05
Octane	~	~	0,09	0,12	0,10	0,12	0,18	0,12	0,27
Styrene	~	~	0,00	0,00	0,00	0,00	0,00	0,00	0,00
p-Xylene	~	~	0,00	0,00	0,01	0,00	0,02	0,00	0,03
Non-1-ene	~	~	0,10	0,19	0,15	0,20	0,07	0,09	0,56
Ethylbenzene	~	~	0,00	0,00	0,00	0,00	0,00	0,00	0,03
Nonane	~	~	0,11	0,09	0,04	0,14	0,00	0,15	0,26
Dec-1-ene	~	~	0,14	0,00	0,00	0,31	0,00	0,00	1,05
Decane	~	~	0,00	0,07	0,05	0,07	0,10	0,06	0,00
Undec-1-ene	~	~	0,04	0,07	0,01	0,07	0,00	0,00	0,14
Undecane	~	~	0,09	0,19	0,13	0,17	1,53	0,15	0,19
Dodec-1-ene	~	~	0,00	0,00	0,00	0,00	0,00	0,00	0,33
Dodecane	> 99	> 99	83,84	90,25	86,70	71,04	83,31	80,92	51,57
Tridec-1-ene	~	~	0,00	0,01	0,00	0,01	0,00	0,00	0,00
Tridecane	~	~	0,01	0,03	0,02	0,03	0,00	0,02	0,04
Tetradecane	~	~	0,01	0,02	0,01	0,02	0,00	0,02	0,02
Gasification rate	0,00	0,00	13,50	6,00	10,00	26,00	10,00	15,00	39,00
Pyrolysis rate	< 1	< 1	16,16	9,75	13,30	28,96	17,00	19,00	48,43
H/C ratio	-	-	0,2011	0,2011	0,1846	0,2050	0,2025	0,1916	0,1982

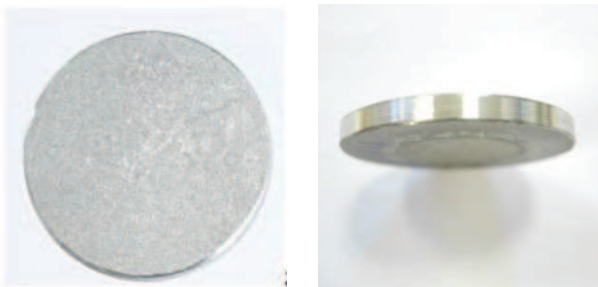
Type of reactor	Tubular reactor		Through porous medium	Tubular reactor
	914K, 10 bar, 50 mg/s	896 K, 10 bar, 100 mg/s	850 K, 35 bar, 65 mg/s	916 K, 60 bar, 100 mg/s
Dodecane	91,61	99,58	51,57	96,44
Gasification rate	7,40	0,00	39,00	1,00
Pyrolysis rate	8,39	0,42	48,43	0,04

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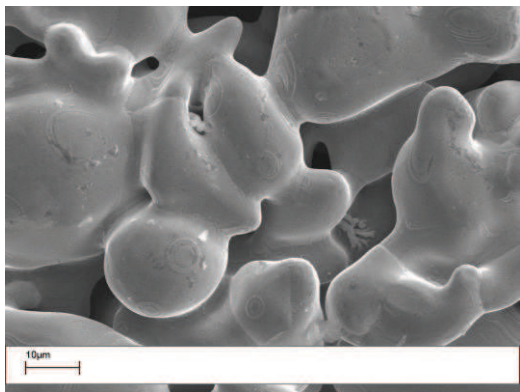
	Tubular reactor		Through porous medium	Tubular reactor
	1328 K, 10 bar, 50 mg	1359 K, 10 bar, 100 mg	850 K, 35 bar, 65 mg	1280 K, 60 bar, 100 mg
Hydrogen	0,00	0,03	0,04	0,01
Methane	4,91	2,32	2,16	1,18
Ethylene	13,06	4,68	3,84	1,03
Ethane	6,90	2,60	6,70	1,79
Propylene	14,47	4,69	7,84	2,49
Propane	1,65	1,68	7,17	2,34
But-1-ene	0,00	3,79	4,45	1,79
Butane	4,80	1,07	3,72	1,68
(E)-Pent-2-ene	0,00	2,62	2,05	2,22
Pentane	3,00	4,53	1,80	3,33
Hex-1-ene	0,06	1,43	1,95	2,98
Hexane	0,04	0,28	0,58	1,40
Benzene	0,00	0,00	0,08	0,08
Hept-1-ene	0,00	0,00	1,29	1,74
Heptane	0,01	0,02	0,54	0,42
Oct-1-ene	0,06	0,08	1,05	0,96
Octane	0,01	0,01	0,27	0,39
Toluene	0,00	0,00	0,18	0,13
Non-1-ene	0,37	0,43	0,56	0,61
Nonane	0,04	0,07	0,26	0,41
Dec-1-ene	1,42	1,24	1,05	0,69
Decane	0,11	0,14	0,14	0,16
Undec-1-ene	0,41	0,39	0,19	0,20
Undecane	0,00	0,14	0,33	0,36
Dodecene	0,00	0,06	0,00	0,06
Dodecane	48,67	67,71	51,57	71,26
Gasification rate	41,00	25,50	39,00	15,00
Pyrolysis rate	51,33	32,29	48,43	28,74



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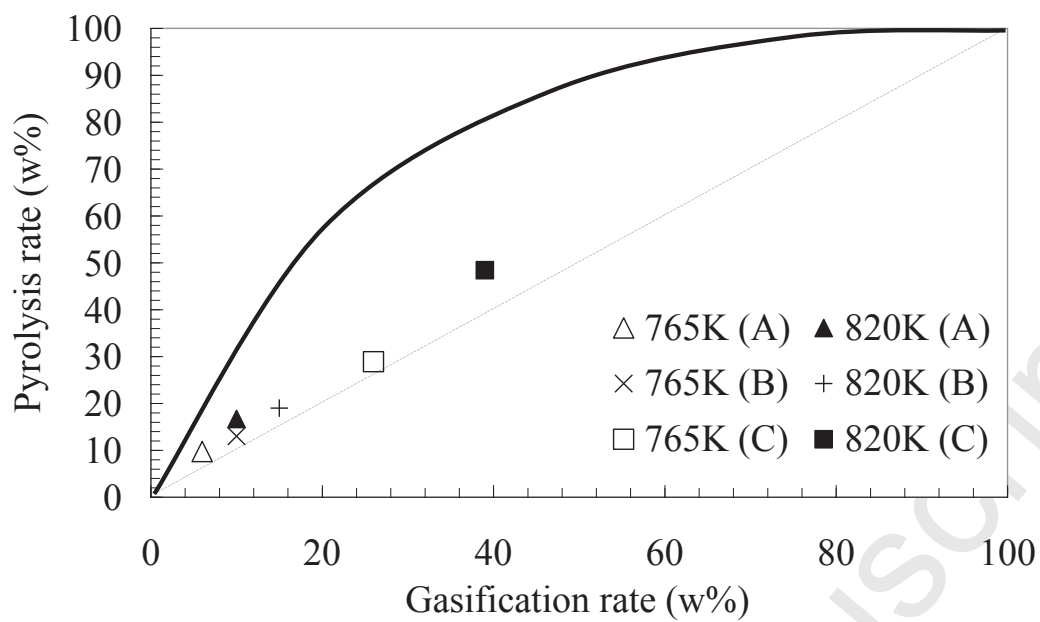


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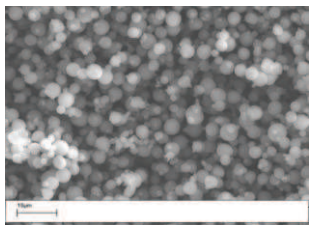
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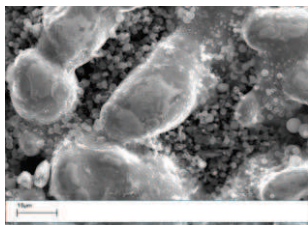
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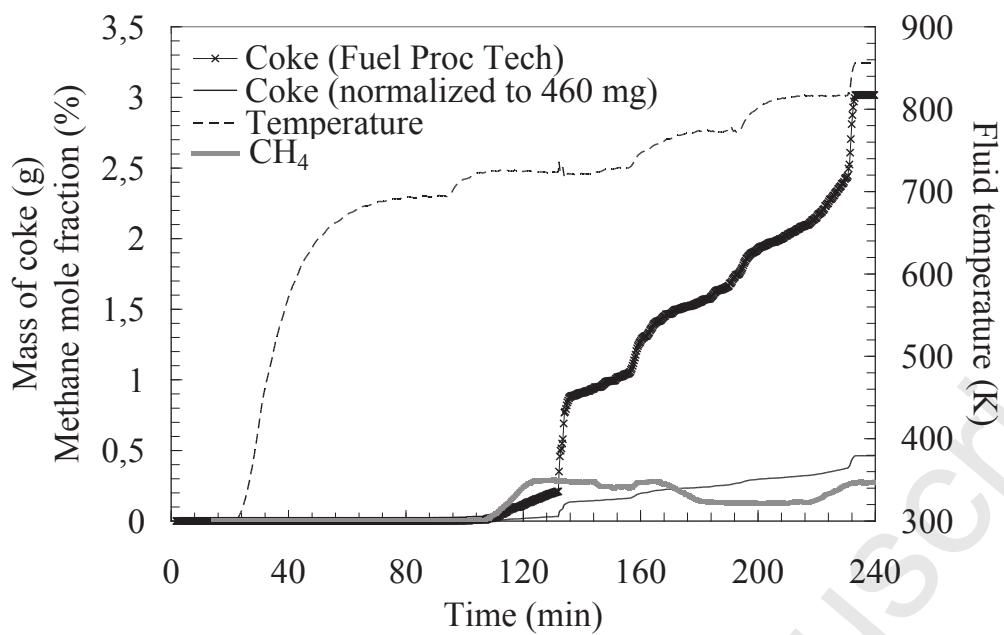


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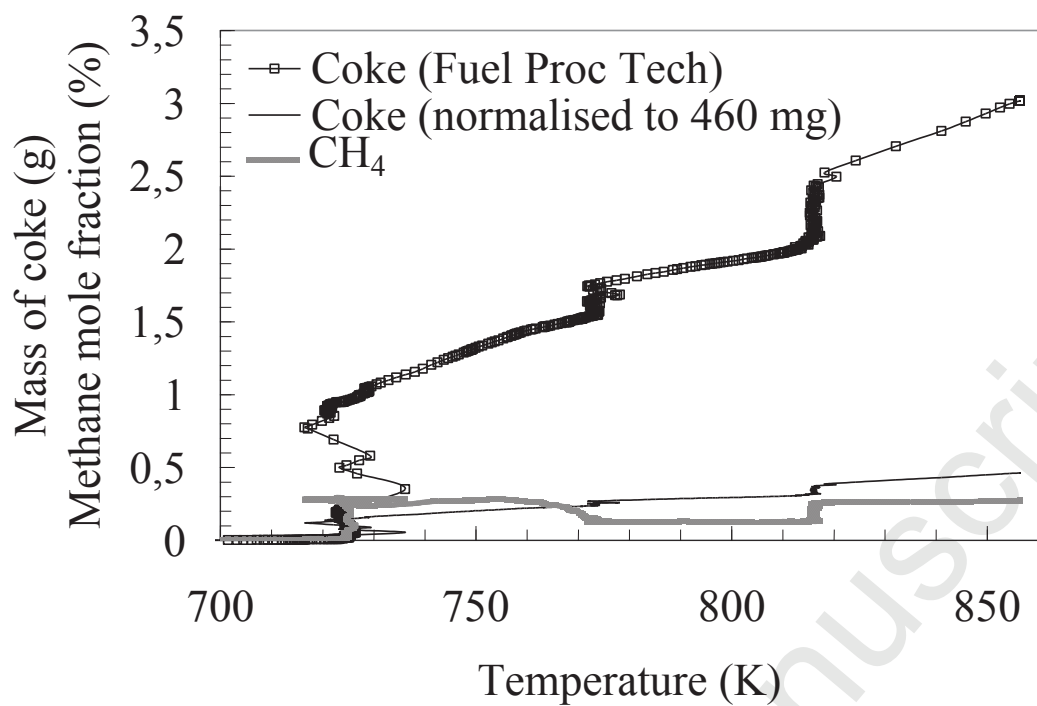


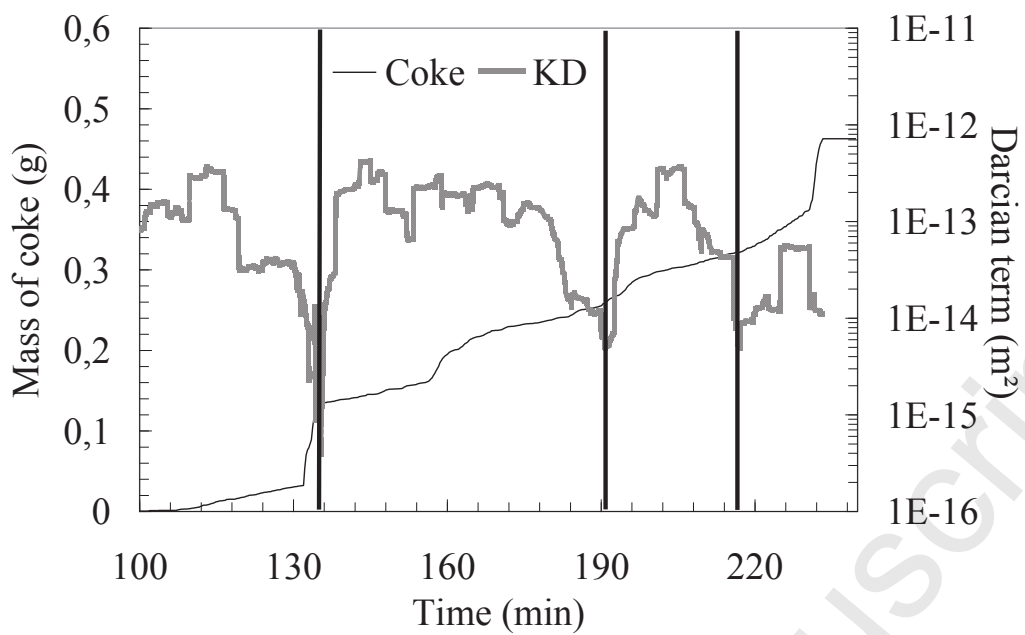
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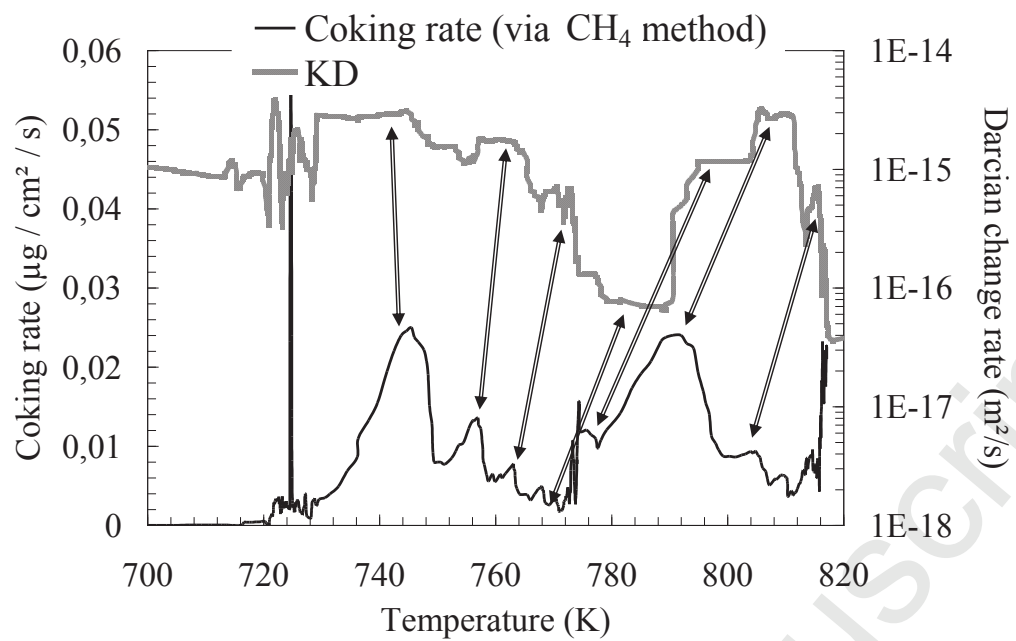


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Highlights

- Hydrocarbon fuel pyrolysis achieved under supercritical state through porous medium
- Spatial profiles of pyrolysis mixture composition obtained for three temperatures
- Unusual production of alkenes, of light species and of coke due to porous medium
- Transient relationship proposed between coke deposit and permeability changes
- Contact surface effect shown through comparisons between plug flow and porous flow

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