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# Numerical Investigations of Chemical Kinetics for Methane Catalysis and Pyrolysis

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Chemical Propulsion Topics

Secondary Technical Area: Environmentally-Friendly "Green" Propellants

## Abstract

In the framework of the active and regenerative cooling of hypersonic and space structures, a kinetic mechanism should be proposed to investigate numerically the fuel pyrolysis and the coke formation with a possible surface effect (catalytic reactions). This chemical mechanism should be suitable for Computational Fluid Dynamics approach (limited number of species and reaction). For this purpose, this work presents some homogeneous and heterogeneous calculations of methane chemistry with metallic catalysts in order to test different kinetic schemes. A parametric study is achieved and several reactors natures are tested.

## 1. Introduction

Hypersonic applications involve the management of a large thermal load applied to the whole structure and more specifically, the engine. The temperature overpasses 1600 K (Mach 6), which imposes an efficient method to cool the materials. In regards with this objective, the circulation at counterflow of an endothermic fuel is explored as a regenerative cooling system [1,2]. The thermal degradation of the fuel would act as a heat sink before entering in the combustion chamber. The choice of the fuel is critical and numerous studies have been conducted in order to explore the potential of several hydrocarbons [3–7]. Based on this bibliography, methane has been selected as a reference fuel for this work. Generally, the pyrolysis of the different fuel is realized in a reactor manufactured in stainless steel, alumina or other metallic materials. Sometimes, it is made with quartz which is an inert material and so prevent from potential reaction between the pyrolyzed fuel and the surface of the reactor. Indeed, it can be assumed that the molecule which compose the inner wall may react with the species present inside the reactor (moreover with the increase of temperature). It would be of great interest to review the studies which deal with that surface catalytic effect and, in particularly, the interaction between pyrolyzed methane and a composite inner wall. Unfortunately, there are a limited number of available works and no study corresponding to the specific conditions mentioned above was found. Consequently, the more appropriate works will be presented below, then several catalytic thermal decomposition studies will be discussed.

The objective of this study is to obtain a mechanism which permits to compute methane pyrolysis considering the surface catalytic effect. This one should be represented by the addition of about a few dozen of reactions.

Studies on the catalytic effect of the inner wall of a reactor are relatively uncommon and were essentially conducted in the seventies. The works of Crynes and/or Albright (et al.) are of prime importance [8–11] even if they deal with simple hydrocarbons (ethane, propane, propylene). Materials of the construction or surface-volume ratio ( $S/V$ ) were considered as an influent factor on the conversion of hydrocarbon and product distribution.

In [8], they studied the pyrolysis of propane in some tubular flow reactors of different natures: stainless steel, low-carbon steel or nickel, treated or not by oxygen, hydrogen sulfide (after  $O_2$  treatment) or steam. The experimental conditions were: temperature range of 873 K – 1023 K, residence time of 2.8 s and atmospheric pressure. For untreated stainless steel reactors, methane and ethylene are the major products. No influence was demonstrated of the ratio variation  $S/V$  and a kinetic model was proposed. Nickel reactors tests lead to similar results. The wall effects have been highlighted for the treated inner surface.

Crynes, in association with Ghaly also explored the wall activity during the thermal cracking of propylene in a flow system [9]. Seven tubular flow reactors (two stainless steel AISI 304, one low-carbon steel AISI 1015, one nickel, one inconel 600, two incoloy 801) were compared under the following conditions: 973 K- 1123 K, atmospheric pressure and residence time of 0.1 s - 3 s. For a reference reactor (stainless steel), the major products were methane and ethylene for a mid-conversion rate (20 %). The carbon yield was also evaluated and Crynes et al. assumed that coke was directly formed by the interaction between propylene and the metallic surface. Indeed, they observed that the carbon yield at low conversion was higher than for inert surface. The authors also calculated the reaction rates and compare them with some precedent data. Even if some differences were noticed, the values were quietly similar. Considering the low-carbon steel reactor, wall activity increased during the first stage of pyrolysis (coke and hydrogen yield increased during the first 20 min) and then dropped and reached a steady-state

after one hour. Reaction rates increased systematically in a range of 25-35 % higher. A quite similar profile was found for nickel reactor. The highest activity was observed at the beginning of the run (slightly higher conversion than reference) before decreasing progressively according to the increase of carbon deposition. At steady-state, propylene conversion was comparable to the reference one but the product distribution remained modified. Inconel and incoloy reactors presented a lower activity. For the first mentioned, a catalytic effect was observed for about 30 minutes with a maximum during the first two minutes. Only product distribution differed during this period and no modifications were noticed for larger time. The same results were found with a reactor made in incoloy with a slight higher activity period (40 minutes). To the authors, wall activity is essentially due to the presence of iron which is a catalyst for carbon and hydrogen production. However, alloys of iron generally contain a significant ratio of chromium which inhibits the activity of iron. So, surface containing active carbon layer such as low-carbon steel may present a higher activity by carrying iron atoms in this layer. Concerning nickel, it is assumed that the active sites have a lower affinity with hydrocarbons than iron. At last, alloys containing both iron and nickel may be less effective than pure metal so that explains the results obtained with inconel and incoloy.

The surface effect was also explored for the pyrolysis of ethane in several flow reactors (stainless steel, incoloy 800 and Vycor glass) [10]. The experimental conditions were closed to the previous studies and surface different treatments have been done for several runs. Hydrogen and ethylene were the dominant decomposed species and coke was also widely represented. Comparison between reactors showed that the ethylene yields is higher while hydrogen amount and coke formation are lower for Vycor glass than for metal. Furthermore, the composition of produced gases changed with the time excepted for the non-metallic reactors. Another observation, the treatment of the metal reactor had an impact on the product distribution as it was

demonstrated in the precedent works. For example, a reduced inner surface leads to a product composition similar at the Vycor glass one. It was also noticed that the ethylene yields varied to the opposite of the hydrogen and coke ones.

Van Der Zwet et al. studied the role of the surface area for several different catalysts (essentially aluminum oxides) on the methane pyrolysis [12]. The experiments were performed in a non-reactive flow reactor made in quartz, at 1398 K and at atmospheric pressure. The authors confirmed that the ratio (S/V) had a clear impact on the product distribution. However, even if the product distribution was modified, the authors noted that the conversion of methane was poorly affected (increase only by a factor 10 when the S/V ratio is increased by 4 orders). To explain such facts, Van Der Zwet assumed that the radical or other dislocations sites of the surface may promote the hydrogen abstraction from CH<sub>4</sub>. Plus due to the autocatalysis phenomenon, the surface also may have an influence on the termination (by capturing from the gas phase the species involved in the autocatalysis). These two opposite effects lead to very complex surface area dependence. Finally, they suggested that a large catalytic surface is favorable to the production of coke and hydrogen while the gaseous and liquid pyrolyzed species are preferentially produced in a reactor with a low S/V ratio. They concluded that the nature of the catalyst has a poor impact in comparison with the surface influence.

The works of Li et al. could be also mentioned [13]. Their study consisted in coating the inner wall of a stainless steel tube by a mixture of different zeolites and a ceramic-like binder. The pyrolysis of two jet fuels (n-dodecane and aviation fuel RP-3) were performed according to supercritical conditions (873 - 898 K and 4 MPa) and continuous flow. Heat sink capacity and conversion rate were both explored. It was demonstrated that those two parameters were enhanced by the zeolite coating: increase of about 25 % for the heat sink capacity and the

dodecane conversion pass from 66 to 80 %. Plus it was also observed that the coke deposit was lower in the case of RP-3 fuel.

Fang and Yeh [14] proposed an extensive analysis considering numerous metal oxides catalysts (24) deposited on a silica gel. Methane pyrolysis was performed at 1400 K and 2.10<sup>-3</sup> MPa in a quartz reactor. 4 g. of catalysts was deposited inside it. The goal of this study was to produce C<sub>2</sub> species from methane so that the catalytic C<sub>2</sub> selectivity of the metals was quantified with regards to CH<sub>4</sub> conversion rate while the dehydrogenation rate of methane served as activity reference. Fang and Yeh have then proposed a criterion to evaluate the catalysts.

A more recent study further explored the interaction between CH<sub>4</sub> and the surface of the catalysts [15]. It exposed the effect of different metallic catalysts (cobalt, nickel, ruthenium, rhodium, iridium and platinum) supported on alumina or silica on the dehydrogenation of methane. A temperature programmed surface reaction (TPSR) of methane from 298 to 873 K (10 K.min<sup>-1</sup>) has been performed in parallel with a temperature programmed hydrogenation (TPH) of the carbonaceous adspecies.

The works of Zadeh and Smith are also of great interest notably for the numerical aspect. They studied the pyrolysis of methane in presence of supported cobalt catalysts (Co-SiO<sub>2</sub>, K-Co-SiO<sub>2</sub>, Co-Al<sub>2</sub>O<sub>3</sub> and K-Co-Al<sub>2</sub>O<sub>3</sub>) [16]. A mixture of CH<sub>4</sub> and Ar (respectively 95 and 5 %) was injected in quartz fixed-bed microreactor heated at 723 K. In those conditions, they observed different phenomenon such as the metal support interaction (MSI) which consists on the migration of the SiO<sub>2</sub> support on the prepared cobalt. The MSI impact is the increase of methane decomposition activity and the facilitation of the migration of carbonaceous species from catalyst surface to the support. This phenomenon is notably increased by the decrease of the initial Co loading. Temperature had also an effect: the higher it is the higher the CH<sub>4</sub> conversion and the

metal coverage. As it was mentioned in the precedent paper, the support had also an effect: The conversion is greater for an alumina support than a silica one.

Numerous other works on the decomposition of methane with metallic catalyst have been conducted those past years, notably according to three main objectives: the production of CO<sub>2</sub>-free hydrogen; the production of carbon nanofibers and the production of heavier hydrocarbons (e.g. [17–20]). Even if the goal of those studies is different of the present one of this paper, it can be cited the works of Hussein et al. [21]. They investigated the catalytic decomposition of methane and the consequent production of H<sub>2</sub> and carbon. Nickel (13 wt %) was chosen as catalyst and titanium oxide as support. The catalysis was conducted at atmospheric pressure and for a temperature range of 823 - 1173 K. Methane was mixed with argon (1:1 in mole) and then injected in a stainless steel reactor where 1 g of catalyst was placed in its center. The reactor dead volume was limited by a filling of quartz particles. No specific analysis on the product distribution was done but the hydrogen and carbon deposit rates as the CH<sub>4</sub> were carefully monitored.

Another work of great interest is the one of Wolf et al. [22] which investigated and developed a model which treats exclusively the reactions that occur at the surface of a platinum catalyst. Neglecting the gas-phase reactions was justified by the studied temperature (300 - 700 K): indeed, the authors showed that there were no or negligible thermal degradation reactions for such low temperature. According to this fact, they created a mechanism composed of 39 elementary surface reactions involving 14 surface species. The species are limited to 2 carbons in order to avoid the very numerous isomerizations reactions that exist for C<sub>3</sub>+ molecules. The kinetic model also permitted to take into account the thin monolayer of carbonaceous overlayer that quickly covers the surface of the catalyst.



This mechanism, in addition with the three precedent ones could be a good base to develop a kinetic model for the catalytic decomposition of CH<sub>4</sub>. Some of the reactions could be implanted in a pure pyrolysis mechanism. Nevertheless, it appears that various adjustments (thermodynamic factors) should be done thanks to experimental results in order to obtain convenient results. Indeed, those described mechanisms were originally developed to predict the catalytic production of species, generally without taking into account the gas-phase reactions (low temperature).

## **2. Numerical simulations and discussion**

The literature survey presented in [23] permitted to identify several interesting surface mechanism which could be added to reduced Hamdullahpur's one [24]. Calculations were performed for methane pyrolysis and they consisted of testing 8 existing kinetic mechanisms. Those models have been compared against experimental data (Gordon [1]; Billaud et al. [2], [3]), numerical data (Davis et al.[4]) and equilibrium data. Then, the most accurate mechanism was selected and a reduction work was achieved by using the dedicated software Workbench. Two methods were tested and associated to this purpose: the Detailed Reduction (DR) which consists of decreasing the number of reactions as a function of their flux; and the Direct Relation Graph (DRG) which limits the number of species and, consequently, the number of reactions. The monitoring of methane decomposition and acetylene prediction served as a first comparison criteria.

Thus, in a first approach, it was planned to integrate the reactions proposed by Wolf et al. in [22]. Unfortunately, it was not possible to gather all the kinetic and the thermodynamic parameters so that this model could not be tested. So, the authors focused on the mechanism

proposed by Deutschmann et al. [25,26]<sup>1</sup>. His team has elaborated several surface mechanisms considering different catalysts: nickel, platinum, rhodium and palladium. These ones were not fully designed for pyrolysis since they integrate reactions with some species containing oxygen (e.g., O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O...). Nevertheless, by removing these molecules, it can be assumed that the surface models were suitable for the purpose of this study.

Hence several comparisons have been made according to the following criteria: the catalyst, i.e., platinum, nickel and rhodium; the site density, which can be estimated considering as one face of a unit cell of a crystal structure. By dividing the number of sites on this face by the area, a first value of the site density is obtained. Typically, the value goes from 10<sup>15</sup> to 10<sup>20</sup> sites/cm<sup>2</sup>. Then, this value should be balanced by each species which could react. By simplification, it was decided to not consider this last element and to fix site density values which would efficiently frame the real ones. Hence, computations were made considering site density going from 10<sup>-10</sup> mole.cm<sup>-2</sup> to 0.1 mole.cm<sup>-2</sup>. Therefore, it must be noticed that a value of 10<sup>-4</sup> mole.cm<sup>-2</sup> should be a theoretical maximum. The reactor design (i.e. closed homogeneous batch reactor or perfectly stirred reactor) was also considered.

#### **a. Platinum catalyst**

Deutschmann's platinum surface mechanism was initially used for the catalytic combustion of methane on platinum (13 species, 24 reactions)<sup>2</sup>. The pure combustion reactions have been deleted and only pyrolysis ones were kept (7 species, 7 reactions). These reactions are then injected in the reduced mechanism of Hamdullahpur

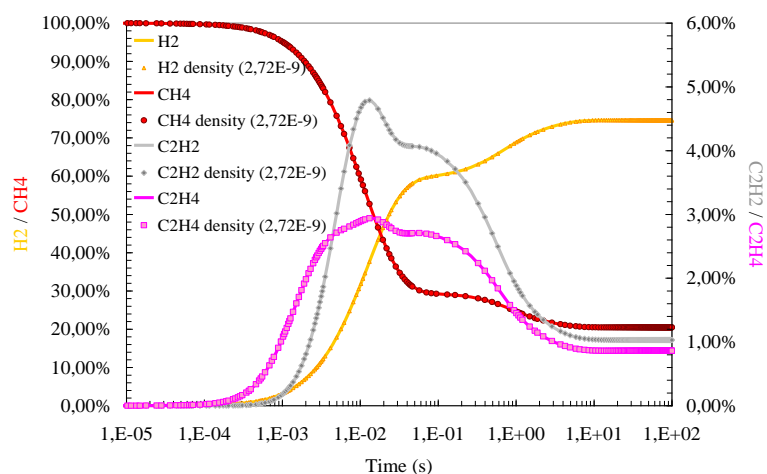
The first computations were performed considering a closed homogeneous batch reactor considering a temperature of 1600 K, a pressure of 1.013 MPa and a residence time of 100 s. The

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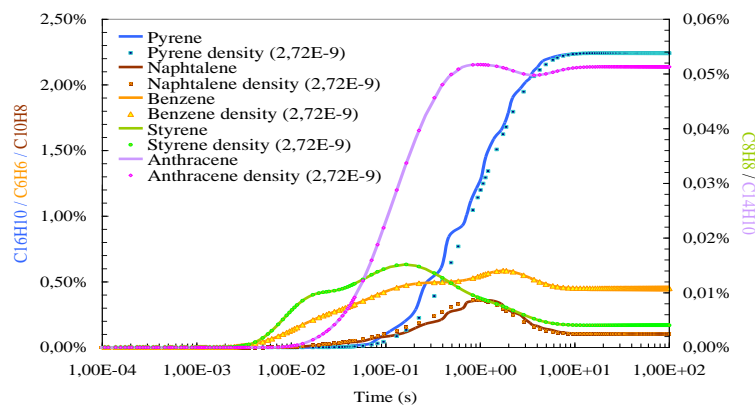
<sup>1</sup> Available mechanisms at: <http://www.detchem.com/mechanisms.html>

<sup>2</sup> Mechanism available at: [http://www.detchem.com/mechanisms/sm\\_Pt\\_CH4\\_O2\\_1.2\\_CHEMKIN](http://www.detchem.com/mechanisms/sm_Pt_CH4_O2_1.2_CHEMKIN)

internal surface of the reactor was fixed at  $1.436 \text{ cm}^2$ , the volume at  $1.6 \cdot 10^5 \text{ cm}^3$  (which correspond to the reference volume and internal area proposed by the software) and the density of sites to  $2.72 \cdot 10^{-9} \text{ cm}^{-2}$  (value fixed by Deutschmann). Firstly, the catalytic results were compared with reference ones, i.e. without surface reactions (Figure 1). Two kinds of species were selected as point of comparison: predominant light species (hydrogen, methane, acetylene and ethylene – Figure 1a) and heavy coke precursors (benzene, styrene, naphthalene, anthracene and pyrene – Figure 1b). It can be noted that no differences are found for the lights while very minor variations are observed for naphthalene and pyrene. Plus, these minor variations do not affect final composition so that they could be neglected.



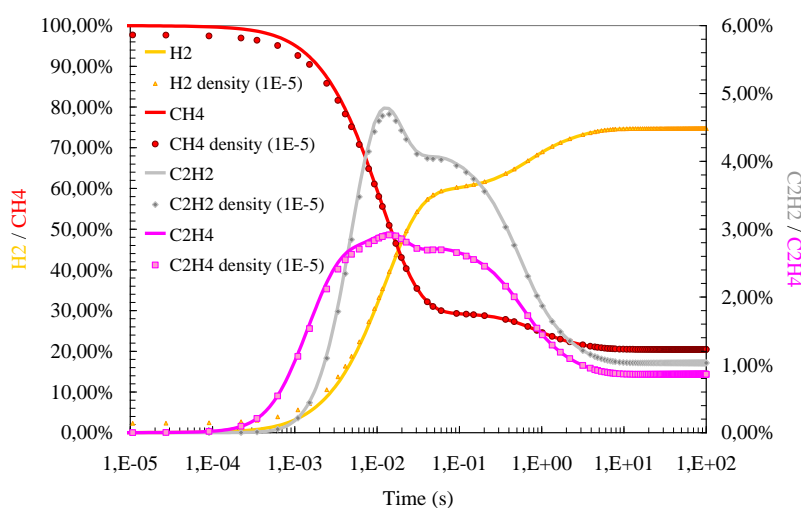
a)



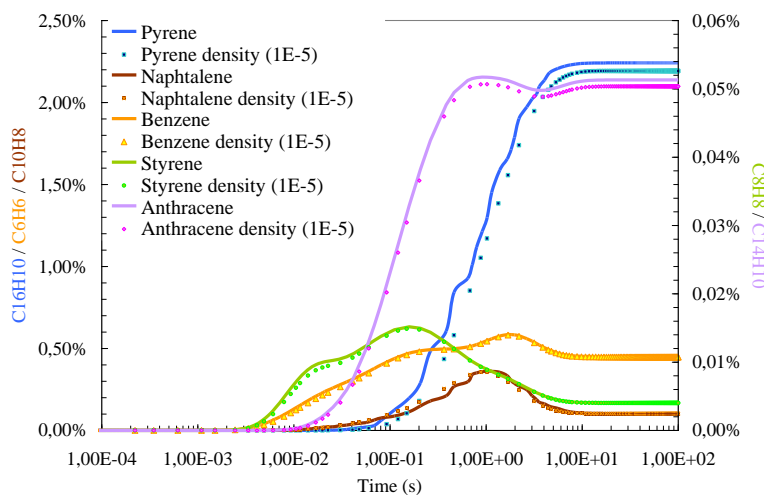
b)

**Figure 1. Comparison between Hamdullahpur's reduced mechanism with and without surface reactions (platinum catalyst, density,  $2.72 \cdot 10^{-9} \text{ mol.cm}^{-2}$ ). a) Light species. b) Heavy coke precursors.**

The site density could be increased up to  $10^{-5}$  mole.cm<sup>-2</sup> (beyond that value, the software could not solve the problem even by increasing the absolute and relative tolerances). In this case, the production is practically not affected. Thus, it can be noticed a very slight decrease of methane consumption before 1 ms of computations but the fractions do not change at the end of the simulation (Figure 2a). Concerning solid PAH, a slight decrease of pyrene and anthracene productions are predicted but as the precedent case, those differences are too minor to be considered.



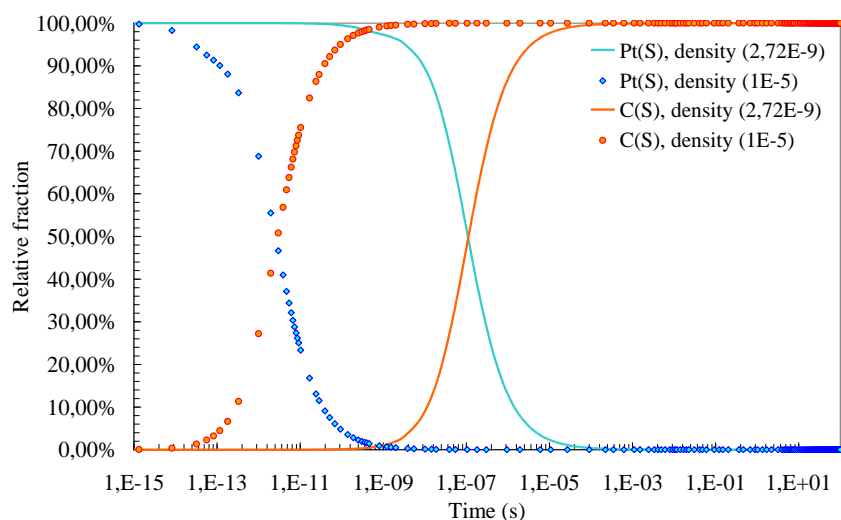
a)



b)

**Figure 2. Comparison between Hamdullahpur's reduced mechanism with and without surface reactions (platinum catalyst, density  $10^{-5}$  mol.cm<sup>-2</sup>). a) Light species (mol.%). b) Heavy coke precursors (mol.%).**

Regarding the repartition of surface species, the coke (C(S)) becomes rapidly predominant and the only surface species whatever the site density (Figure 3). The rise of the site density has a visible effect, i.e., it critically accelerates the production rate of coke (more than 4 orders) with a faster consumption of platinum sites. The surface is quickly deactivated by the coke deposit so that the catalytic effect is suppressed by this wall of solid carbon. No particular effect of the platinum site density is found up to  $10^{-5}$  mole.cm<sup>-2</sup> on light and heavy coke precursors. Higher site density may conduct to an increase of its effect (as it will be seen for other catalysts). Nevertheless, as it is mentioned above, higher values of site density should be not realistic so that it can be assumed that platinum has no impact on methane pyrolysis for such conditions (considering Deutschmann mechanism). Thus, the experimental results presented in section III should not be affected by the presence of platinum coil and can be considered representative of pure methane thermal degradation.



**Figure 3. Surface species distribution in mol.% (platinum catalyst).**

## **b. Nickel catalyst**

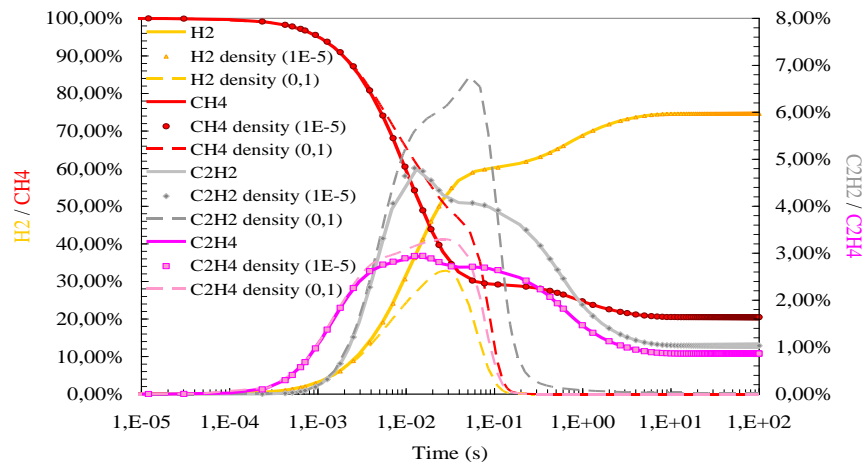
Deutschmann developed a specific mechanism to predict the reforming and oxidation of methane on nickel (42 reactions involving 13 species)<sup>3</sup>. By removing the oxidized molecules, the number of species fell to 7 species and the reactions one to 11.

This mechanism was injected in the Hamdullahpur's one and tested according to the same conditions described above. A first comparison was made according to the increase of site density (Figure 4). It can be noted that as for platinum catalyst, the site density has no impact up to  $10^5$  mole.cm<sup>-2</sup> for light species (Figure 4a). Nevertheless, for heavy coke precursors, some differences have been found (Figure 4b). Indeed, whereas no notable variation is found from C<sub>6</sub> to C<sub>14</sub>, a high difference is predicted for the initial production of pyrene (C<sub>16</sub>H<sub>10</sub>) which the formation is clearly delayed. This phenomenon is not fully understood considering the fact pyrene is issued from lighter species (notably acetylene) which productions are not affected. Finally, such deviation may be caused by a delayed production of intermediary species which intervene in the reaction pathway of pyrene.

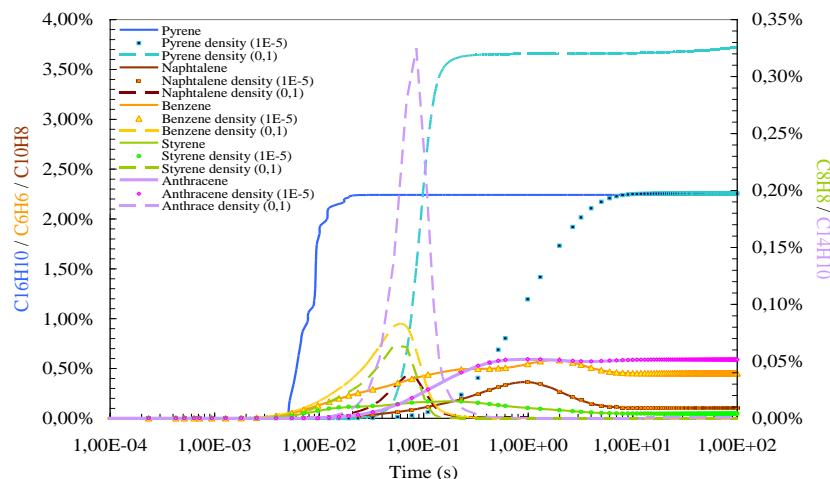
Regarding surface molecule profiles (Figure 5), strong variations can be noticed. A higher delay is observed for the decrease of Ni(s) and the increase of H(s) ratios while the C(s) production is delayed and clearly lower. These phenomena, notably the lower consumption of nickel sites, appeared to be understandable because its absolute amount is higher considering a higher site density, so that both the “saturation” and the surface coke formation required a longer delay. Thus, it can be assumed that the different dynamic of anthracene production is linked to these surface variations.

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<sup>3</sup> Available at: [http://www.detchem.com/mechanisms/sm\\_Ni\\_CH4\\_H2O\\_CO2\\_O2\\_1.2\\_CHEMKIN](http://www.detchem.com/mechanisms/sm_Ni_CH4_H2O_CO2_O2_1.2_CHEMKIN)



a)

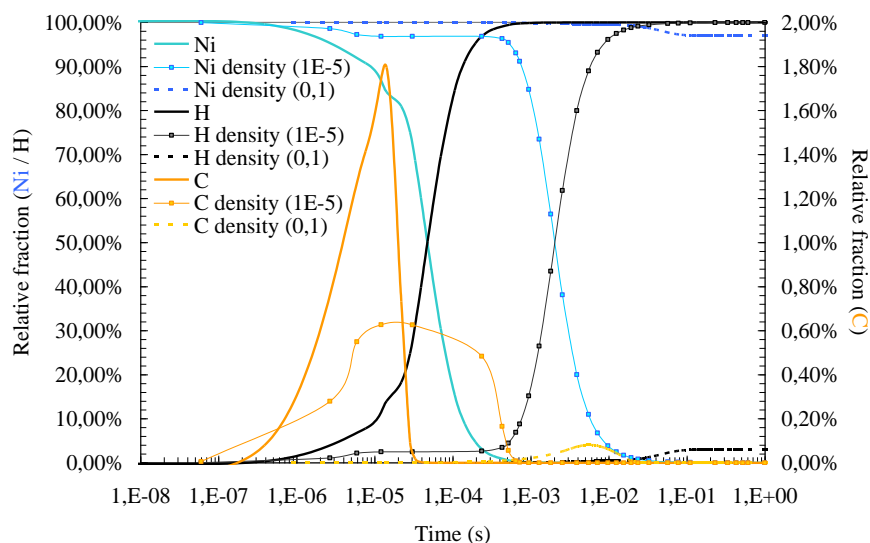


b)

**Figure 4. Comparison between Hamdullahpur's reduced mechanism with and without surface reactions (nickel catalyst). a) Light species (mol.%). b) Heavy coke precursors (mol.%).**

Considering this surface mechanism, the software can solve a problem with a higher value of site density (up to  $0.1 \text{ mole.cm}^{-2}$ ) and reveals strong differences in the gas and surface specie productions. For the lights, the critical difference is the total consumption of methane (Figure 4a). As a consequence, the production of other lights, if it could be higher for the first milliseconds of computation ( $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ ), it becomes null after 0.1 s for hydrogen and ethylene and after 1 s for acetylene. In parallel the production of heavy coke precursors is also affected (Figure 4b). Excluding pyrene ratio, the production of the other species is earlier and more important but felt to 0 after 1 s of computation. The pyrene production is delayed of about one order and reached a

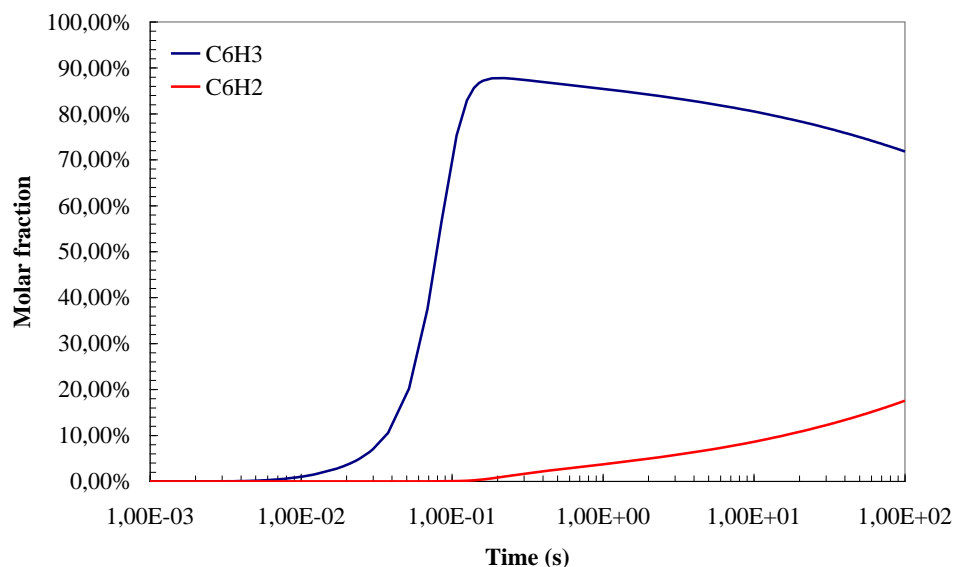
higher value (about 3.6 % against 2.1 %). After 100 s of computations, its formation is not still stabilized. At last, the dynamic of surface species appears to be strongly slower: the Ni site ratio remaining higher than 90 % while the H(S) and C(S) ones are limited (respectively < 10 % and < 0.2 %). This is probably due to the quick extinction of methane and the high density of sites.



**Figure 5. Comparison between the surface specie predictions (mol.%) of Hamdullahpur's reduced mechanism with catalytic reactions according to different site density ( $2.66 \cdot 10^{-9}$  mole. $\text{cm}^{-2}$ ,  $10^{-5}$  mole.  $\text{cm}^{-2}$  and 0.1 mole.  $\text{cm}^{-2}$ ).**

Then due to the fact that all those gas species are totally consumed since 0.1 s, this should be balanced by the production of other species. The computations reveal that  $\text{C}_6\text{H}_3$  becomes the main gas species after 1 ms and  $\text{C}_6\text{H}_2$  the second one (Figure 6).  $\text{C}_6\text{H}_2$  is a precursor of  $\text{C}_6\text{H}_3$  which is notably involved in the production of acetylene. The accumulation of such precursors is questionable since they are highly hydrogenated compared to methane. This may be related to the validity of the mechanism and further analysis of the catalytic effect should be provided with help of specialists.





**Figure 6. Predominant species (mol.%) in gas phase after the total consumption of methane.**

All these observations suggest that nickel catalyst enhances the methane production (up to its total consumption) and favors the coke formation. It is also noted that the higher the site density the faster the decomposition and the more important the amount of coke (illustrated by the presence of anthracene as only heavy coke precursors).

Finally, the well-known catalytic effect of Nickel is qualitatively verified notably with an increase of coking effect.

### **c. Rhodium catalyst**

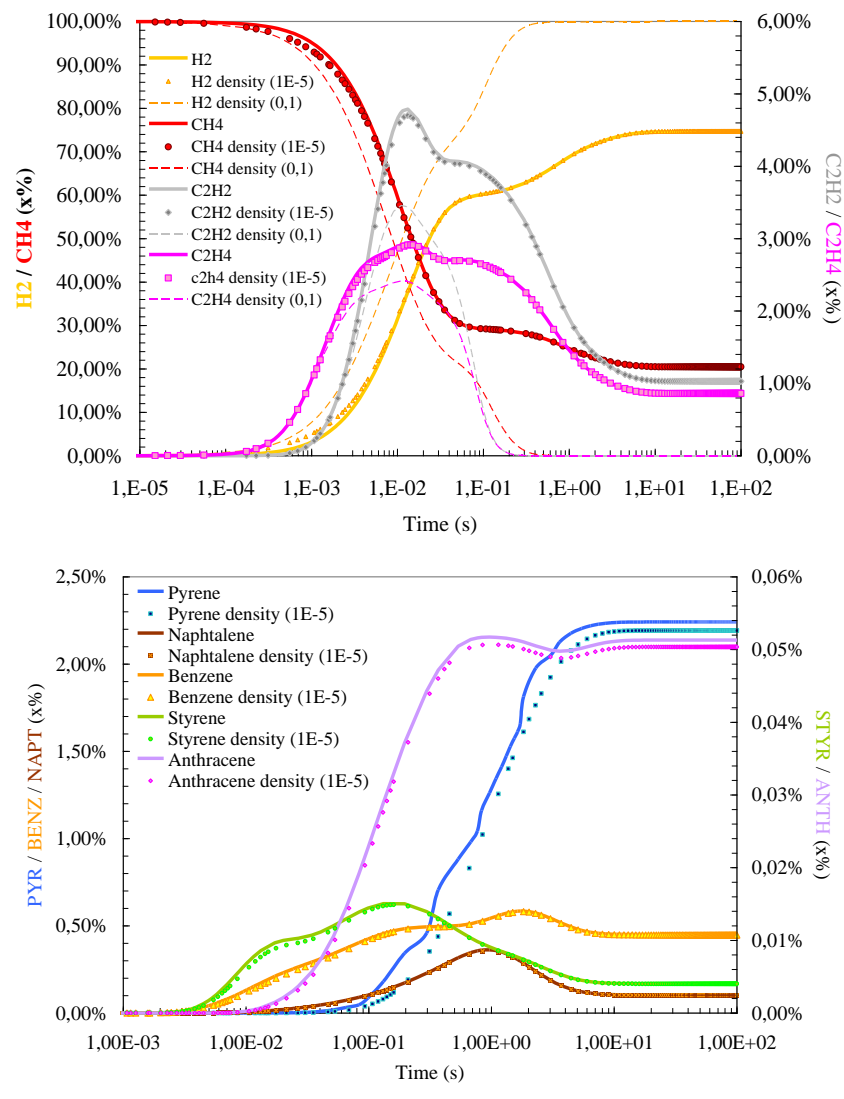
This mechanism was developed by Deutschmann's team in order to simulate the partial oxidation of methane on rhodium<sup>4</sup>. This kinetic model is more complex than the precedent ones, involving 12 species in 38 reactions (which represents 7 species for 12 reactions).

As the precedent case, the impact of the site density was investigated. As the nickel case, a higher value of site density could be treated (up to 100 mole.cm<sup>-2</sup>). Strong differences are found

<sup>4</sup> Available at : [http://www.detchem.com/mechanisms/sm\\_Rh\\_CPO\\_CH4\\_1.0\\_CHEMKIN](http://www.detchem.com/mechanisms/sm_Rh_CPO_CH4_1.0_CHEMKIN)

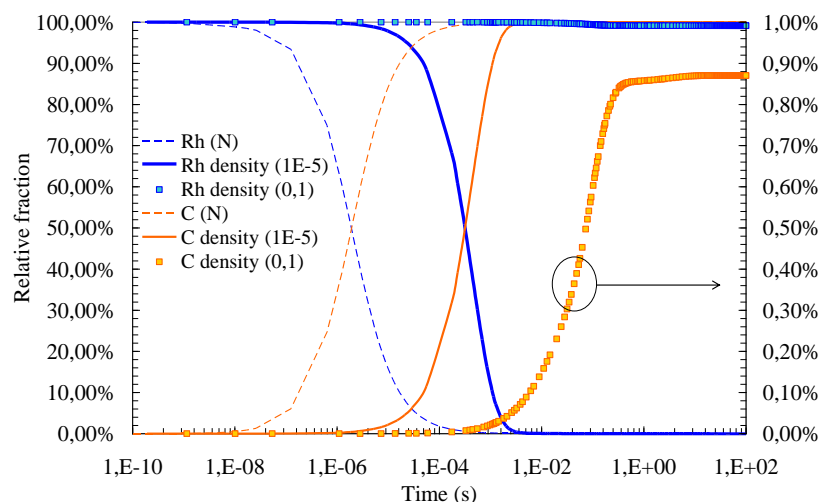
considering this catalyst. Thus, for light species, a moderate site density ( $10^{-5}$  mole.cm<sup>-2</sup>) has a very relative effect on the kinetics dynamic: the consumption of methane as the production of hydrogen are faster for the first milliseconds (Figure 7a). Regarding the heavy species, it can be considered that only the pyrene production is slightly affected by the presence of rhodium (< 1 % - Figure 7b). For surface species, the consumption of rhodium is delayed (same profile as nickel catalyst) and coke becomes the dominant species after a few ms of computation (Figure 8). For a higher value of site density (0.1 mole.cm<sup>-2</sup>), the profile is totally modified. Indeed, a complete consumption of methane occurs before 1 ms. In parallel, acetylene and ethylene are produced transiently while H<sub>2</sub> ratio rapidly reached 100 % (Figure 7a). As a consequence, the carbon atoms initially present in methane are adsorbed at the surface. Since the surface species also take the Rhodium into account, which is largely predominant, only 1 % of C is found (Figure 8). Nevertheless, this 1 % represents the totality of initial carbon. Furthermore, it is difficult to provide a mass balance of the atoms in the heterogeneous calculations because of the two phases (solid and gas/liquid). The species are quantified independently in each phase.

Finally, using rhodium as catalyst lead to a faster and complete decomposition of methane associated with a huge production of hydrogen (which became the only produced species) while solid carbon is deposited on the surface (Figure 8). This signs the critical impact of a catalyst which may involve, in case of large excess, the total decomposition of methane at the reactor surface into gaseous hydrogen and solid carbon (equilibrium state).



**Figure 7. Comparison between Hamdullahpur's reduced mechanism with and without surface reactions (rhodium catalyst). a) Light species (mol.%). b) Heavy coke precursors (mol.%).**

A site density of  $10^{-5}$  mol.cm<sup>-2</sup> clearly shows a site saturation around 0.01 s, which shows that the catalytic effect get negligible for test duration over 10 ms. However, for very high site density (0.1 mol.cm<sup>-2</sup>), the Rhodium sites are still around 100%, which clearly reveals that no site saturation is found. The catalytic effect can continue, up to 100 s here.

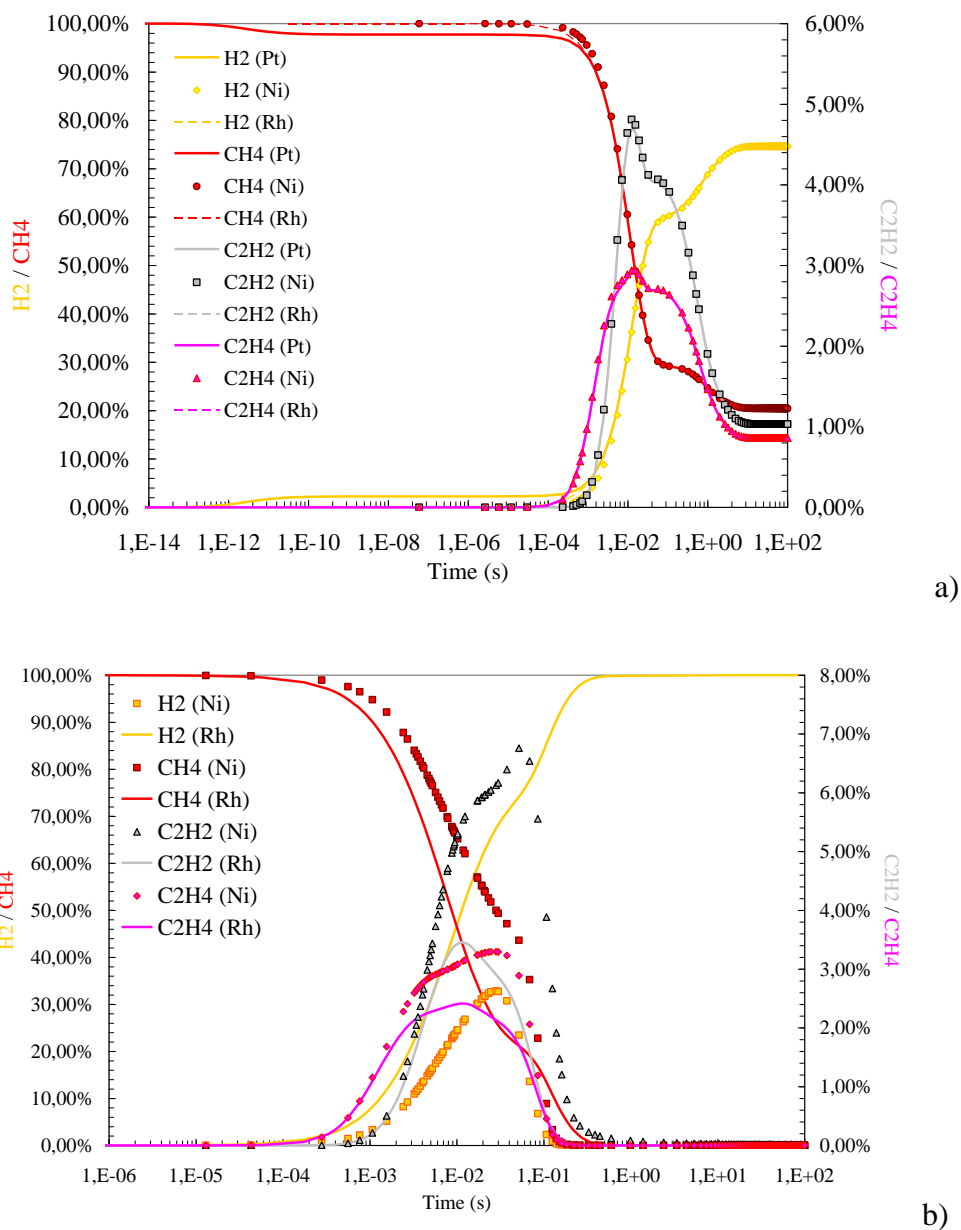


**Figure 8.** Comparison between the surface specie predictions (mol.%) of Hamdullahpur's reduced mechanism with catalytic reactions according to different site density ( $2.72 \cdot 10^{-9}$  mole. $\text{cm}^{-2}$ ,  $10^{-5}$  mole.  $\text{cm}^{-2}$  and  $0.1$  mole.  $\text{cm}^{-2}$ ).

#### d. Comparison of catalytic mechanisms

A comparison was made according to site density and catalyst nature. The results are given, for the light species in Figure 9, for heavy coke precursors in Figure 10 and for surface species in Figure 11.

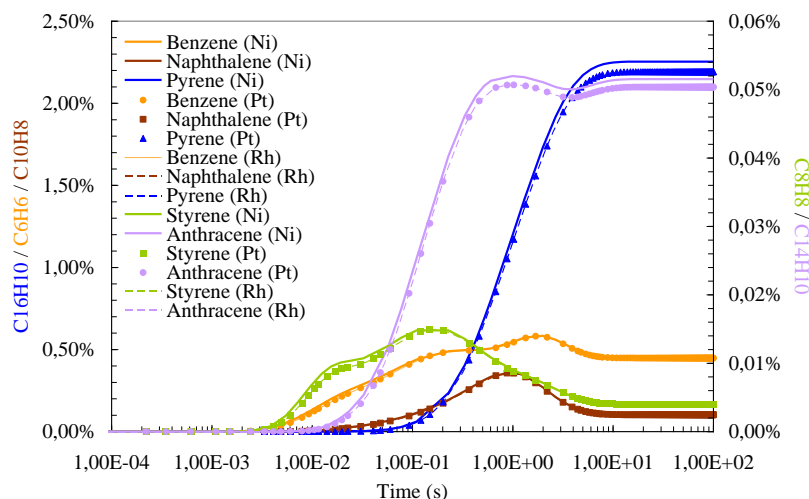
For lights, two values were retained  $10^{-5}$  mole. $\text{cm}^{-2}$  (Figure 9a) and  $0.1$  mole. $\text{cm}^{-2}$  (Figure 9b). Considering the first value, the differences are very limited between the three catalysts (i.e. faster but limited production of hydrogen linked with methane decomposition in presence of platinum). On the contrary, strong variations are found for a higher amount of site density. Methane is totally consumed after 1 ms of computation (faster consumption considering rhodium). Nevertheless, whereas for nickel, only transient precursors ( $\text{C}_6\text{H}_3$  and  $\text{C}_6\text{H}_2$  – Figure 6) and pyrene remain in the gas phase after 1 ms,  $\text{H}_2$  is the only remaining gas specie considering rhodium catalyst for the same computation delay.



**Figure 9. Effect of catalyst nature on light specie production (mol.%).**

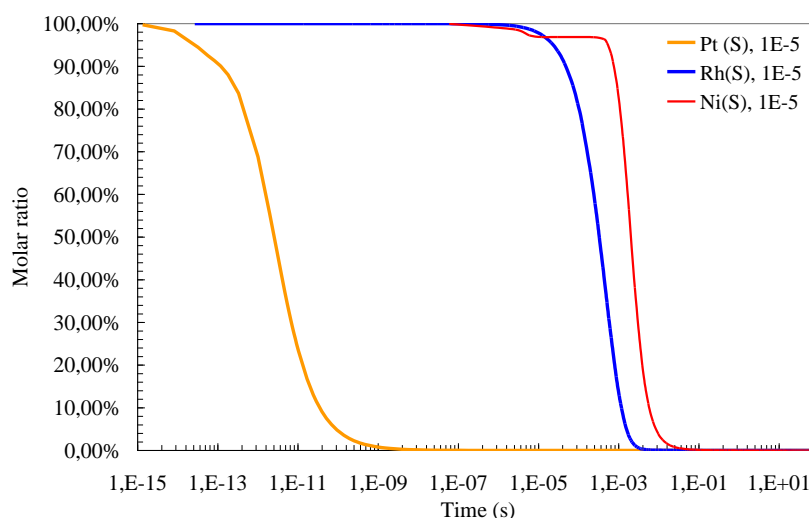
**a) Site density =  $10^{-5}$  mole.cm $^{-2}$ . b) Site density =  $10^{-1}$  mole.cm $^{-2}$ .**

For heavy coke precursors, the differences are negligible for a site density of  $10^{-5}$  mole.cm $^{-2}$  (Figure 10). For a higher value, the production is practically null with rhodium catalyst while anthracene (4 %) is predominant considering nickel.



**Figure 10. Effect of catalyst nature on heavy coke precursor ratio (mol.%) for a site density of  $10^{-5}$  mole.cm $^{-2}$ .**

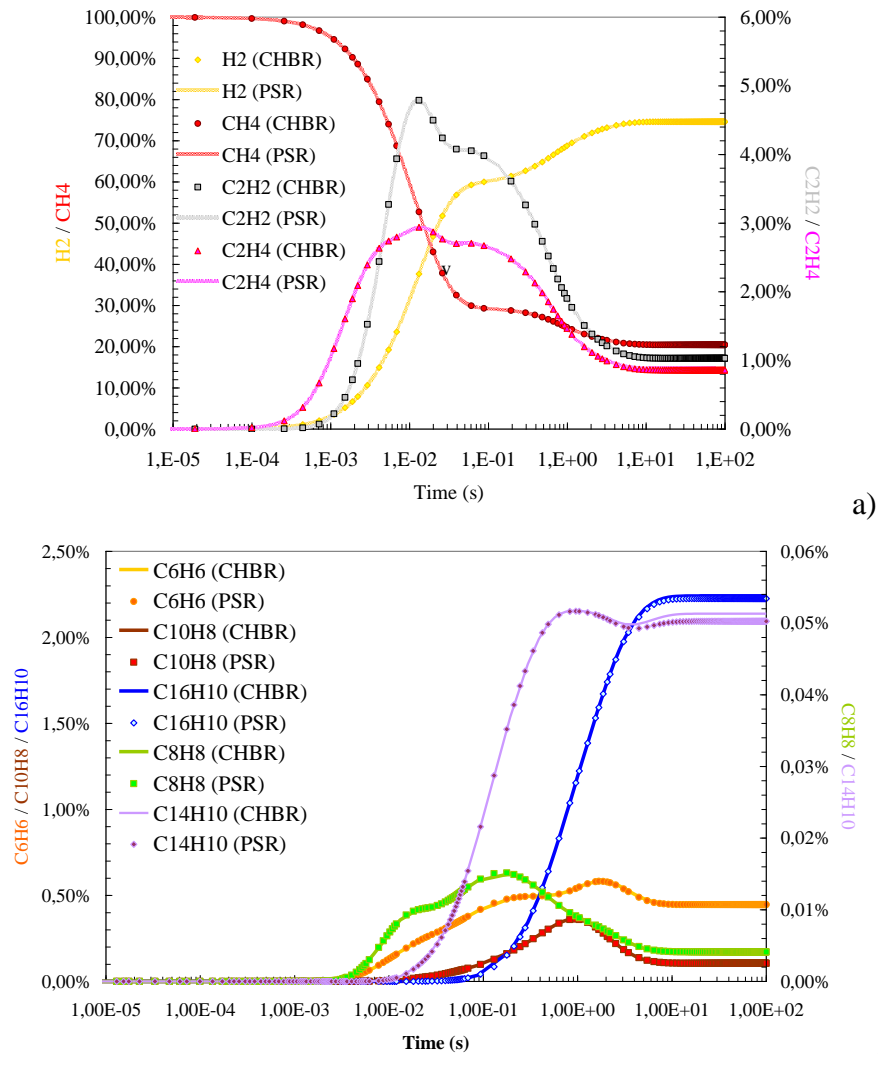
The consumption of site density is complete whatever the catalyst (Figure 11). This consumption is clearly faster for platinum (1 ns) while for the two others, the profiles are similar (1 ms for Rh and above 10 ms for Ni). Coke is mainly and quickly produced with platinum (and with a certain delay for rhodium) while H(S) is predominant considering nickel catalyst. This could explain why a strong amount of asphaltic coke formation is expected in presence of nickel while a catalytic one is predicted with other catalysts.



**Figure 11. Consumption of catalyst sites (mol.%) for an initial density of site =  $10^{-5}$  mole.cm $^{-2}$ .**

### e. Impact of the reactor configuration on catalytic computations

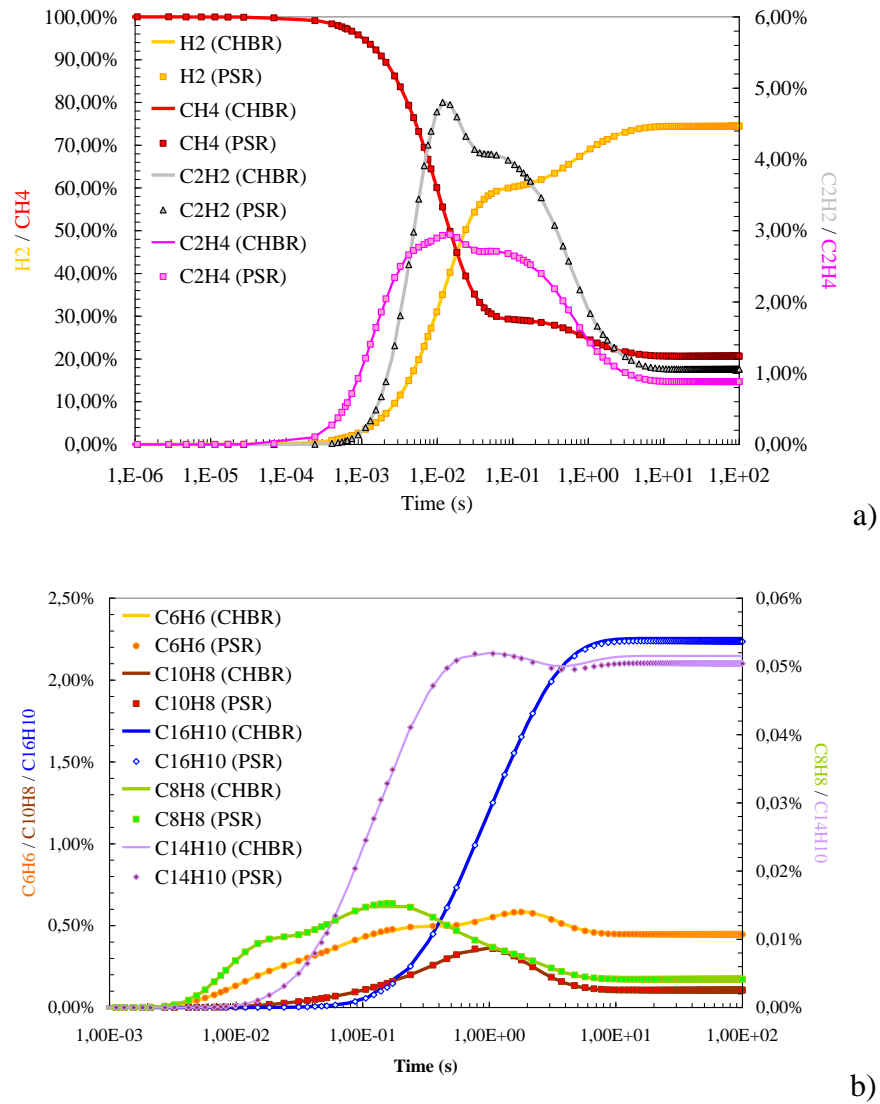
The precedent computations were realized considering a closed homogeneous batch reactor (CHBR). Nevertheless, it was shown in the precedent study [27] that the product distribution obtained during the pyrolysis of reactive fuel through a porous media was quite similar with the one obtained in perfectly stirred reactor (PSR). The CHEMKIN software permits to make the computations regarding PSR. Thus, first simulations were made to compare CHBR and PSR with the same software. No differences are found using only Hamdullahpur's mechanism (Figure 12).



**Figure 12. No prediction differences considering PSR or CHBR for the reduced mechanism.**

**a) Light species (mol.%). b) Heavy coke precursors (mol.%).**

Then, a comparison was done with nickel catalyst and a site density of  $10^{-5}$  mole.cm<sup>-2</sup> but as previously, no significant variations are found (Figure 13).

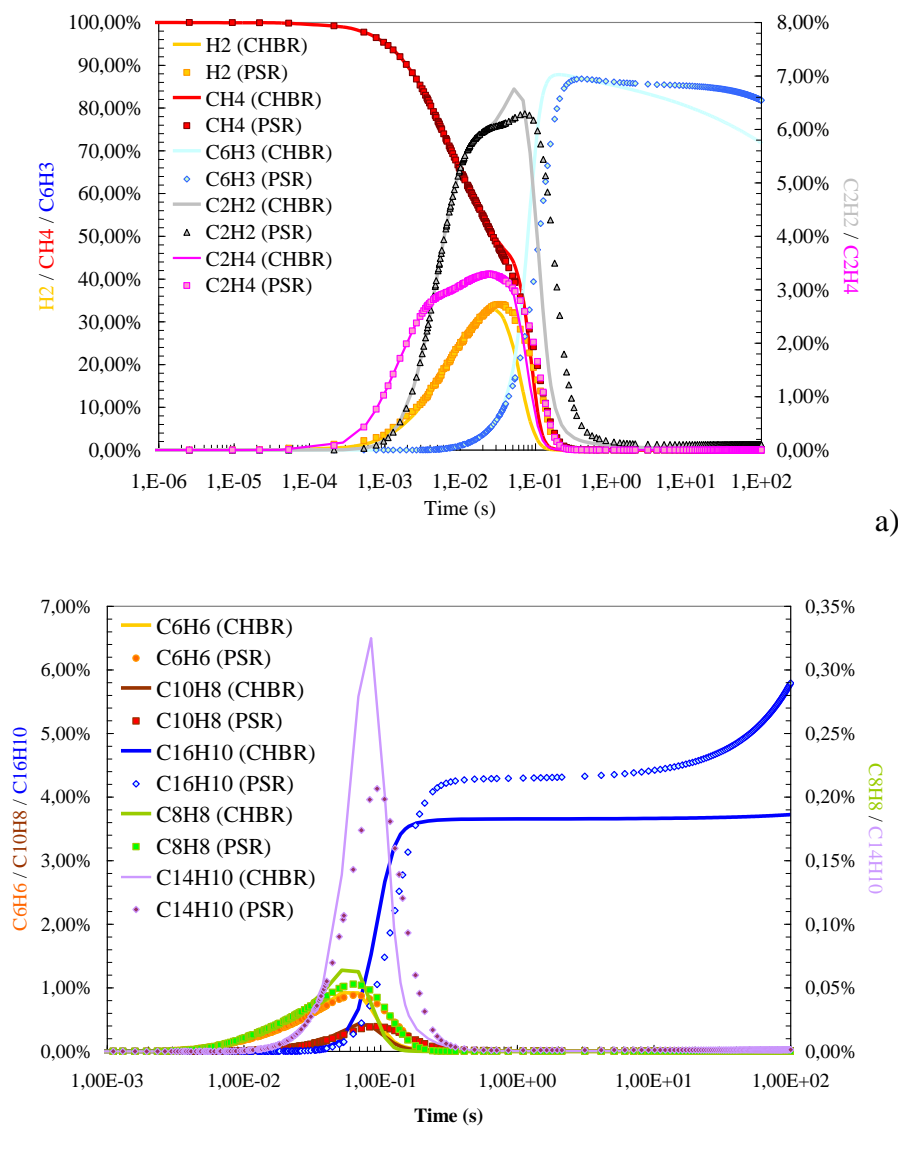


**Figure 13. No prediction differences considering PSR or CHBR with nickel catalyst (site density =  $10^{-5}$  mole.cm<sup>-2</sup>). a) Light species (mol.%). b) Heavy coke precursors (mol.%).**

The site density has to be increased to a value of  $0.1$  mole.cm<sup>-2</sup> to notice relative discrepancies. The CHBR presents a residence time equal to the computation time (closed system) while the PSR (open system) has a residence time around 1000 s (linked to the mass flow rate  $0.5$  g.s<sup>-1</sup> and methane density at 625 K –  $3.0812$  kg.m<sup>-3</sup>). For both reactors, the surface/volume ratio is constant to have a similar catalytic effect. The predictions for lights are



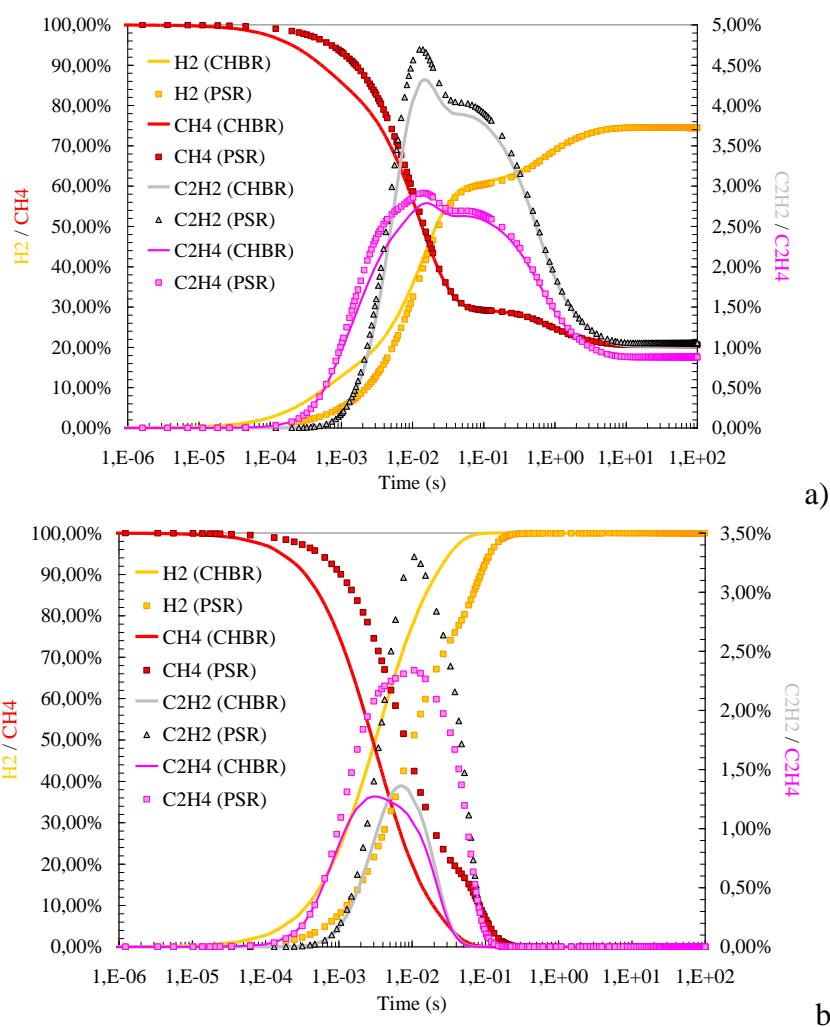
closed excluding  $C_6H_3$  ratio which the fall is faster and stronger in the PSR configuration (Figure 14a). This drop is notably compensated by the increase of pyrene ratio which rises after 1 s of computations (Figure 14b).



**Figure 14. Comparisons between PSR and CHBR predictions with nickel catalyst (site density = 0.1 mole.cm<sup>-2</sup>). a) Light species (mol.%). b) Heavy coke precursors (mol.%).**

Finally regarding nickel catalyst, the ratio predictions are closed whatever the reactor nature so that the reactor configuration cannot be considered as a significant criterion for the study computations. This fact is also confirmed for platinum catalyst.

Therefore, for rhodium mechanism, the predictions are more affected by the reactor type especially for a high value of site density ( $0.1 \text{ mole.cm}^{-2}$  – Figure 15b). The consumption of methane is delayed of about one order (which delayed the production of other species). The ethylene ratio is multiplied by 2 while the acetylene one by 3. Finally the transient production varies according to the reactor nature but after a few seconds of computations, the final composition remains unchanged with a  $\text{H}_2$  ratio of 100 % (which is high –equilibrium state- thus questionable).



**Figure 15. Comparisons between PSR and CHBR predictions (mol.%) with rhodium catalyst.**

**a) Site density =  $10^{-5} \text{ mole.cm}^{-2}$ . b) Site density =  $0.1 \text{ mole.cm}^{-2}$ .**

Finally, the choice between PSR and CHBR is numerically of secondary importance regarding the final composition and the conditions imposed by the authors.

### **3. Conclusions and Perspectives**

Regenerative and active cooling represents a large subject gathering several domains as material withstanding or reactive fuel thermal decomposition. Methane was chosen as a reference fuel. The goal was to select an available mechanism which could predict its pyrolysis for a large set of conditions. The size of the kinetic model should be restricted in order to easily implement it in a CFD code. In parallel, a work has been done on the integration of catalytic reactions into the kinetic model. Several catalysts has been considered (because a number of materials are found in cooling systems where methane is used as a coolant). Rhodium, platinum and nickel mechanisms were studied and injected in the reduced Hamdullahpur's mechanism. The effect of these catalysts on the methane conversion has been observed. The chemical mechanisms were extensively tested to estimate the site density effect and the effect of the material nature. Experiments are expected in order to obtain data for nonmetallic materials for which no heterogeneous kinetic scheme has been found.

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