

## Soot formation during methane reforming at high temperature: experiments and modelling

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One way to obtain a gas suitable for Fischer-Tropsch synthesis is a two-step process constituted by a fluidized bed, for the biomass pyrolysis/gasification, followed by a high temperature reforming reactor. Raising the syngas to high temperatures (1600-1800 K) in presence of steam is a way to purify it by lowering the concentration of tars, and to increase the mass yield by reforming CH<sub>4</sub> and tars into CO and H<sub>2</sub>.

Methane reforming experiments were performed in a pilot scale facility (gas flow rate: about 1 Nm<sup>3</sup>.h<sup>-1</sup> for a residence time of 2 s). Methane was introduced in a mixture of synthetic gases (CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O) representative of the gas released during biomass pyrolysis at high temperature (1100 K) and fast heating rate. During these experiments, the massive formation of soot was observed, leading to the fouling of the filtering devices. The soot particles were analyzed and observed using an Electron Scanning Microscope. Their steam gasification reactivity was then characterized using TG analysis.

The experiments were simulated then using the plug-flow assumption. The model computes the gas composition using CHEMKIN II subroutines. A good agreement between experiments and modeling was found for the main gases. The soot precursors (PAH) formation was also modeled.

### 1. Introduction

For the production of diesel fuels, lignocellulosic biomass gasification is followed by Fischer-Tropsch synthesis which requires a high quality syngas. To match the gas specifications, the tars concentrations should be below their dew point (Boerrigter and Rauch 2006). Furthermore, in order to maximize the gasification yield (into CO and H<sub>2</sub>), methane content should be as low as possible.

Biomass gasification at temperatures below 1000°C produces gas which contains methane and too much tar for liquid fuel synthesis. To upgrade and purify the gas, it can be heated to high temperatures. A high methane conversion, as well as a very low tar content are expected at the outlet. Thermal cracking of methane has been largely studied over a wide range of temperature (Roscoe and Thompson 1985; Olsvik and Billaud 1994; Ranzi, Sogaro et al. 1994; Holmen 1995). Although the influence of hydrogen on the methane cracking has been demonstrated, the influence of steam has rarely been studied, especially in absence of O<sub>2</sub>, and mostly with different objectives and operating conditions than ours (Kunugi, Tamura et al. 1961; Jönsson 1985).

C<sub>2</sub>-species formation is expected during syngas thermal treatment, which corresponds to methane oxidation under extremely fuel rich conditions (Warnatz, Maas et al. 2006). These by-products have to be minored for different reasons. First, the formation of C<sub>2</sub>-species reduces the methane conversion into CO and H<sub>2</sub>. Second, acetylene is considered as the principal intermediate species on the reaction path to formation of Poly-Aromatic Hydrocarbons (PAH) species, commonly considered as soot precursors (Appel, Bockhorn et al. 2000; Richter and Howard 2000; Warnatz, Maas et al. 2006).

Experimental tests were performed in a pilot scale facility to investigate the methane reforming in a gas produced by wood pyrolysis. The main tested parameters were temperature (from 1273 to 1773 K) and the initial composition. During the experiments, production of soot particles was observed but not measured precisely; these particles increased the difficulty to perform the tests, because they rather rapidly induced high pressure drop in the filters at the reactor exit.

The experimental gas compositions were then compared to 1D plug-flow modeling results, using detailed kinetic schemes. Furthermore the model was used to predict the production of soot precursors, for different operating conditions.

## 2. Experimental

The experimental part of this work was performed in collaboration with Gaz de France, within the project CINE-HT, partially funded by the French National Research Agency (ANR).

### 2.1 Description of the facility

The experimental facility, referred to as PEGASE, has been designed to study the reforming of methane, light hydrocarbons and tars at high temperatures (between 1273 and 1773 K). Figure 1 is a schematic diagram of the facility. The external water cooled vessel measures about 4 m in length by 0.6 m in diameter; it is made of stainless steel to sustain a pressure of 4 bars. The hot reactor zone is made of alumina tubes, heated by molybdenum silicide heaters. Small overpressure of argon is maintained between the vessel and the reactor to prevent reactive gas to flow into the reactor.

The reactive mixture injected into the reactor using massflow controllers is rapidly heated up to the desired temperature in the preheating zone ( $L = 1$  m; i.d. = 15 mm) before flowing into the isothermal hottest part ( $L = 0.84$  m; i.d. = 70 mm). After leaving the reaction zone, the gas is cooled down, flows through filters and steam condenser, and is analyzed using a micro Gas Chromatograph ( $\mu$ GC) coupled with a Thermal Conductivity Detector (TCD). The compounds which can be detected are: Ar, CO<sub>2</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>. The total mass flowrate of the dry exit gas is measured by a Coriolis mass flowmeter.

### 2.2 Conditions of the experiments

The experimental conditions are listed in

Table 1. The main studied parameter is temperature. For a few tests, residence time, H<sub>2</sub>O or H<sub>2</sub> contents are also varied. Residence time is adjusted by changing the initial gas flowrates.

Table 1: Conditions of experiments

Temp. (K)	Res. time (s)	CO (mol%)	CO <sub>2</sub> (mol%)	CH <sub>4</sub> (mol%)	H <sub>2</sub> (mol%)	H <sub>2</sub> O (mol%)
1265-1783	2.1	19	14	7	16; 32	15; 25; 30

\*:Standard conditions in bold characters

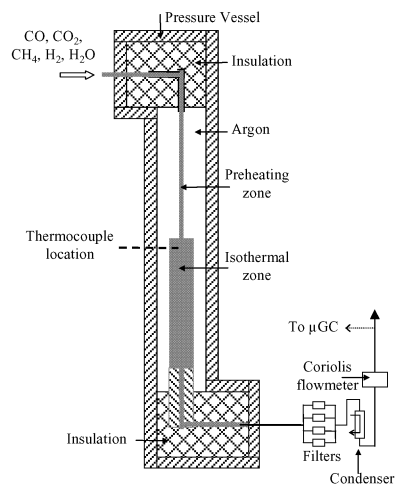


Figure 1: Schematic diagram of the gas reforming reactor, PEGASE.

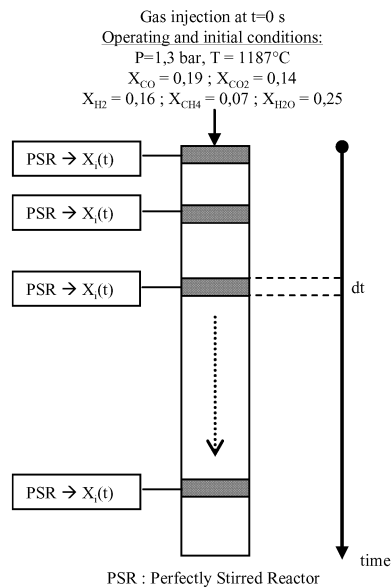


Figure 2: Schematic representation of the 1D plug-flow reactor model.

The pressure in the reactor was equal to 1.3 bar. The temperature indicated with the results is measured by a type B thermocouple located in the top part of the isothermal zone (see Figure 1).

H<sub>2</sub>O exit flowrate was calculated by measuring the mass of condensed water; however, we estimated that 89 to 100% of the steam really condensed, so the H<sub>2</sub>O flowrate may be underestimated. It was not possible to close a mass balance, as soot particles were not weighed at the end of each test. For most tests, more than 94% of the carbon was measured in the gas at the exit.

### 3. Chemical reactions modeling

CFD computations (for more details see (Valin, Cances et al. to be published 2008)), have shown that the PEGASE reactor could be modeled using a 1D plug-flow model: PEGASE is separated in elementary section, each of them being a Perfectly Stirred Reactor (PSR). At each time step a PSR is modeled using subroutines of the CHEMKIN II software (Kee, Rupley et al. 1989). Pressure and temperature are set for each simulation and they are supposed to remain constant over time. Figure 2 depicts the 1D model and the standard operating and initial conditions.

A lot of detailed chemical mechanisms devoted to combustion are published in the literature, but it was impossible to find one kinetic scheme developed for steam reforming of methane. Moreover, the typical operating conditions of syngas reforming

are relatively specific: high concentrations of  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ . However, the intrinsic radical chemistry should be the same, whatever the initial gas composition.

The kinetic mechanism used for the present was proposed by Skjøth-Rasmussen and coworkers (Skjøth-Rasmussen, Glarborg et al. 2004). This mechanism (159 species, 773 reactions) is suitable for the calculation of soot precursors, mostly Polycyclic Aromatic Hydrocarbons (PAH), and is one of the most recent mechanisms available in the literature.

## 4.4. Results

### 4.1 4.1 Output gas composition

Figure 3 shows the output gas composition, after 2s residence time in PEGASE, as a function of temperature. The main components are plotted in Figure 3(a), whereas the  $\text{C}_2$ -species formed in the reactor are represented in Figure 3(b). The experimental results are compared to the Skjøth-Rasmussen's models mechanisms predictions. The  $\text{CO}$  and  $\text{H}_2$  contents increase with temperature, whereas the  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  contents decrease. These evolutions are the most significant between 1373 and 1573 K and tend to be slighter above 1573 K. The agreement between the experiments and the calculations is very good for  $\text{CO}_2$  and  $\text{CH}_4$ . The  $\text{H}_2$  content is slightly overestimated by the models. The discrepancy gap between experiments and models for  $\text{H}_2\text{O}$  above 1450 K can be related to the higher experimental uncertainty for  $\text{H}_2\text{O}$ . Figure 3(b) presents  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  concentrations as functions of temperature. The measured  $\text{C}_2\text{H}_6$  content was below the quantification limit (20 to 30 ppm). The computed  $\text{C}_2\text{H}_6$  concentration is much lower than the  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  ones (of about a factor of 100). Results from experiments and models show a peak for the concentrations at temperatures lying between 1300 and 1500 K. The agreement between modelling and experiments is not so good for  $\text{C}_2\text{H}_2$ .

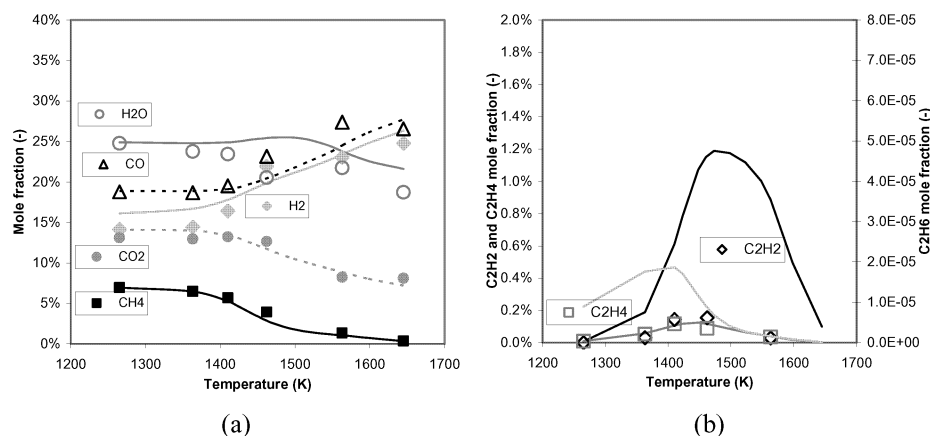


Figure 3: Mole fraction evolution vs. temperature for a 2 s residence time; (a) main components; (b)  $\text{C}_2$ -species; Experimental (symbols) and predicted (lines) values.

#### 4.2 4.4 Soot formaproduction

The mass of mass of soot was not measured soot particles werewas not quantified during the the experiments. However, the soot particles theythe particles were collected on filters, and the pressure loss in these filters was measured. Comparing the pressure drop of all the experiments provides qualitative indications about soot formation.

- In standard conditions (see Table 1), the the soot yield presents a peak between 1363 K and 1645 K.
- With a standard initial composition (see Table 1), a temperature of 1783 K and a residence time of 3.5 s, the the soot yield is quite low.
- By increasing the hydrogen content from 16 % to 32 % (15 % of H<sub>2</sub>O, others: see Table 1) at 1460 K, the the soot yield decreases drastically.

The soot particles collected during the experiment in standard conditions at 1560 K are composed in mole of C : 91,6 %, H : 1,8 %, N : 0,9 %, O: 5,7 %. They were observed using a Scanning Electron Microscope (SEM). Figure 4 shows spherical particles smaller than 1  $\mu\text{m}$ . Their smooth aspect suggests a small reactive surface and thus a small chemical reactivity. This point was confirmed when their steam gasification reactivity was characterized using Thermo-Gravimetric (TG) analysis. Figure 5 shows the temporal evolution of the conversion rate of the mass of soot at final temperature of 950°C and 1000°C. The gasification starts only when the final temperature is reached. The soot reactivity is very low: at 1000°C, 4 h are necessary to convert 90% of the sample, and 5h at 950°C.

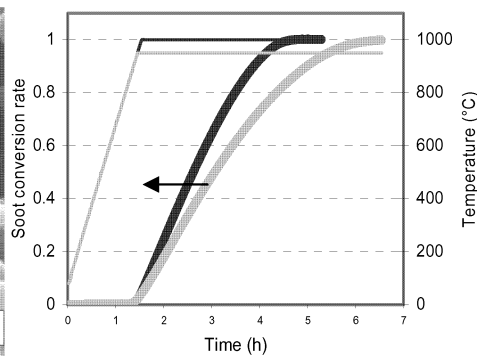
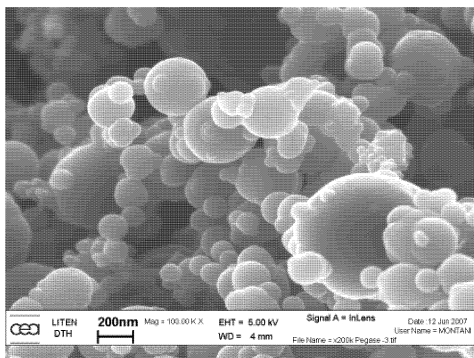


Figure 4: SEM photograph of the collected soot particles. Figure 5: Soot steam gasification reactivity in TG analysis conditions.

the Soot particles are formed through the conglomeration of polycyclic aromatic hydrocarbons (PAH) molecules. Although Even if these PAH species were not measured, their concentrations were computed using the chemical mechanism of Skjøth-Rasmussen, which has been validated over a wide range of conditions (Richter

and Howard 2000; Warnatz, Maas et al. 2006). However, without experimental validations, the following interpretations have to be very careful.

The temperature evolutions of the predicted mole fraction of several soot precursors are plotted in Figure 6. In this diagram, the symbols A1 refers to benzene ( $C_6H_6$ ), A2 denotes naphthalene ( $C_{10}H_8$ ), A3 represents anthracene ( $C_{14}H_{10}$ ), and A4 symbolises pyrene ( $C_{16}H_{10}$ ). Benzene is the most concentrated of these selected PAH species of one order of magnitude, whereas the mole fraction of heavier hydrocarbons increases with their ring number ( $X_{A4} > X_{A3} > X_{A2}$ ). Figure 6 also clearly shows a peak value of the mole fraction of the different species between 1400 and 1600 K, which concords agrees with the experimental observations mentioned above concerning soot particles.

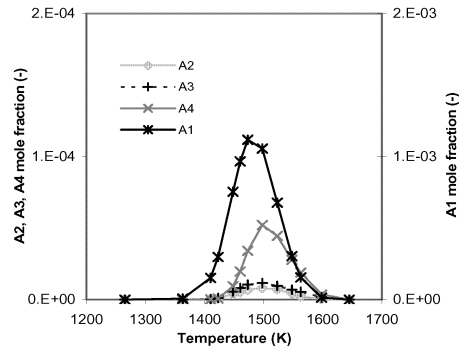


Figure 6: Modeled PAH mole fractions vs. temperature, after 2 s residence time. A1 = Benzene; A2 = Naphthalene; A3 = Anthracene; A4 = Pyrene

#### 4.3 Parametric analysis

As for the main gaseous products, the impact of the changes of the injected initial gas composition  $H_2$  and  $H_2O$  contents on the main components and PAH species was investigated. The bar diagrams plotted in Figure 7 represent the relative variation of the main output species (Figure 7(a,b,c)) and of the PAH species (Figure 7(d)), compared to the reference composition of the output gas. The operating temperature was set at 1400 K, and the theoretical residence time was 2 s., for variations of initial concentration of species (i.e.  $H_2O$ , and  $H_2$ ). The reference case for Figure 7(a) and (b) corresponds to the standard conditions mentioned in

Table 1. The modeled relative variations match the experimental values relatively well.

When  $H_2O$  was decreased by 40 %, from 25 to 15 vol.% (see Figure 7(a)), the  $CH_4$  and  $H_2$  concentrations at the outlet were reduced by 8 %. This impact of the initial  $H_2O$  mole fraction was confirmed when the steam content injected in PEGASE was increased by 20 %, from 25 to 30 vol.% (see Figure 7(b)): the mole fraction of  $CH_4$  and  $H_2$  increase by 4 %. Surprisingly, the methane conversion seems to be inhibited by steam.

The relative variations due to the change of the hydrogen initial content are plotted in Figure 7(c). Since the  $H_2O$  mole fraction was 15 %, the reference case used for the relative calculations was the one depicted in Figure 7(a). It appears clearly that  $H_2$  has a strong inhibiting effect on the methane conversion.

The impact of these variations of the initial gas composition on the PAH molecules formation. (i.e.  $\text{H}_2\text{O} = 15 \text{ vol.}\%$ ;  $\text{H}_2\text{O} = 30 \text{ vol.}\%$ ; and  $\text{H}_2\text{O} = 15 \text{ vol.}\%$ ,  $\text{H}_2 = 32 \text{ vol.}\%$ ) is depicted in Figure 7(d). When the steam content is reduced/increased (from 25 to 15 or 30 mol vol.%) plotted in Figure 12, the model predicts/forecasts/predicts the lower/increase formation of the PAH species: reducing/doubling the initial steam content by 40% causes an increase/decrease of A4 by 650%. The reducing effect of  $\text{H}_2\text{O}$  on the soot concentration was validated by the augmentation of the initial steam content from 25 to 30 vol.%. The impact of the  $\text{H}_2$  initial content in the injected gas is strong: as the  $\text{H}_2$  content was doubled (from 16 to 32 mol %), and the PAH concentration was reduced by more than 60% for all the PAH, and almost of 100% for pyrene (A4). These results are again in agreement with the experimental observations on soot formation mentioned above.

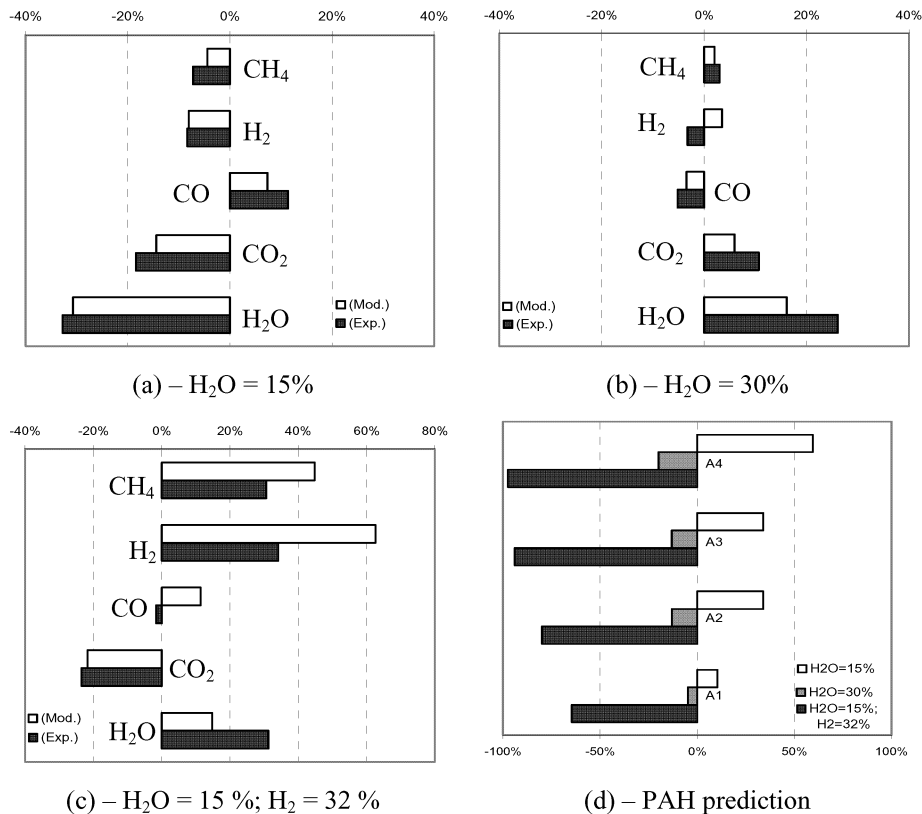


Figure 7: Relative variations of the output gas for changes of the composition of the injected gas at 1460 K for 2 s residence time. Comparison between experimental (Exp.) and predicted values for the main components: (a)  $\text{H}_2\text{O} = 15\%$ ; (b)  $\text{H}_2\text{O} = 30\%$ ; (c)  $\text{H}_2\text{O} = 15\%$ ;  $\text{H}_2 = 32\%$ . (d) PAH prediction.

## 5. Modelling

### 5. Conclusion

Soot formation was observed during experiments of methane reforming under syngas conditions, in the PEGASE pilot scale reactor. These tests were reproduced by means of a 1D plug-flow model coupled with CHEMKIN II subroutines, using the detailed mechanism of Skjøth-Rasmussen, which provides results in good agreement with the experimental data. The model allows the formation of PAH species that are soot precursors to be predicted.

The temperature effect was investigated, showing a peak value for the C<sub>2</sub>-species and PAH formation between 1400 and 1600K. A parametric analysis on the injected composition was performed. It appears that high steam and H<sub>2</sub> content have favourable effects on the PAH formation, but their influence is negative in terms of methane conversion, which is one of the purpose of the PEGASE reactor. The choice of the industrial operating conditions will necessarily be a compromise between the different evocated parameters.

Some particles were collected, analyzed and observed using SEM microscopy. Their steam gasification reactivity was tested in a TG analysis device; the very slow conversion indicates that soot elimination through gasification under 1000°C will require very long residence time devices.

Further investigations with artificial PAH and real syngas injection are now planned. Developments will be carried out to precisely measure the PAH and soot formed in the PEGASE reactor. Moreover theoretical investigations have to be conducted to understand the formation and interaction mechanisms of soot under syngas conditions.

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