HYDRODYNAMIC MODELLING OF A PLASMA PROCESS FOR CARBON BLACK PRODUCTION.

INFLUENCE OF CARBON SOOT ON THE HEAT AND MASS TRANSFER

Isabel Dème¹, Laurent Fulcheri¹ and Gilles Flamant²

¹ CENERG Ecole des Mines de Paris, Sophia Antipolis, France
² IMP-CNRS, Font-Romeu, France.

ABSTRACT

The development of a new plasma process involving high temperature gas-solid interaction requires the analysis of hydrodynamic phenomena. In this context, CFD modelling is a key tool for the design, the control and the optimisation of the process. In a previous step, the general flow inside the reactor in the absence of carbon particles has been studied and a simplified approach to take into account the influence of the rotating electromagnetic forces (3-phase AC) has been developed. In the next step, whose preliminary results are presented in this paper, the injection of a gaseous hydrocarbon is considered and a 2D model taking into account the radiation of carbon particles is developed in parallel.

1. INTRODUCTION

The world-wide production of carbon black accounts to about 6 million tonnes per year. More than 99% of the carbon black is presently produced by partial combustion processes. The furnace process is the main carbon black production process. Although the partial combustion processes are able to produce carbon blacks at very low price, satisfying for a large extend the present demand, the fact remains that the operating conditions are limited by the interacting reactions: Fuel combustion, feedstock cracking and product synthesis. Depending on the feedstock and on the quality of the product, the furnace process achieves poor carbon yields varying between 35 and 65%. As a consequence, a high level of gaseous emissions accompanies this process.

A new route for the production of carbon black and hydrogen using a thermal plasma process is under development since 1993 by Ecole des Mines de Paris and CNRS in association with industrial partners. The main objectives of this new route are:
- The set-up of a new environmentally friendly process.
- The production of new carbon nanostructures thanks to realisation of temperatures and enthalpies unreachable by combustion processes.

One of the main features of the process is related to the growth of ultra fine solid carbon particles in the gas flow that will radically affect the heat transfer and the flow inside the reactor.

The results presented in this paper correspond to a first step in the modelling of the pilot reactor in 2D. This model is developed to take into account the presence of carbon
particles during the injection of gaseous hydrocarbons. The model is validated against experimental data by adjusting the control parameters.

2. PRESENTATION OF THE TECHNOLOGY

![Electrical Power Supply (200 kW)](image)

The plasma gas is introduced in the upper part of the reactor. Each electrode is connected to one of the phases of the power supply (3-phase AC). The hydrocarbon is introduced radially downstream the plasma flow; it is decomposed into carbon black and hydrogen. Carbon black is separated from the gas and collected in a bag filter [1].

Figure 1. Pilot plant for the production of carbon black and hydrogen

3. 2D HYDRODYNAMICS MODELLING

In parallel with the experimental work carried out on the pilot plant, CFD modelling has been used as a tool for the control, the optimisation of the process and the scaling up of the process to an industrial scale.

Hydrodynamic study of the reactor started with B. Ravary [2]. The main points developed and implemented in a CFD code by Ravary were the influence of the electromagnetic forces induced by the arc current in the arc zone and the mixture of two gases of the same nature. The model is described in detail in references [2] and [3].

3.1 Preliminary calculation

In the next step, whose preliminary results are presented in this paper, the hydrocarbon injection is considered. The presence of a solid carbon phase is expected to radically affect the heat transfer due to the two-phase medium radiation (absorption, emission and scattering).

The plasma-particle system is considered as a continuous homogeneous and semi-transparent gas [4]. Therefore, the injection and mixing phenomena are not treated. For radiation modelling, the discrete ordinate model is applied. One of the main difficulties is related to the knowledge of physical coefficients. The evaluation of these coefficients is possible under special approximations or assumptions [5]. As a conclusion of this consideration the semi-transparent medium is purely absorbent and the absorption coefficient can be expressed as follows:

\[
a = \frac{3}{2} \int \frac{\partial F(\nu)}{\partial \nu} \nu \, d\nu
\]

where \( \lambda \) is the wavelength of radiation, \( f_\nu \), the particle volume fraction, with the function

\[
F(\nu) = \frac{24n_\nu k_\nu}{(n_\nu^2 - k_\nu^2 + 2)^2 + 4n_\nu^2 k_\nu^2} \quad [6],
\]

\( n = n_\nu - ik_\nu \), the spectral complex index.
The reactor design allows an efficient separation between the plasma and the reaction zone where the hydrocarbon is injected (see Figure 1). In the plasma zone (no particles) the plasma is considered as a transparent medium and the absorption coefficient is set to zero. In the reaction zone, the distribution of particles being homogeneous, the absorption coefficient is constant (all parameters of Equation (1) are considered constant) [4]. This approach allows studying the influence of the absolute value of the absorption coefficient on the temperature field and the heat transfer.

3.2 Method

The injection of the hydrocarbon involves the decomposition of the hydrocarbon and the formation of solid particles. This causes some difficulties as it involves the mixing of two different fluids at different temperatures. The hydrocarbon injection temperature is about 300K and the zone where the hydrocarbon is injected has a mean temperature of about 2000K. At very high temperatures a vast number of chemical species can be formed from the different elements in the mixture. This decomposition corresponds to non-thermodynamic equilibrium phenomena (gas into condensed phase) and the chemical reaction is irreversible. The distribution of the particles resulting from its decomposition is heterogeneous.

The mixing between the plasma and a hydrocarbon feedstock requires special consideration. For the simplification of the problem, the kinetic of the chemical reaction is not modelled. The plasma gas and the feedstock methane are considered as two non-reactive species. Input parameters of the model are the physical thermodynamics and transport properties of the plasma and the methane, as well as their molecular masses. For the calculation of the properties of the mixture plasma - methane the mixture formulation based on kinetic theory is used. Thereby, the properties are functions of the mass fraction of each species as follows:

\[
\begin{align*}
\mu_{\text{mix}} &= x_{\text{CH}_4} \mu_{\text{CH}_4} + x_{N_2} \mu_{N_2} \\
C_p \text{mix} &= x_{\text{CH}_4} C_p \text{CH}_4 + x_{N_2} C_p \text{N}_2
\end{align*}
\]

\[
k_{\text{mix}} = x_{\text{CH}_4} k_{\text{CH}_4} + x_{N_2} k_{N_2}
\]

\[
\rho_{\text{mix}} = \frac{1}{\frac{x_{\text{CH}_4}}{\rho_{\text{CH}_4}} + \frac{x_{N_2}}{\rho_{N_2}}}
\]

In these equations, \(x_{\text{CH}_4}\) and \(x_{N_2}\) are the mass fractions of methane and nitrogen, respectively, \(\mu_{\text{mix}}, \mu_{\text{CH}_4}\) and \(\mu_{N_2}\) are the viscosities of mixture, methane and nitrogen; \(k_{\text{mix}}, k_{\text{CH}_4}\) and \(k_{N_2}\) the thermal conductivities of mixture, methane and nitrogen; \(C_p \text{mix}, C_p \text{CH}_4\) and \(C_p \text{N}_2\) the heat capacities of mixture, methane and nitrogen; \(\rho_{\text{mix}}, \rho_{\text{CH}_4}\) and \(\rho_{N_2}\) are the densities of mixture, methane and nitrogen, respectively.

This calculation has the major disadvantage to only take into account the temperature and the concentration of the species but not the composition of the mixture.

The absorption coefficient allows taking into account the presence of solid particles. The variation of the absorption coefficient only depends on the volume fraction of the carbon particles. For the determination of the particle fraction volume it is assumed that the dissociation of the hydrocarbon into carbon and hydrogen is total and instantaneous, all carbon present is of solid nature.

Therefore, the particle fraction volume in the mixing can be expressed as:

3183
\[ f_v = \frac{\rho_c}{\rho_r} \cdot \frac{M_{CH_4}}{M_c} x_{CH_4} \]

where \( \rho_c \) is the density of the solid carbon, \( M_{CH_4} \) and \( M_c \) the molecular weight of methane and solid carbon, respectively. The overall absorption coefficient is evaluated from Equation (1), with the new value of particle volume fraction given by Equation (6).

3.3 Results

Calculations were carried out for nitrogen and methane as plasma gas and hydrocarbon at flow rates of 9 Nm\(^3\)/h and 0.56 Nm\(^3\)/h, respectively and a total electric power input of 49.4 kW. Figure 2 shows the distribution of the absorption coefficient along the reaction zone and Figure 3 the temperature field in the reaction zone.

![Figure 2](image1.png) ![Figure 3](image2.png)

Figure 2. Absorption coefficient in the reaction zone. Figure 3. Temperature field of the reaction zone.

In the zone close to the injection of the hydrocarbon (zone (1), see Figure 2), the value of the absorption coefficient calculated is very high (order of magnitude 24 m\(^{-1}\)). The mass fraction of methane in this zone is approximately 1; there is only solid carbon. The results in this zone are wrong because the decomposition of the methane to solid carbon did not take place yet as the temperatures are not high enough (the injection temperature is equal to 300 K). The model overestimates radiation flux. Wall and gas temperature are uniform as shown in Figure 3, except for zone (2) (see Figure 2) where the cold hydrocarbon is injected. Temperature and heat transfer characteristics are used for model validation against experimental data. At present state, no method is in place to experimentally determine the absorption coefficient.

This approach must be improved, as it does not take into account the formation of the solid particles.

4. Validation: Comparison of experimental and numerical data

Temperature and heat flux are used for model validation [8]. The temperature on the axis of the reactor is measured by thermocouples in positions H3, H5 and H6, and by an optical pyrometer measuring the wall temperature from window H4 (The different points of measurement are represented in Figure 3). The thermal balance is carried out by calorimetric measurement.
The control parameter allowing model adjustment are the thermal conductivities of the vertical and horizontal walls of the reactor. The horizontal wall is also called the top of the reactor. The vertical walls are the walls of the reactive zone 1 (ZR1) and reactive zone 2 (ZR2).

These control parameters were adjusted with three experiments without injection of hydrocarbon. The horizontal thermal conductivity was adjusted to 13 W m\(^{-1}\) K\(^{-1}\) and the vertical thermal conductivity was adjusted to 1.2 W m\(^{-1}\) K\(^{-1}\). The change of the thermal conductivity of the top of the reactor has little influence on the temperature fields, but it allows adjusting the heat flux.

For the test 1, calculations were carried out for nitrogen as plasma gas at a flow rate of 6 Nm\(^3\)/h and a total electric power input of 44.1 kW.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>T in H3</th>
<th>T in H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>1753</td>
<td>1273</td>
</tr>
<tr>
<td>Model without thermocouple</td>
<td>2588</td>
<td>2155</td>
</tr>
<tr>
<td>Model with thermocouple</td>
<td>2588</td>
<td>1123</td>
</tr>
</tbody>
</table>

Table 1. Temperature at different points of measurement in the reactor for the test 1

The results presented in Table 1 show the comparison between the experiment, the model with the modified thermal conductivity and the model with the same conductivity, but including the modelling of the thermocouple (diameter 2 mm) at the position H5. Temperature is overestimated by the models compared to the temperature measured with the thermocouple. In fact, these measurements by thermocouple indicate temperatures lower than the real fluid temperature as the effects of radiation from and to the wall have not been accounted for.

Finally, the adjusted 2D model was used to numerically simulate the reactor including feedstock injection. Validation was carried out against experimental data obtained the experiment 2 with nitrogen as plasma gas. Calculations were carried out for nitrogen and methane as plasma gas and hydrocarbon at flow rates of 9 Nm\(^3\)/h and 0.56 Nm\(^3\)/h, respectively and a total electric power input of 49.4 kW.

<table>
<thead>
<tr>
<th>Total heat flux (kW)</th>
<th>Top</th>
<th>ZR1</th>
<th>ZR2</th>
<th>Exit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 2</td>
<td>22.6</td>
<td>18</td>
<td>6.9</td>
<td>0.08</td>
</tr>
<tr>
<td>Model without injection</td>
<td>18</td>
<td>17</td>
<td>10</td>
<td>3.2</td>
</tr>
<tr>
<td>Model with injection</td>
<td>19.2</td>
<td>20</td>
<td>9.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2. Comparison of experimental 2 and numerical data for total heat flux (kW) in the reactor.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>T in H4</th>
<th>T in H5</th>
<th>T in H6</th>
<th>T in exit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 2</td>
<td>1749</td>
<td>1565</td>
<td>1188</td>
<td>649</td>
</tr>
<tr>
<td>Model without injection</td>
<td>1489</td>
<td>2171</td>
<td>1667</td>
<td>1203</td>
</tr>
<tr>
<td>Model with injection</td>
<td>1466</td>
<td>996</td>
<td>654</td>
<td>512</td>
</tr>
</tbody>
</table>

Table 3. Comparison of experimental 2 and numerical data for temperatures at different points of measurement in the reactor.

Results obtained from experimental and numerical investigations are compared in Tables 2 and 3. The results include firstly the comparison between the experiment and the model with the injection, secondly the comparison between the models without and with injection.
The wall temperature in position H4 is not affected by the injection. On the other hand, the temperatures along the axis of the reactor (H5 and H6) are underestimated by the model. The heat transfer increases in the top section of the reactor (Top and ZR1), and decreases in the bottom section (ZR2 and Exit). That is explained by the temperature evolution. As expected, the results show that the presence of solid particles strongly affected the heat transfer and the temperature distribution inside the reactor.

5. CONCLUSION

As a conclusion, the effects of the presence of particles have been studies in 2D. The presence of solid particles strongly affects the heat transfer and the temperature distribution inside the reactor. This approach must be improved, as it does not take into account the formation of solid particles. In spite of approximations and assumptions, the model shows good performance when compared against experimental data.

ACKNOWLEDGEMENT

This study was partially funded by the European Commission under contract N°GRD1 1999 10671

REFERENCES