Computational Study of Carbon Nanoparticle Formation during Thermal Decomposition of Methane

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Abstract: Thermal decomposition of methane is a suitable and eco-friendly way to simultaneously produce hydrogen and carbon black. A parametric study is made on a two-dimensional model of methane thermal decomposition reactor. This modelling attaches utmost importance in the radiation phenomenon and particle population evolution.

Keywords: Methane Reforming, Population Balance, Coagulation, Carbon Black

1. Introduction

High temperature thermal decomposition of methane is a promising route for a large-scale co-production of hydrogen and carbon black with little CO_2 emissions [1-3]. The economic viability of this technique relies on obtaining the desired properties of the carbon black produced [4], and therefore on the control of the nucleation, growth, and coagulation of carbon particles. The production of high value carbon black necessitates high temperatures, usually in the range of 1600 to 2200 K [5, 6]. Two main direct and environmental friendly thermal decomposition pathways have been proposed in the last decades. The first one is a plasma process using electricity as the source of energy and reactivity [5-8] whereas the other one involves the use of concentrated solar energy [9-11]. Aside these experimental works, Computational Fluid Dynamic (CFD) simulations have been performed in order to have better insights of the thermal methane decomposition and the particle formation for each specific reactor configuration [4, 12, 13]. More recently, a two dimensional model of methane decomposition has been presented by Caliot and Flamant [14]. The two-dimensional axis-symmetric simulation of Caliot successfully describes fluid flow, conduction, convection, radiation heat transfer, gas-phase kinetics, particle formation, growth and coagulation. Like Patrianakos [13], Caliot used a class method [15] to solve the population balance equation [16] of carbon particles. Caliot and Flamant [14] also added a detailed multi-grey radiative model with a particle size population dependency over the absorption coefficient. Based on the work previously made by Caliot and Flamant [14], this study models the methane decomposition in a tubular heated wall reactor in order to see the influence of temperature and pressure on the carbon particle formation and growth.

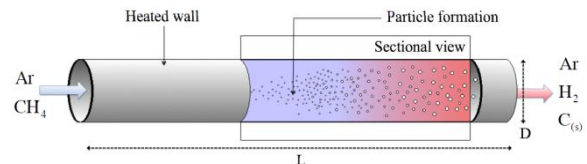## 2. Thermal decomposition of methane reactor

Fig. 1. Scheme of the reactor

The reactor, shown Figure 1, is a cylinder made of graphite with a length L of 0.6 m and a diameter D of 15 mm. The opaque graphite tube receives a constant amount of heat energy used for the thermal decomposition of methane. The temperature profile of the wall is imposed and constant. The temperature boundary condition at the wall goes from 300 K to 1800 K. The inlet gas is a mixture of argon and methane, at 50/50 proportion in mole fraction. The velocity of the inlet flow is about 0.7 m/s at standard temperature and pressure conditions. The flow is assumed axisymmetric.

3. Formulation of the model

The model formulation closely follows considerations reported by Caliot and Flamant [20]. The reaction of methane decomposition is modeled using the single overall kinetic reaction given by Eq. 1:

$$CH_4 \rightarrow C_{(s)} + 2H_2 \qquad (1)$$
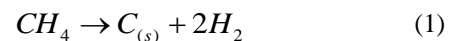
Taking into consideration the small volume fraction of the solid phase produced by Eq.1, the gas flow is assessed not to be disturbed by the particle population; and that embedded solid particles have the same velocity that the gas phase. In the same way, the small size of these solid particles leads to a high specific surface, which indicates that thermal inertia of these particles can be neglected. In consequence, the temperature of the particle is equal to the gas phase temperature. Given the previous assumptions, the biphasic flow is treated as a single-phase fluid flow. The system of local steady state governing equations describing the gas-particle flow can be written as:

$$\nabla \cdot (\rho_m \mathbf{u}) = 0 \qquad (2)$$

$$\nabla \cdot (\rho_m \mathbf{u} \otimes \mathbf{u}) = -\nabla p + \nabla(\mu \nabla \cdot \mathbf{u}) \qquad (3)$$

$$\nabla \cdot (\mathbf{u}(\rho_m E + p)) = \nabla \cdot \left(k_{eff} \nabla T - \sum_j h_j \mathbf{J_j} \right) + S_{rad} + S_{chem} \qquad (4)$$

$$\nabla \cdot (\rho_m Y_{g,j} \mathbf{u}) = -\nabla \cdot (-\rho_m D_j \nabla Y_{g,j}) + S_{j,chem} \qquad (5)$$

where E is the total energy, h the total enthalpy, h_k the enthalpy of the species k and D_j the diffusion coefficient of the gas species j. chemical source terms S_{chem} and $S_{j,chem}$ take into account homogeneous reactions of methane dissociation in gas phase and heterogeneous reactions of methane condensation on the carbon particle surface. The thermal conductivity of the mixture, denoted k_{eff}, is calculated by a parallel model; eq. 6. The radiative model uses a multi grey approach. The RTE is solved using the Discrete Ordinates (DO) radiative model. The participating medium is the methane-carbon particle mixture. Absorption and emission from both constituents of the mixture, methane and solid particles, are modeled according to the considerations of Caliot [14]. An absorption distribution function model (ADF) [17] is used as the global spectral model for methane. It is derived from the narrow band radiative properties of methane at high temperature provided by Perrin and Soufiani [18]. Mie theory is applied to calculate the mean Planck absorption coefficient of the particle [19].

$$k_{eff}^{-1} = \left(\frac{\sum_i \alpha_{p,i}}{k_c} + \frac{1 - \sum_i \alpha_{p,i}}{k_{gas}} \right)^{-1} \qquad (6)$$

The particle size distribution is returned by solving the equation system 7 with i from 0 to M-1. This system represent a class method [15] in order to solve the Friedlander equation [20] which governs the size particle population. Particles are assumed spherical. The volume discretization is made with a minimal diameter of 0.256 nm and a maximal one of 8 μm. This diameter interval covers reliably the particle size scale in this process [14]. The volume discretization is ruled by a geometric progression with common ratio 2.

$$\nabla \cdot (\rho_c \alpha_{p,i} \mathbf{u}) = -\nabla \cdot (-\rho_c D_{p,i} \nabla \alpha_{p,i}) + p_c V_i (H_{het,i-1} N_{i-1} - H_{het,i} N_i) - S_{i,coag} + \delta_D(i) S_{nuc} \qquad (7)$$

The diffusion coefficient for carbon particles, denoted $D_{p,i}$, is calculated using the Stokes-Einstein formulation. This formulation takes into account the dependency of the diffusion coefficient with the particle size. The total volumetric heterogeneous reaction rate, $H_{het,i}$, is calculated using Eq. 8,

$$H_{het,i} = \frac{k_{het} h_{CH_{4,i}}}{k_{het} + h_{CH_{4,i}}} N_A [CH_4] \frac{V_0}{V_i} s_i \qquad (8)$$

with :

k_{het} : heterogeneous reaction rate expressed by an Arrhenius law,

$h_{CH_{4,i}}$: mass transfer diffusion coefficient for methane,

V_i : particle volume of the i particle section,

s_i : particle surface of the i particle section.

The nucleation source term is based on an Arrhenius law for homogeneous methane dissociation in gas phase. The coagulation source term, denoted $S_{i,coag}$, is expressed by the equation system 9.

$$S_{0,agg} - \rho_c V_0 \sum_{j=0}^{M-1} \beta_{0,j} N_0 N_j \qquad (13)$$

$$S_{i,agg} = -\rho_c V_i \sum_{j=0}^{M-1} (1 - 0.5\delta_{i-1,j}) \frac{(V_j + V_{i-1}) - V_{i-1}}{V_i - V_{i-1}} \beta_{i-1,j} N_{i-1} N_j$$
$$+ \rho_c V_i \sum_{j=0}^{i} (1 - 0.5\delta_{i,j}) \frac{V_{i+1} - (V_i + V_j)}{V_{i+1} - V_i} \beta_{i,j} N_i N_j$$
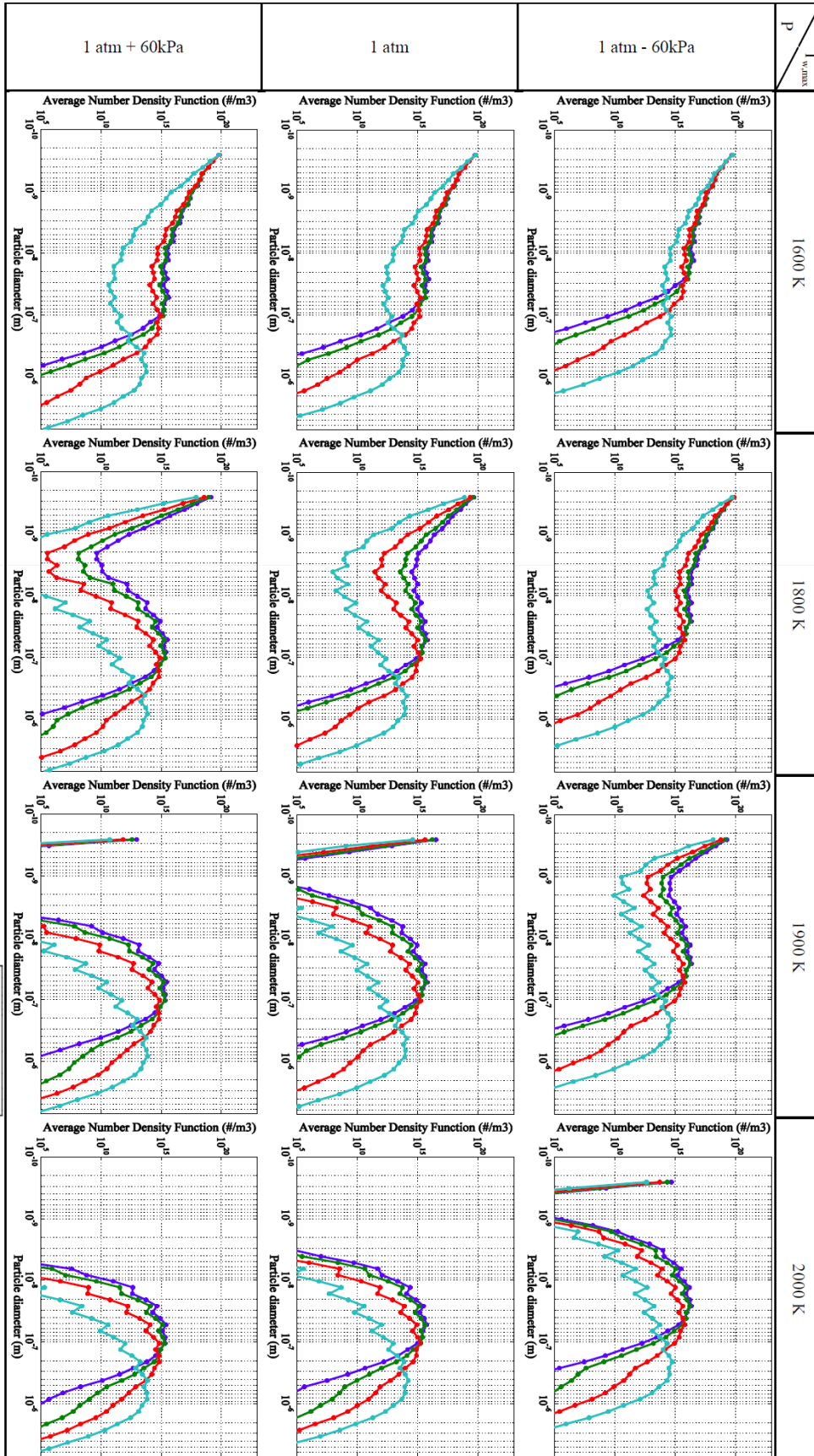$$- \rho_c V_i \sum_{j=0}^{M-1} \beta_{i,j} N_i N_j \qquad , \quad i \in \{1; 2; ...; M-1\}$$

Fig. 2. Influence of temperature and pressure on the particle size distribution at the outlet of the reactor

The coagulation kernel, β, is calculated with the Fuchs formulation [21]. This formulation assumes no-charged particle and instantly coalescent after collision.

4. Results of the parametric study

Fig. 2 presents the particle size distribution at the end of the reactor with different operating pressures and different maximum wall temperatures. The figure also shows the particle size distribution for different radial positions. The first significant observation is that the temperature has more influence on the particle size distribution than the pressure in this range of temperature and pressure. For high temperature and pressure conditions, the coagulation rate is more important compare to the nucleation rate in a way there is no existing monomer at the end of the reactor. Every new emerging solid particle instantly coalesces with an already existing particle. Consequence of the coagulation process, an interesting observation is the narrowing of the particle range at the end of the reactor for the highest temperature and pressure conditions. It can be expected that for even higher temperature and pressure, the size population of carbon particle could be considered as monodispersed which would be advantageous in the desire of high value carbon black production.

5. Conclusion

Simulations of the formation and growth of carbon nanoparticles inside a thermal methane decomposition reactor under different temperature and pressure conditions have been performed. These modelings include species transport, chemical kinetics with homogeneous and heterogeneous reactions, energy conservation, and a detailed radiative model coupled with a sectional method. The present study gives understandings of the effect of varying operating pressure and temperature on the particle size distribution. Particularly, in this case, an increase of pressure and/or temperature provide a narrower particle size population. Particles size tend to be about equal in diameter in a range between 100 and 300 nm. This trend could be interesting with the aim to produce high value carbon black. Further improvements in the presented model are expected in future works such as a more detailed nucleation model [22].

6. Acknowledgments

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