

Flow of chemically reacting carbon vapor

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Abstract. Numerical simulation of a chemically reacting flow of an expanding gas flow consisting of carbon C and its clusters (C₂ - C₅) is presented. It is shown how the chemical composition of the mixture flow changes when it expands and its temperature decreases. The temperature range in which the nonequilibrium chemical model including separate direct and inverse cluster formation reactions should be used is determined. Variations in the effective adiabatic index in the C-C₅ mixture and along the nozzle axis are given.

1. Introduction

Flows with chemical reactions, including cluster formation reactions, are of great interest because of use of high-speed plasma jets for material testing and surface modification [1,2]. Typically such jets are produced in plasmatrons. A novel method for obtaining pulsed plasma jets involves the use of an electromagnetic rail generator (railgun) [3]. Of major importance is the fact that the plasma composition in the railgun channel is determined by the material of electrodes (rails) because of erosion that occurs when a plasma piston moves along it. By using a railgun with graphite electrodes, supersonic plasma jets with the velocities as high as 14 km/s [4] can be obtained. Such a high-speed carbon plasma jet can be used to form carbon coatings at different materials.

After an expanding plasma jet leaves the railgun channel, it experiences a considerable temperature drop due to expansion. This leads to changes in its chemical composition. The cluster formation process starts. This is an exothermal process, and the reacting jet is cooled to a lesser degree than a jet of a nonreacting gas. Because of a short outflow time a great role in the jet is played by nonstationary chemical processes. In this paper we report numerical simulation of a nonstationary flow of the mixture consisting of carbon C and its clusters C₂ - C₅.

2. Numerical model

We consider flows in the absence of external heat exchange and take into account the thermal effect of chemical reactions. In this case the Euler equations in the form of conservation laws in the rectangular coordinate system will acquire the form

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$$\begin{aligned}
\frac{\partial \rho}{\partial t} + \nabla(\rho \vec{V}) &= 0 \\
\frac{\partial}{\partial t}(\rho \vec{V}) + \nabla(\rho \vec{V} \vec{V}) &= -\nabla p \\
\frac{\partial}{\partial t}(\rho h_s) + \nabla(\rho \vec{V} h_s) &= W_T \\
\frac{\partial}{\partial t}(\rho Y^{(s)}) + \nabla(\rho \vec{V} Y^{(s)}) &= W_s
\end{aligned} \tag{1}$$

where ρ is the flow density, \vec{V} is the velocity vector, p is the pressure, h_s is the enthalpy, W_T is the change in the mixture energy due to chemical reactions, $Y^{(s)}$ is the mass fraction of mixture component s , and W_s is the change of the s component of the mixture due to chemical reactions.

The heat capacity of each component of the mixture and also enthalpy and entropy are calculated by using relevant polynomials as functions of T

$$\begin{aligned}
\frac{C_{pk}^0}{R} &= a_{1k} + a_{2k} T_k + a_{3k} T_k^2 + a_{4k} T_k^3 + a_{5k} T_k^4 \\
\frac{H_k^0}{RT_k} &= a_{1k} + \frac{a_{2k}}{2} T_k + \frac{a_{3k}}{3} T_k^2 + \frac{a_{4k}}{4} T_k^3 + \frac{a_{5k}}{5} T_k^4 + \frac{a_{6k}}{T_k} \\
\frac{S_k^0}{R} &= a_{1k} \ln T_k + a_{2k} T_k + \frac{a_{3k}}{2} T_k^2 + \frac{a_{4k}}{3} T_k^3 + \frac{a_{5k}}{4} T_k^4 + a_{7k}
\end{aligned} \tag{2}$$

Coefficients $a_{1k} \dots a_{7k}$ for chemical components are taken from the NIST database [5] and tables of thermodynamic properties of different species [6].

To calculate the dependence of the reaction rate constant on temperature, a standard Arrhenius equation is used

$$k_i = A_i \exp(-T_a / T) . \tag{3}$$

The reactions in carbon vapor used in this simulation are listed in Table 1. Formation and dissociation of carbon cluster C2-C5 are included in this set. The coefficients for all of these reactions are also given in Table 1.

Table 1. Reaction coefficients for carbon cluster formation (f) and (r) reactions [5].

N	Reaction	$A, (m^3/kmol \cdot s), (1/s)$	T_a, K
1	$C + C \rightarrow C_2$	$2 \cdot 10^{11}$	0
1r	$C_2 \rightarrow C + C$	$2.9 \cdot 10^{15}$	74000
2	$C_2 + C \rightarrow C_3$	$2 \cdot 10^{11}$	0
2r	$C_3 \rightarrow C_2 + C$	$1.9 \cdot 10^{16}$	84814
3	$C_2 + C_2 \rightarrow C_3 + C$	$2 \cdot 10^{12}$	8616
3r	$C_3 + C \rightarrow C_2 + C_2$	$1.3 \cdot 10^{13}$	22142
4	$C_2 + C_2 \rightarrow C_4$	$2 \cdot 10^{11}$	0
4r	$C_4 \rightarrow C_2 + C_2$	$3.6 \cdot 10^{16}$	66474

5	$C3 + C \rightarrow C4$	$2 \cdot 10^{11}$	0
5r	$C4 \rightarrow C3 + C$	$5.6 \cdot 10^{15}$	52900
6	$C + C4 \rightarrow C5$	$2 \cdot 10^{11}$	0
6r	$C5 \rightarrow C4 + C$	$1.1 \cdot 10^{16}$	80482
7	$C2 + C3 \rightarrow C5$	$2 \cdot 10^{11}$	0
7r	$C5 \rightarrow C2 + C3$	$2.2 \cdot 10^{16}$	62142

3. Results

First of all let us consider equilibrium molar concentrations of C atom and C2-C5 carbon clusters at different temperatures. Previously such an estimation were made by using not a forward and reverse reaction but by using equilibrium constant [8,9]. Fig. 1a and 1b show such dependence for two pressures. It is clearly seen that for a lower pressure ($p = 10^4$ Pa) there is only C5 clusters up to 1500 K. A further temperature increase leads to changes in mixture composition and when temperature becomes higher than 5500 K only C atoms exist in the mixture. For a higher pressure ($p = 10^6$ Pa) the dependence is similar, the only difference is that the change of the mixture composition from C5 to C occurs in a broader temperature range (1500 - 8000 K). It is also interesting to note that there are few C4 clusters at any temperature in the equilibrium case. C3 and C2 cluster concentrations have maxima at different temperatures and the maximum concentration of C2 clusters are lower than that of C3 clusters for both pressures. The process of carbon mixture composition variation occurs in the following way: if we start with a low (less than 1500 K) temperature, only C5 clusters exist, after 1500 K the processes of C5 cluster dissociation and C3 cluster formation start. Near the maximum value of C3 cluster molar concentration (3000 K for 10^4 Pa and 4000 K for 10^6 Pa) the process of C2 cluster formation begins and C atoms appear in the mixture. When the temperature becomes higher than 3000 K for 10^4 Pa and 4000 K for 10^6 Pa, the number of C atoms increases and the amount of C2 clusters at first increases and beginning from 4000 K for 10^4 Pa and 5500 K for 10^6 Pa decreases. Only the amount of C atoms increases after these temperatures. Finally only C atoms exist in the mixture. No doubt, ionization of C atoms starts at higher temperatures but the consideration of this effect is out of the scope of this paper. In any case the ionization becomes important at the temperatures higher than 10000 K.

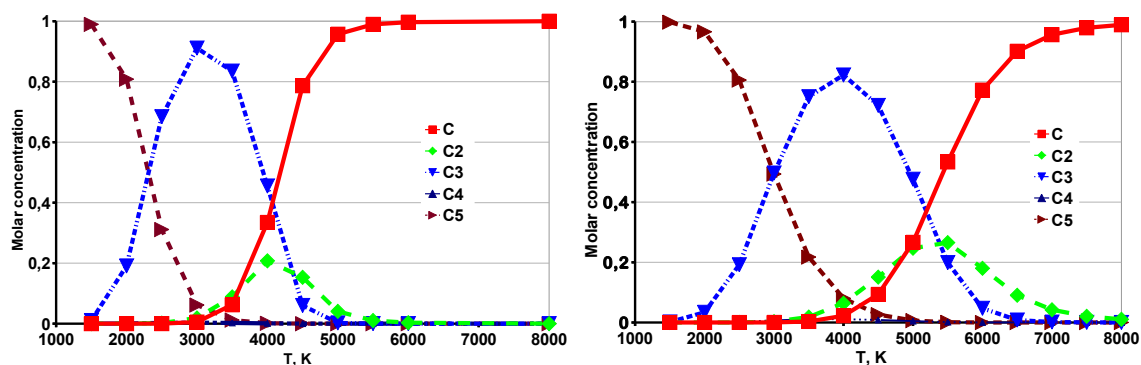


Figure 1. Molar concentrations of C atoms and C2-C5 clusters at different temperatures under equilibrium conditions. (a) pressure $p = 10^4$ Pa, (b) pressure $p = 10^6$ Pa

The expanding flow parameters can be solved analytically in the case of a constant adiabatic index. In order to see whether this is applicable to our case, i.e., carbon vapor flows, we need to calculate the range in which the adiabatic index of the C-C5 mixture changes at different temperatures. Fig.2 shows variations in the adiabatic index under equilibrium conditions for two pressures. It can be seen that

there is a strong change in the adiabatic index. This is caused by changes in the mixture composition (see Fig.1). At low temperatures, when the mixture consists of C5 clusters alone, the adiabatic index is about 1.1 and it increases up to 1.65 with increasing temperature. It can also be seen from Fig.2 that the adiabatic index of the mixture exhibits different behaviors for different pressures.

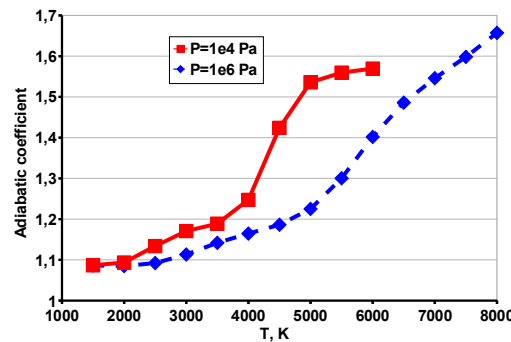


Figure 2. Adiabatic index for C-C5 mixture at different temperatures under equilibrium conditions.

To show how a chemical transformation of the C-C5 mixture affects the expanding flow parameters, we simulated a flow in the axis-symmetric nozzle. The nozzle critical cross-section had a radius of 1.45 mm and nozzle wall angle was 12°. Fig.3 shows the geometry of the calculation zone and a computational mesh. Two simulations were made to show how inlet values of temperature affect the flow parameter distribution along the nozzle axis. For the first simulation, the temperature at the critical cross section of the nozzle was $T^*=4200\text{K}$ and for second simulation $T^*=6000\text{K}$, the pressure was 10^4 Pa for both cases. It can be seen from Fig.1 that for the case of $T^*=6000\text{ K}$ only C atoms exist in the critical cross-section, and for $T^*=4200\text{ K}$ the mixture includes C atoms, C2 and C3 clusters. The code based on the OpenFOAM [10] platform was used for these simulations.

Fig.4 shows the adiabatic index variation along the nozzle axis for the case $T^* = 6000\text{ K}$. It can be seen that there is a decrease in the adiabatic index along the axis. If we compare this figure with Fig.2, we can conclude that we see a typical behaviour of the adiabatic index, i.e. its fall with decreasing temperature.

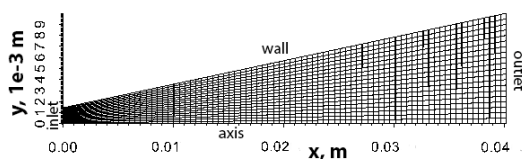


Figure 3. Geometry, mesh and boundary types of computational domain.

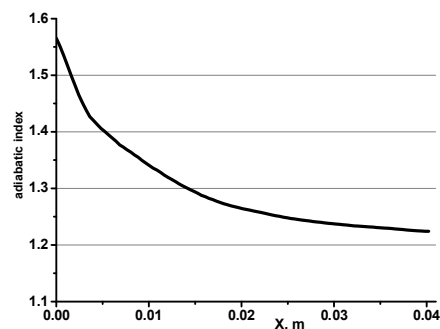


Figure 4. Adiabatic index for C-C5 mixture along the nozzle axis for the simulation with temperature in critical nozzle cross-section $T^*=6000\text{ K}$.

Fig.5 shows the change in the normalized temperature T/T^* along the nozzle axis. The x-axis is the normalized nozzle cross-section A/A^* . To show how the temperature decreases at a constant adiabatic index γ , the lines for $\gamma = 1.1, 1.2, 1.3, 1.4, 1.5, 1.6$ and 1.7 are plotted in the figure. There are also two lines for our simulation at $T^*=4200\text{K}$ and $T^*=6000\text{K}$, i.e., for a varying adiabatic index. It is seen that

there is a difference between two simulations. The normalized temperature for the case $T^*=4200\text{K}$ decreases faster than for the case $T^*=6000\text{K}$.

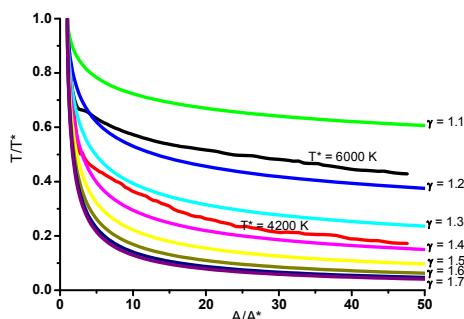


Figure 5. Normalized temperature T/T^* as a function of normalized nozzle cross-section A/A^* .

If we compare the lines for the constant adiabatic index, it can be seen that at the initial stage of expansion the temperature drop in both simulations corresponds to a relatively high adiabatic index (1.3 for $T^*=6000\text{ K}$ and 1.5 for $T^*=4200\text{K}$). After the initial stage of expansion the adiabatic index decreases and becomes about 1.2 for $T^*=6000\text{ K}$ and 1.4 for $T^*=4200\text{ K}$.

4. Conclusion

Numerical simulation of a chemically reacting flow of an expanding carbon vapour consisting of carbon C and its clusters C2-C5 has been carried out. It has been shown that it is necessary to take into account the nonequilibrium chemical model including separate direct and inverse cluster formation reactions when temperature of the mixture is higher than 1500 K and lower than 5000 K for the mixture pressure lower than 10^4 Pa . It has also been shown that the mixture parameters (e.g. temperature) during expansion of the flow in the nozzle are strongly affected by the parameters at the nozzle inlet. For the case of temperature in the critical cross-section of the nozzle $T^*=6000\text{ K}$ the adiabatic index along the nozzle axis changes in the range 1.2-1.6.

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