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Numerical simulation of synthesis of fullerenes by the arc discharge method

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Abstract. A mathematical model of the fullerene formation process by carbon vapor clustering in an arc discharge camera was developed. Numerical simulation of formation of fullerene clusters up to C_{60} and C_{70} from carbon vapor produced by an arc discharge in a plasma reactor camera was carried out. A geometrical model of the reactor was built, and a numerical model of the processes occurring in the gas flow in the reactor and at clustering of carbon vapor including 82 components and 522 chemical reactions was developed.

1. Introduction

Fullerenes and their derivatives are recently discovered forms of carbon. They attract the interest of researchers due to new, unexpected properties, which are the result of an unusual molecular structure of a hollow cage. Investigations of physical and chemical properties of fullerenes show a potential of these materials for use in many fields of science and technology, such as electronics, optoelectronics, electrochemistry and chemistry. [1]

At present few applications of fullerenes in industry are commercialized, which is due to a very high cost of fullerene production. In order to make fullerene production cost efficient, a detailed study of fullerene formation in arc discharge reactors is needed.

Arc discharge is the most commonly used method of fullerene production, it provides the maximum yield (up to 12% from the raw soot) and also enables one to control the composition of raw soot (ratio C_{60}/C_{70} etc.) by varying production process parameters (such as pressure, temperature, camera configuration, etc.). Numerical modeling is a necessary stage for development and optimization of technology. The major goal is to find the conditions which provide the maximum content of fullerenes in raw soot.

2. Mathematical model

To describe a turbulent flow of a multicomponent gas mixture, Reynolds-Averaged Navier-Stokes (RANS) equations are used. As a result of solution of these equations, averaged characteristics of the flow are obtained.

The continuity equation and the balance mass of the mixture components are

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_j}{\partial x_j} = 0, \tag{1}$$

$$\frac{\partial \rho Y_\alpha}{\partial t} + \frac{\partial \rho u_j Y_\alpha}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\frac{\mu}{Sc} + \frac{\mu_t}{Sc_t}\right)\frac{\partial Y_\alpha}{\partial x_j} + \rho\, \dot{r}_\alpha, \qquad (2)$$

the equation of momentum transfer is

$$\frac{\partial \rho u_i}{\partial t} + \frac{\partial \rho u_j u_i}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} + \rho g, \qquad (3)$$

i=1,2,3,

the equation of enthalpy transfer is

$$\frac{\partial \rho h}{\partial t} + \frac{\partial \rho u_j h}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\frac{\mu}{Pr} + \frac{\mu_t}{Pr_t}\right)\frac{\partial h}{\partial x_j} - \frac{\partial q_{rj}}{\partial x_j}, \quad (4)$$

The equations of kinetic energy of turbulence and dissipation velocity are

$$\frac{\partial k}{\partial t} + \overline{u}_j \frac{\partial k}{\partial x_j} = \tau_{ij}\frac{\partial \overline{u}_i}{\partial x_j} - \varepsilon + \frac{\partial}{\partial x_j}\left[\left(v + v_t/\sigma_k\right)\frac{\partial k}{\partial x_j}\right], \quad (5)$$

$$\frac{\partial \varepsilon}{\partial t} + \overline{u}_j \frac{\partial \varepsilon}{\partial x_j} = C_{\varepsilon_1} f_1 \tau_{ij}\frac{\varepsilon}{k}\frac{\partial \overline{u}_i}{\partial x_j} - C_{\varepsilon_2} f_2 \frac{\varepsilon^2}{k} + \frac{\partial}{\partial x_j}\left[\left(v + v_t \sigma_\varepsilon\right)\frac{\partial \varepsilon}{\partial x_j}\right]. \quad (6)$$

These equations are formulated for the case of essentially subsonic flows at a constant pressure. Here $\dot{r}_\alpha$ are the sources of the mass of the mixture components due to chemical reactions, ρ is the density, u is the velocity, h is the enthalpy, Y_a is the mass fraction of component a, *Sc* is the Strouhal number, μ is the dynamic viscosity, τ_{ij} are the components of stress tensor, *Pr* is a Prandtl number, ξ is the velocity of dissipation, k is the kinetic energy, v and v_t are the kinematic viscosity and turbulent kinematic viscosity, respectively, *C* and *f* are the model coefficients, and q_{rj} are the heat sources due to chemical reactions (equal to the negative reaction enthalpy $q_r = -\Delta H_r$)

The scheme of chemical reactions of carbon vapor condensation used in our study is based on a generalization of experimental data [2].

There are no thermodynamic data in the literature for all the clusters of carbon higher than C_{10} (excluding fullerenes), and the simplest piecewise-linear approximation is used in the model. This method of evaluation of thermodynamic data provides a smooth change in the Gibbs free energy as a function of cluster size required by the model and, apparently, is sufficient to solve a number of problems.

The thermal effect of a reaction is calculated as

$$\Delta H_r^0 = \sum H_{prod} - \sum H_{reac} = \sum_i v_i(a_{1i}RT + a_{6i}R) - \sum_j v_j(a_{1j}RT + a_{6j}R), \quad (5)$$

where *v* are the molar coefficients in chemical reactions, a_{ni} and a_{nj} are the coefficients in the equations of enthalpy of the resulting and initial reagents of the reaction, respectively.

The model also uses the equation of state of an ideal gas to describe the flow of helium

$$P = R\rho T \sum_{\alpha \neq C} \frac{Y_\alpha}{M_\alpha} \cdot , \qquad (6)$$

where P is the gas pressure, R is the gas constant, ρ is the density, Y_a is the mass fraction of component a, and M_a is the molar mass of component a.

To calculate the temperature dependence of the rate constant of a reaction, standard Arrhenius formula is employed

$$k_i = A_i T^{\beta_i} \exp\left(-\frac{E_i}{RT}\right), \qquad (7)$$

where A_i, β_i are the coefficients in Arrhenius equation, and E_i is the activation energy.

3. Results and discussion

The numerical experiment is performed in OpenFOAM (Open Source Field Operation And Manipulation CFD ToolBox) - freely available software for numerical simulation of problems in mechanics. [3] The use of OpenFOAM for the simulation of arc discharge reactors is possible because OpenFOAM is oriented at numerical simulation of flows of multicomponent gases, the chemical interaction between components in the multicomponent gas mixture being considered.

At present there is no complete physical model of the electric arc with strong evaporation of electrodes, and exact calculations of these parameters are impossible. Thus, it is useful to calculate a 2-dimensional model of a turbulent jet coming from the anode electrode, which is an idealized representation of the flow of a helium-carbon mixture in the interelectrode gap. Similar calculations are presented in [2]. In this model the following boundary conditions were established: a fixed velocity v = 29.34 m/s and fixed temperature T=3000 K were set at the jet inlet, the gas mixture consisted of 90% He and 10% C; constant pressure P=50 kPa and zero gradient for velocity and temperature were set at the outlet.

As a result of calculations of simplified tasks, concentrations of carbon clusters in the mass fractions after the establishment of an equilibrium concentration at the point of maximum output of fullerenes (at the jet center) were obtained (Fig.1). The mass fractions of most stable fullerenes C_{60} and C_{70} after establishment of the equilibrium composition of the gas mixture were calculated (the mass fraction of C_{60} was found to be 0.78‰ and mass fraction of C_{70} was found to be 0.10‰, the total content of carbon clusters in the gas mixture was 61‰, thus the total content of fullerenes C_{60} and C_{70} was 1.45%). Fig.2 shows the temperature distribution at the jet center.
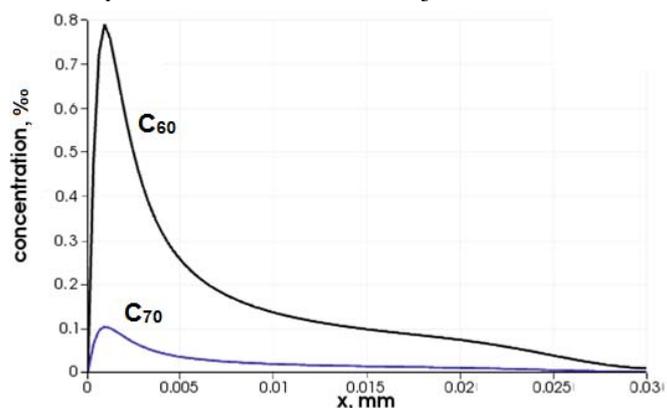

Figure 1. Concentrations of fullerenes C_{60} and C_{70} along the jet central line (X axis).
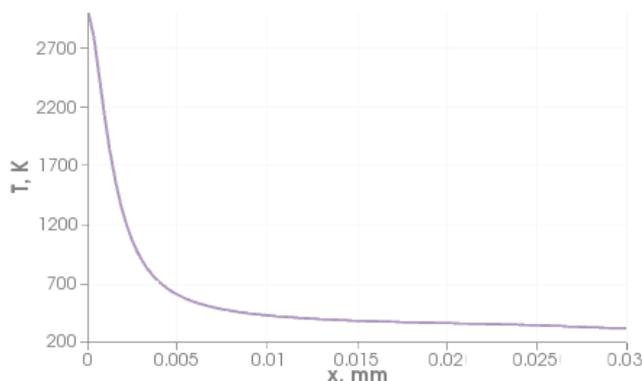
Figure 2. Temperature distribution along the jet central line (X axis).

The calculation of the tasks in the real geometry was conducted in several steps. First the helium flow was calculated, the chemical interaction being excluded. The calculations were performed by solver sonicFoam (for calculations of the flow of a viscous compressible gas) to establish the velocity field. The flow model was turbulent and the k-epsilon model of turbulence was selected.

Fig. 3 shows the fields of temperature and concentration of fullerene C_{60} in the cross section of the arc discharge camera. The maximum content of fullerenes is in a fairly narrow temperature area. In the high temperature field (near the interelectrode gap) the content of the fullerenes is negligible.
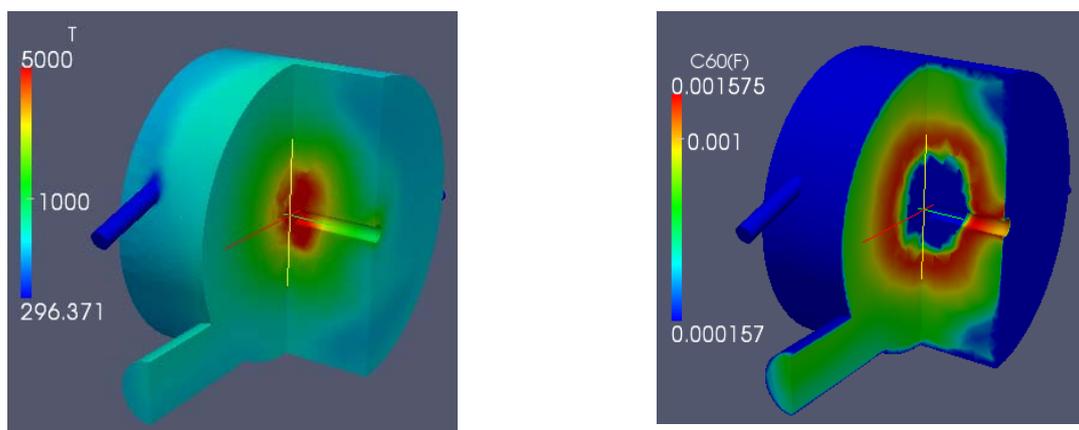

Figure 3. a) temperature and b) C_{60} concentration fields in the camera cross section.

4. Conclusions

The mathematical model of fullerene formation from a carbon vapor in an inert environment (helium in our case) has been developed. The numerical simulation of this process includes 82 components of the gas mixture and 522 chemical reactions. A strong dependence of the rate of carbon cluster formation on temperature has been revealed. The problem of a carbon vapor jet flow in the two-dimensional geometry has been solved. The distribution of the concentrations of the components has been obtained, the formation of fullerenes C_{60}, C_{70} has been shown and the temperature zones in which the speed of fullerene formation is maximal have been defined.

Modeling of the flow in a three-dimensional reactor using the real geometry of the setup built at Ioffe Physico-Technical Institute has been performed. Distributions of velocity and temperature in the reactor chamber have been found and the distribution of fullerene C_{60} in the camera has been obtained. It is important to note that in order to improve the model it is necessary to sort out the chemical reactions that make major contributions into fullerene formation and exclude insignificant reactions.

This is a complicated task because the formation of fullerenes of carbon vapor occurs sequentially as the cluster size increases.

To clarify the kinetics of the process it is necessary to include the coefficients of the dependence of the reaction rate constants on temperature and pressure into the Arrhenius equation, to find E_a values in the Arrhenius equation (in our model it is zero for most reactions), and also to include the reactions with participation of carbon ions.

The model can also be improved by introducing electromagnetic interactions.

Acknowledgments

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