A meshless method based on computational model of fullerene production by the electric arc-discharge method

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Abstract

The molecules from fullerene family have garnered a lot of attention in scientific and engineering circles due to their unique properties and possible applications. High demand for these materials has revealed a necessity to understand the process of fullerene formation and numerous attempts have been made to optimize the yield of respective apparatus. Since the fabrication technique has a large impact on the properties of the material, several methods have been developed. Among many production techniques available now, the arc-discharge method seems to be the most appropriate for industrial production.

In this paper, the arc-discharge method, where the fullerenes are formed by vaporizing the graphite electrodes in a low pressure inert gas atmosphere is described, together with a physical model proposed to approximate the physical behaviour of the plasma, coupled with nonlinear chemical reactions. The governing equations of the suggested model will be solved with a Local Radial Basis Functions Collocation Method (LRBFCM), structured on multiquadrics radial basis functions with five-noded influence domains and explicit time stepping. The local pressure-velocity coupling is used to solve the governing equations.

KEY WORDS: arc-discharge, fullerene synthesis, computational model, meshless method

1. Introduction

The discovery of C_{60} molecule in 1985 [1], multi-wall carbon nanotubes in 1991 [2] and single-wall carbon nanotubes in 1993 [3], [4] and the remarkable properties these carbon allotropes exhibit, have lead scientists to design several production methods such as laser ablation technique, chemical vapour deposition, high pressure monoxide and arc-discharge methods. At present the most efficient production technique is the arc-discharge method, designed by Krätchmer [4], or one of its modifications (e.g. [5]).

Since the fullerene formation has yet to be completely understood, several authors ([7], [8], [9]) have suggested various models. All of the authors agree that the fullerene formation can be described by four types of governing equations: continuity, momentum, energy and species conservation for each of the constitutients. In this paper, the model of [7] is suggested to be used for numerical simulations.

The governing equations of the suggested model are solved numerically with meshless method. This novel computational approach has several advantages over standard numerical methods, because its solution is based on points instead on polygons, thus simplifying the calculations of complex geometries or non-uniform discretization. The strong form of the governing equations can be used and unlike as with the finite element method, no integrals are needed. The meshless method used in the present model is the recently developed LRBFCM [13].

2. Fullerene synthesis procedure

The most common techniques in fullerene production today are the arc-discharge method

[4], the chemical vapour deposition [6] and the laser vaporisation technique [1]. The techniques vary in catalysts and inert gas type, yield, purity and type of material produced (fullerene, single-wall nanotubes, multi-wall nanotubes). The cheapest and easiest method to obtain significant amount of fullerene material is the arc-discharge method. However, this method produces a mixture of components and therefore requires a separation of the desired product from the soot and catalytic particles that are usually present in the crude product.

2.1 Arc-discharge method

Most common laboratory scale, carbon arc reactor consist of a typically water cooled chamber, which is filled with an inert gas, usually argon or helium. Two cooled graphite rods are placed in the enclosure and the distance between them is adjusted in order to maintain a constant voltage between these electrodes. The anode is generally made of carbon and filed with catalysts (Co, Fe, Ni, Y, or the mixture of these elements) and the cathode is normally made of pure graphite. A current that passes through electrodes creates plasma in the space between them. A direct current is used for nanotube production and an alternating current is used for fullerene production. The process starts at the contact point of the anode and the cathode. The electrodes are kept in contact until the current generated temperature is high enough to ignite the plasma and cause the anode material to evaporate. Carbon species and catalysts vapour that are produced in the hot plasma zone, build up a deposit on the cathode. By maintaining the desired gap between the growing deposit on the cathode and the burning anode, a constant anode erosion rate is assured and the plasma, ignited between the cathodes, is stable. Efficient operation is assumed to exist in such conditions. Most of the anode material is vaporised due to high temperatures near the anode and high energy density in the plasma. Since the cathode is water-cooled, the quench at the edges of the electrode leads to high levels of super cool or supersaturated vapour in which fullerens and nanotubes are formed. The products of the arc discharge reactor are deposit on the cathode, rubber-like collaret around the cathode deposit, web-like structures between the cathode, and reactor walls and soot on the reactor walls.

Fullerenes are formed outside the inner electrode gap and are found in the soot on the reactor walls. Multi-walled carbon nanotubes (MWNT) are formed only in the inter-electrode gap, where the current is flowing and thus require a maximization of cathode deposit. The single-wall carbon nanotubes (SWNT) are found in the collaret. The abundance of carbon forms is strongly dependent on the input power, the current type and intensity applied on the electrodes, the distance between the electrodes, their cooling, the chemical composition of the anode, the nature and the pressure of the inert gas, the temperature of plasma, the energy transfer and the geometry of the reactor.

3. Models of fullerene growth

Extensive study of fullerene production has been made ([7], [8], [9]) in order to optimize the parameters necessary to increase the fullerene yield. The process of fullerene formation is very complex as it involves numerous variables and the complete picture of its kinematics is still unknown. Even though the precise kinematics of fullerene growth is yet unknown, many models exist that are in satisfactory agreement with experiments. The models are reviewed in [8].

By posing the potential differential equations of continuity mechanics for the velocity, temperature, carbon mass fraction and current intensity fields in the arc-discharge reactor, fullerene synthesis can be described mathematically.

A physical model for fullerene production, based on the assumptions of Bilodeau et. al [7] is proposed in the following section.

3.1 Physical model

The model consists of a set of partial differential equations: continuity, momentum, energy and species conservation equations. The governing equations describe velocity, pressure, temperature, and species fields.

In order to be able to solve these equations, certain assumptions have to be made [7]. It is assumed that the flow is axisymetric and laminar with Re < 10, that a unique temperature represents plasma and thus ensures local thermodynamic equilibrium, that the system is in a steady state as long as the gap distance between electrodes is kept constant, that the anode erosion rate over the surface of the electrodes is uniform, that the deposition on the cathode is governed by the diffusion, that the gravitational and magnetic fields are present in order to ensure higher yield, that the input of energy in the arc is due to the ohmic heating and the enthalpy flux of the electrons, that the enthalpy diffusion due to species transport is present and that the radiation losses are accounted for by the net emission coefficient.

By taking all this into account, the following four general equations, describing the process of fullerene synthesis can be derived. The first one is the continuity equation that is written in the following form: $\partial\rho/\partial t + \vec{\nabla}\cdot(\rho\vec{u}) = S_m$, where ρ is mass density, $\vec{u}$ gas velocity and S_m mass source term. Another is momentum equation which describes the plasma flow behaviour in the arc generator: (2)

$$D(\rho\vec{u})/Dt = -\vec{\nabla}P + \mu\vec{\nabla}^2\vec{u} + \rho\vec{g} + \vec{j}\times\vec{B} + \rho\vec{f},$$

where P is gas pressure, $\vec{g}$ is gravitational acceleration, $\vec{j}$ is current intensity, $\vec{B}$ is magnetic field intensity and $\vec{f}$ is vector of body force per unit mass. The equation for conservation of energy is given by

$$\frac{D(\rho c_p T)}{Dt} = \vec{\nabla}\cdot(k\vec{\nabla}T) + \frac{j_z^2}{\sigma} + \frac{5}{2}\frac{k_b}{e}c_p\vec{j}\cdot\vec{\nabla}T - (k-\rho D_C c_p)\vec{\nabla}(T_C - T_g)\cdot\vec{\nabla}Y_C - Q_{rad} + S_h, \quad (3)$$

where c_p stands for heat capacity at constant pressure, k for thermal conductivity, $\vec{j}$ for current intensity, σ for electrical conductivity, k_B for Boltzmann's constant, e for electron charge, S_h for enthalpy source term, D_C for diffusion coefficient of the carbon species, T_C and T_g for temperatures of pure carbon and pure buffer jet respectively, and Q_{rad} for radiation losses. The fourth equation is species conservation equation

$$D(\rho Y_C)/Dt = \vec{\nabla}\cdot(\rho D_C\vec{\nabla}Y_C) + S_{in}, \quad (4)$$

where S_{in} represents a negative source term due to condensation and Y_C carbon gas-phase fraction. In our case a simplified version: $D(\rho Y_i)/Dt = M_i\omega_i$ will be first taken into account. In this eq. M_i describes molecular weight for species i, ω_i chemical production rate of species i and Y_i gas-phase species mass fraction. To calculate species mass fractions, a reduced kinetic model for chemical reactions proposed by Krestinin and Moravsky [9] and improved by Scott [10] will be used.

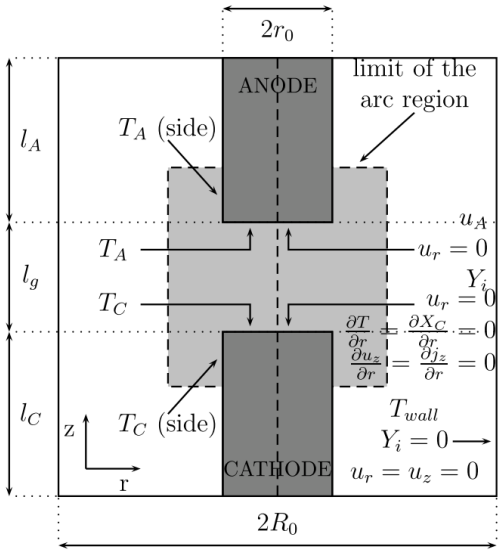
The terms S_m, $\rho\vec{f}$, S_h and S_{in} depend on the specific conditions in the arc reactor.

3.2 Initial and boundary conditions

Initial and boundary conditions for the governing equations posed are represented in Figure 3.2.

4. Numerical method

Governing equations describing fullerene synthesis are a function of space and time. In order to be able solve the problem of the process of fullerene growth numerically, continuum



equations describing the velocity, temperature, carbon mass fraction and current intensity field in the arc must be replaced by their discrete approximations. Hence, the continuous equations are replaced by formulae with finite degrees of freedom, thus reducing the problem to the solution of algebraic equations. Several numerical methods such as the finite differences method, finite elements method, finite volumes method or meshless method are applicable. In this case the meshless method or mesh-reduction technique is adapted for spatial discretization and the finite differences method is applied for the explit time discretization.

4.1 Meshless solution procedure

Meshless method or mesh-reduction technique is an approximation technique in which solution is represented on a set of arbitrary distributed nodes both on the boundary and within the computational domain. Among the variety of meshless methods such as Element-free Galerkin method, Meshless Local Petrov-Galerkin method, Gradient and adaptive gradient smoothing method, etc. [11], the Radial Basis Functions Collocation Method (RBFCM) [12] is the simplest. In our case, its local version developed by Šarler and Vertnik [13] is applied. The respective fluid flow simulations with a local pressure correction have been shown in [12]. The idea behind (LRBFCM) is to approximate a function locally over a set of neighbouring nodes by using radial basis functions (RBFs) as a basis, and the collocation to determine the coefficients. Among the most commonly used RBFs namely Gaussian, multiquadric, inverse multiquadric and thin plate splines, multiquadric (MQ) RBF is chosen to be applied in our case. The adopted RBF is expressed as: $\psi(\vec{r}) = \sqrt{r^2 / c^2 + 1}$, where r is the distance between the reference point and its neighbours and c is a shape parameter, which is either predetermined or set as a part of the solution.

The value of approximation function Θ is known only for a set of N points $\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N$, which correspond to data values $\theta_1, \theta_2, \ldots, \theta_N$ and radial basis functions $\psi_1, \psi_2 \ldots, \psi_N$. The interpolation is given by $\Theta(\vec{p}) \approx \sum_{i=1}^{N} \alpha_i \psi_i(\vec{p})$, where α_i are the expansion coefficients. By considering a collocation condition $\Theta(p_i) = \theta_i$ a linear system of N algebraic equations is obtained $\Psi \vec{\alpha} = \vec{\theta}$, where Ψ is a matrix of radial basis functions. Expansion coefficients can than be determined from $\vec{\alpha} = \Psi^{-1} \vec{\theta}$, but only when the number of domain nodes matches the number of the basis functions and when the matrix Ψ is nonsingular.

In order to be able to solve the partial differential equations of the mathematical model, first and second derivatives of the approximation function $\Theta(\vec{p})$ must be calculated. The operator applied on approximation function calculated on the influence domain is expressed as: $\partial^\iota / \partial^\iota p_i^\iota \Theta(\vec{p}) \approx \sum_{n=1}^{N} \alpha_n \partial^\iota / \partial^\iota p_i^\iota \psi_n(\vec{p})$, where index ι denotes the order of the derivative.

The boundary values are computed either from Dirichlet or Neuman boundary conditions. The implementation of Dirichlet boundary

condition, which specifies the value of the function an a surface is straightforward and can be expressed as $\Theta(\vec{p}) = \Theta_{BC}$, where Θ_{BC} is the value on the boundary. The application of Neuman boundary condition requires the use of collocation and thus the boundary condition is expressed as $\Theta_{BC} = \sum_{i=1}^{N} \alpha_i \partial / \partial \vec{n} \psi_i(\vec{p})$, where $\vec{n}$ represents a normal to the boundary.

4.2 Time - stepping

The time derivative is discretized in an Euler backward (explicit) finite difference method (FDM) $(\partial\Theta/\partial t)_k = (\Theta(\vec{r}, t_{k+1}) - \Theta(\vec{r}, t_k))/\Delta t$ where Δt is the time difference between time t_{k+1} and t_k.

4.3 Solution procedure

The spatial derivatives are approximated with LRBFCM whereas the time derivatives are approximated with FDM. As an example the continuity equation from above mentioned model is presented here. Equation 1 thus becomes: (11)

$$\rho(r_i, t_{k+1}) = \rho(r_i, t_k) + \Delta t \left[S_{mi}(t_k) - \sum_{n=1}^{N} \{ \alpha_{xn} \frac{\partial}{\partial x_i} \psi_n(r_i) + \alpha_{yn} \frac{\partial}{\partial y_i} \psi_n(r_i) \} \right].$$

Equations of momentum, energy and species conservation are discretised in a similar way.

5. Conclusions

In this paper the synthesis of fullerenes in electric-arc discharge reactor is presented. A definition of the physical model suggested to be used to describe the process of fullerene formation is given as well as a description of a numerical solution procedure that will be applied to solve the governing equations of the model.

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