Numerical Simulation of the Carbon Combustion Synthesis of Oxides Particles

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Abstract: An increasing number of studies of the synthesis of nanostructured complex oxides have recently been conducted to support their growing array of emerging technological applications. A few prominent examples are nanoenergetic materials, advanced nanoelectronics, memory devices, digital pigments, biomedical imaging contrast agents, drug delivery and biosensors. Nanoparticles generally have unique novel properties different from those of bulk materials. Due to their active surface area they are becoming a core component of advanced materials that have many practical applications. The rapidly growing market demand for nanostructured complex oxides particulates calls for cost-effective and environmentally friendly technologies for their large-scale production. Recent experimental and numerical studies of Carbon Combustion Synthesis of Oxides (CCSO) have revealed that the gas transport behavior is rather complex with respect to traditional Self-propagating High temperature Synthesis (SHS) systems. It involves at least two gaseous components: oxygen (oxygenator) as the main and practically unique gaseous reagent in SHS for gas-solid reactions and carbon dioxide which is released in the post combustion zone in CCSO. The goal of this study is to develop Two Gas Flow (2GF) filtration combustion model counting resistance distribution in a porous reacting media and enabling the numerical investigation of the complex gas dynamics behavior during CCSO. In contrast to classical filtration combustion (FC) models the proposed 2GF model for CCSO is capable of considering and predicting potential gas motion as well as complex vortex flows.

Keywords: Combustion, reacting two phase flow, multi-scale resolution, and high accuracy, porous media.

1 Introduction

Recently Martirosyan and Luss [1-3] developed a new, simple, economical and energy efficient synthesis of submicron and nanostructured complex oxides from inexpensive reactant mixtures. In
this process, referred to as Carbon Combustion Synthesis of Oxides (CCSO), the exothermic oxidation of carbon (C+O$_2$=CO$_2$, $\Delta H_{\text{CO}_2}^{\text{298K}}$=-393.5 kJ/mol) generates a steep thermal reaction wave (temperature gradient of up to 1000 °C/cm) that propagates at a velocity of 0.1-3 mm/s through the solid reactant mixture (oxides, carbonates or nitrates) converting it to the desired oxide product by the reaction:

$$\sum_{i=1}^{n} \mu_i \chi_{i}^{(s)} + \alpha C^{(s)} + \beta O_2^{(g)} = \sum_{j=1}^{m} P_{j}^{(s)} + \delta CO_2^{(g)} + (-\Delta H)$$

where $\chi_{i}^{(s)}$ is a solid compound (such as an oxide, super oxide, nitride, or carbonate, chloride, or oxalate) containing the metal needed to form the oxide, $P_{j}^{(s)}$ the solid complex oxide product, $\mu$, $\beta$ and $\delta$ stoichiometric coefficients and $(-\Delta H)$ the heat of the reaction, $x$ is the carbon weight percent in the mixture and $M_i^{(s)}$ the molecular weight of the $i$-th reactant.

CCSO is a modified form of Self-propagating High temperature Synthesis (SHS) [4] with gas filtration that maintains the advantages of SHS and circumvents some of its disadvantages. Specifically, it enables a more efficient synthesis of complex oxides with nano and submicron structure. The carbon used in CCSO is not incorporated in the product and is emitted from the sample as a CO$_2$. A large gas emission provides a convective cooling mechanism through the sample that reduces local temperature and prevents product partial melting and particles growth. CCSO does not require use of expensive fuel reactants and complex equipment and can be scaled up for continuous mass production [5, 6]. The combusted carbon is emitted from the sample as carbon dioxide and its high rate of release increases the product porosity and friability [7].

Well established theoretical models for filtration combustion (FC) [8-11] deal traditionally with only one gas as well as with the Darcy law or the Euler equation, but do not account for the loss of enthalpy by the released CO$_2$ and the reaction-induced change in the physical properties such as thermal capacity and density and the counter(co) -flow filtration of oxygen and carbon oxide in the reacting sample. Two opposite countercurrent flows of oxygen and carbon dioxide take place inside the CCSO sample [3, 12] Markov et al [13, 14] demonstrated that the complicated finger front instability can be eventually developed during the carbon combustion synthesis due to the limited access of oxygen into the reaction zone by counter-flow filtration. These gas dynamic features affect the propagating front velocity, maximum temperature, combustion mode and stability. In addition, it was shown that the mechanism of heat transfer during the CCSO is rather thermal conduction than gas convection or radiation [13].

The goal of this study was to develop Two Gas Flow (2GF) filtration model of combustion to investigate numerically the complexity of gas dynamics features during the CCSO. In proposed 2GF model we used the Navier-Stokes equations [15] as well as the concept of distributed resistance of a porous reacting medium [16] which lead to a more general version of energy, impulse and momentum conservation. Briefly, the method can be described as follows. The authors [16] consider a generalization of the Hook law expressing the pressure gradient during FC as a function of gas velocity. The linear part of this function corresponds to the well-known Darcy law while the non-linear part of it reflects a possible vortexes and flow turbulization. In addition to the pressure gradient-gas velocity bound the equations of energy, impulse and impulse moments are imposed in accordance with the transport phenomena theory [17]. To describe numerically the CCSO complex gas dynamic features in a cylindrical sample in porous media we use the two-level approach developed by Markov [18, 19] investigating of cooperative multiphase processes in course of Chemical Vapor Deposition (CVD). The splitting numerical technique is developed for multiscale transport simulation.

### 2 Problem Statement

The kinetics of volume and surface chemical reactions is based on the following scheme:

$$\text{BaCO}_3 \xrightarrow{k_1 \frac{Q}{Q_1}} \text{CO}_2 + \text{BaO} \quad \text{TiO}_2 + \text{BaO} \xrightarrow{k_2 \frac{Q}{Q_2}} \text{BaTiO}_3$$
\[ \text{BaO} + \text{BaTiO}_3 \xrightarrow{\frac{k_s}{Q_s}} \text{Ba}_2\text{TiO}_4 \quad \text{TiO}_2 + \text{Ba}_2\text{TiO}_4 \xrightarrow{\frac{k_a}{Q_a}} 2\text{BaTiO}_3 \]

We use the non-dimensional variables for the macroscopic problem formulation. A particle is characterized by non-dimensional parameter \( z = \frac{I_0 \rho_0}{b_0 \rho_p} \) where prime is used for dimensional values, \( I_0 \) is a characteristic macroscopic scale. The Damkehl numbers \( \tau_{ij} \) \((1=V,S,p; i=1,2; j=f,r)\) are defined as the ratios of time scale for forward, backward chemical reaction and condensation to the time scale for advection transport. These scales as well as the Reynolds and Peclet numbers are included in the coefficients of governing equations. The basic governing equations are the Navier–Stokes equations supplemented by the terms resulting from microscopic analysis together with relaxation equations for the chemical species. The governing equations represent the mass conservation for gas species, particle number density and size variation, the momentum and energy conservation for carrier gas flow. The flow occurs through a region containing fine-scale geometrical porous structures whose effects, being too small to be numerically resolved within the overall calculation, are represented instead as distributed momentum 'sinks' or 'resistances'. We use actual densities of gas \( \rho = \chi \rho \), and solid species \( \rho_s = (1-\chi) \rho_s \) where \( \chi \) is the porosity coefficient, bars are related to actual values of density. The Navier–Stokes model of reacting isotropic gas are written as follows (bars for densities are omitted)

\[
\frac{\partial \rho C_j}{\partial t} + \nabla \cdot (\rho C_j \mathbf{u}) = \nabla \cdot (\rho \mathbf{u} \mathbf{C}^T \mathbf{C}) + J_{\text{macro}}^{\rho C_j}
\]

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = -M^{-2} \nabla \rho + \text{Re}^{-1} \nabla \cdot \mathbf{\tau} ; \quad \mathbf{\tau} = \mu \left[ \nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3}(\nabla \cdot \mathbf{u}) \mathbf{I} \right]
\]

\[
\frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \text{Re}^{-1} \nabla \cdot \mathbf{\tau} ; \quad \mathbf{\tau} = \mu \left[ \nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3}(\nabla \cdot \mathbf{u}) \mathbf{I} \right]
\]

\[
\frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = \mathbf{S}_V - \mathbf{M}^{-2} \nabla \rho + \text{Re}^{-1} \nabla \cdot \mathbf{\tau} ; \quad \mathbf{\tau} = \mu \left[ \nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2}{3}(\nabla \cdot \mathbf{u}) \mathbf{I} \right]
\]

where \( \rho = \sum_{i=1}^{K} \rho_i, \quad \rho \mathbf{u} = \sum_{i=1}^{K} \rho_i \mathbf{u}_i, \quad \rho_i = \rho C_i \). The full momentum equations are solved using the porous resistance introduced by a (negative) momentum source term in the form: \( \mathbf{S}_V = -\rho \mathbf{K}_e, \quad \mathbf{K}_e = \chi \rho \mathbf{u} + \mathbf{K}_r, \quad i=1,2,3 \). The state equation for perfect gas is used to complete the macroscopic equation set. Initial and boundary conditions are imposed at the entrance and/or exit of tube (sample) and at its lateral surface [18, 19]. Here the surface is assumed to be chemically neutral and adiabatic.

3 Darcy Law and the Distributed Resistance Porous Model

To simulate and obtain in practice gradient properties of filtering elements the authors of [16] have for the first time used the model of distributed porous resistance which corresponds to the following dimensionless pressure gradient as a function of the 1D flow velocity:
\[
\frac{\partial \tilde{P}}{\partial \tilde{x}_i} = -M^2 \left\{ \tilde{K} \tilde{\rho} \tilde{V}_i \left| \tilde{V}_i \right| + \frac{\tilde{f}}{D_h} \tilde{\rho} \tilde{V}_i \left| \tilde{V}_i \right| \right\} - M^2 \tilde{C} \tilde{V}_i ,
\]  \hspace{1cm} (8)

The Darcy law is written as \( M^{-2} (\nabla p) = -u \zeta_i \). The Navier-Stokes resistance model is applied in the form:
\[
M^{-2} (\nabla p)_i = -u_i \left( \alpha_i \left| u_i \right| + \zeta_i \right) - \frac{\partial \chi \rho u_i}{\partial t} + \left( \nabla \cdot (\chi \rho \mathbf{u} \mathbf{u}) + \nabla \cdot (\tau) \right),
\]  \hspace{1cm} (9)

At the sufficiently low Mach numbers \( M \ll 1 \) the nonlinear term in (9) has almost no effect on the pressure gradient and it (the gradient) is related to the flow velocity linearly. Therefore, at these \( M \) model (9) appears to be completely equivalent to the Darcy law. While at the sufficiently high \( M \) \( M \approx 1 \) the nonlinear terms are of major impact producing nevertheless low pressure gradients \( \frac{\partial \tilde{P}}{\partial \tilde{x}_i} \approx 0 \), at \( |u_i| \ll 1 \), and corresponding at this limit to the well known quasi-isobaric approximation [8].

### 4 Results and Discussion

Ignition was initiated at the left section of cylindrical sample (see Figures 1-3) and at the right section of cylindrical sample (see Figures 4-7) Our calculations by using model (9) and the Darcy law presented in Figures 1-3 with the sufficiently high Mach numbers \( M \) are qualitatively in agreement, however there is the quantitative difference between gas pressure, temperature and velocities. It is noted that this difference is sufficient not only for gas velocities, but also for pressures and temperatures. We may expect that conditions of vortex formation are also strongly related with the effect of non-linear terms in model (9). Nevertheless, this problem can be solved in our future work.

Our calculations have revealed that the equivalence or discrepancy between model (9) and the Darcy law is determined not only by the Mach number but also by the relation of the characteristic thermal scale to the size of particles. Thus, from our calculations we may conclude that the non-linear terms in model (9) generate vortexes in course of CCSO. The vortexes produced by the Darcy law are much weaker and the gas movement is much closer to a potential one.

Figure 4 shows the distributions of the non-dimensional temperature \( \tilde{T} = \frac{(T - T_i)}{RT_i^2} \) and axial velocity generated by the CCSO reaction front. The temperature has been introduced in accordance with the Frank-Kamenetsky transformation [21], where \( T^* = 1000 \) \( ^\circ \)C. Therefore the part of distribution with \( T \geq T^* \) corresponds to positive \( \tilde{T} \), while the other with \( T \leq T^* \) presents negative non-dimensional temperatures. Thus, the complex reaction kinetics that localized at the combustion front is highly activated by thermal processes. Figures 3-8 present the pressure, gas density, intermediate oxide \( BaO \), final oxide product \( BaTiO_3 \), and dimensional temperature distribution along symmetry axis and in cylindrical sample at various instances of time.
Figure 1. Micro step calculation of intermediate oxide $BaO$ distribution along the distance from spherical particle at subsequent time instances.

Figure 2. Ignition was initiated at the left section of cylindrical sample. Non-dimensional temperature $\tilde{T} = \frac{(T - T_i) E}{RT_i^2}$ distribution along the symmetry axis for Mach number $M = 0.2$, model (9) $\alpha_i = 0$, $\zeta_i = 10^3$, $Re = 10^3$.
Figure 3. Ignition was initiated at the left section of cylindrical sample. The discrepancy in percent between temperature calculation along the axis of symmetry for the Darsy law and model (9) for Mach number $M = 0.2$, $\alpha_i = 0$, $\zeta_i = 10^3$, $\text{Re} = 10^3$ $\alpha_i = 0$, $\zeta_i = 10^3$, $\text{Re} = 10^3$ at subsequent time instances $t_n = n\times10$, $n = 1, 2, ..., 10$.

Figure 4. Non-dimensional temperature $\tilde{T} = \frac{(T - T_e) E}{R T_e^2}$ distribution (a) and gas longitudinal velocity (b) distribution along the symmetry axis for Mach number $M = 0.1$, model (9) $\alpha_i = 0$, $\zeta_i = 10^3$, $\text{Re} = 10^3$ at $t = 20$ (dashed line) and $t = 80$ (solid line).
Figure 5. Gas pressure via axial coordinate for Mach number $M = 0.1$, model (9) $\alpha_i = 0$, $\varphi_i = 10^3$, $Re = 10^3$ at $t = 20$ (dashed line) and $t = 80$ (solid line).

Figure 6. (left) - The increasing of gas density along the symmetry axis for Mach number $M = 0.1$ at subsequent time instances $\rho_g : t_n = n \times 10, n = 1, 2, ..., 10$, $\alpha_i = 0$, $\varphi_i = 10^3$, $Re = 10^3$; (right) - The increasing in time of intermediate oxide $BaO$ along the symmetry axis for Mach number $M = 0.1$ at subsequent time instances $BaO : t_n = n \times 10, n = 1, 2, ..., 10$, $\alpha_i = 0$, $\varphi_i = 10^3$, $Re = 10^3$. 
Figure 7. The increasing in time of final oxide product $BaTiO_3$ along the symmetry axis for Mach number $M = 0.1$ at subsequent time instances $BaTiO_3: t_n = n \times 10, n = 1, 2, \ldots, 10$, $\alpha_l = 0, \xi_l = 10^3$, $Re = 10^3$.

Figure 8. Dimensional temperature distribution (ignition from the top) for various time at $M=0.1$, model (9) $\alpha_l = 0, \xi_l = 10^3$, $Re = 10^3$. 
Concluding Remarks

Two Gas Flow (2GF) filtration model describing the complex gas dynamic features during carbon combustion synthesis of oxide was developed. It has been analytically shown that the model is completely equivalent to the Darcy law at the sufficiently low Mach numbers. At high Mach numbers there is a huge discrepancy between them, the results of analytical research have been checked numerically. They appear to be in a good agreement with the calculations in some parametrical regions. Under the other equal conditions the calculations revealed that the ratio of a temporal particle size to the characteristic thermal scale affects on the CCSO parameters and the thermal wave distributions.

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Nomenclature

\( b \) — Radius of temporal condensed particle;

\( b_1, b_2 \) — Contribution of two temporally condensing components into the mass fluxes for a particle;

\( b_{cr,j} \) — Critical particle radius with respect to phase-transition reaction \( j \);

\( C_b \) — Particle specific heat capacity at constant pressure, J/(kg K);

\( C_j \) — Mass fraction of species \( j \), dimensionless;

\( c_{j,b}^{sat} \) — Concentration of the saturated vapors of reaction products, mol/m^3;

\( c_{j,\infty}^{sat} \) — Concentration of the saturated vapors of the condensing component over a plane surface, mol/m^3;

\( C_{pk} \) — Specific heat capacity of substance \( k \) at constant pressure, J/(kg K);

\( D_j, D_{ki} \) — Diffusivity, m^2/s;

\( E_i \) — Activation energy for reaction \( i \), J/mol;

\( h = c_p T \) — Overall enthalpy of the gas mixture, J/kg;

\( J_{j \rightarrow g}^{macro}, J_{S \rightarrow g}^{macro}, J_{iS}^{macro} \) — Material fluxes caused by chemical reactions and phase conversions, kg/(s m^3);

\( J_{S \rightarrow g} \) — Condensation flux, kg/(s m^3);

\( K_{ej} (T) \) — Equilibrium reaction constant;

\( k \) — Microscopic heat transfer coefficient, J/(m^2 s K);

\( k_{ph}^j \) — Rate of condensation;

\( k_{r}^{S}, k_{f}^{S} \) — Rate constants and thermal effects for surface reactions;

\( k_{r}^{vol}, k_{f}^{vol} \) — Rate constants for forward and backward bulk reactions;

\( l_0 \) — Reference length, m;
References