On fine particles synthesis using three-zone reactor

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Abstract. This paper reports a numerical study on thermal and mass dispersion in carbon combustion synthesis of oxides (CCSO) in porous media. A volume averaging of the microscopic conservation equations over an elementary volume is applied to derive the macroscopic conservation equations for convective and conductive heat and mass transfer in a porous media consisting of gas components mixture and solid particles of reactant species. The governing system of macroequations is the conservation of momentum, mass and energy for multicomponent gas-solid media using the heat and mass exchange between gas and solid phases. The model developed in dimensionless variables and similarity parameters is applied to numerical simulation of barium titanate micron particles synthesis in three-zone reactor using the thermal and mass dispersion. The results are in satisfactory agreement with experimental measurements. The dispersion strongly influences on the thermal front propagation as well as on the barium titanate synthesis rate. The three-zone reactor is more efficient compared to the flow-reactor.

1. Introduction
Due to very high dielectric constant at room temperature, barium titanate (BaTiO₃) is one of the most important materials in ferroelectrics [1,2]. Also, BaTiO₃ ceramics present a ferroelectric–paraelectric transition at the Curie temperature, showing the so-called positive temperature coefficient of resistivity effect. In the ceramic industry, BaTiO₃ powder is frequently obtained after calcinations of TiO₂ and BaCO₃ raw materials. Regarding this matter, industry requirements need to balance energy consumption, calcination time, and the quality of the final particulate product. The objective of present paper is to analyze the effects of hydrodynamic dispersion [3] on the heat and mass transfer that occurs in CCSO [2]. We consider the flow reactor [2] and so called three-zone reactor that is similar to a diesel particulate filter an efficient device for particulate matter removal from the engine [4]. A volume averaging of the microscopic conservation equations over an elementary volume using [3,5,6] allows us to derive the macroscopic conservation equations for convective and conductive heat and mass transport in a porous mixture of gas components and solid powder of reactant species. The deviations of temperature and gas species densities from the corresponding mean values are applied as
the dispersion terms caused by temperature and mass fluctuations. The closure scheme of the set of governing equations is based on experimentally verified results [5] for gas-solid thermal nonequilibrium combustion. The model developed for dimensionless variables is applied to numerical simulation of barium titanate synthesis in three-zone reactor using kinetics schemes [1,2]. The simulation results are in satisfactory agreement with experimental data [7]. The thermal dispersion and reactor geometry strongly influence on the thermal front propagation as well as the barium titanate synthesis rate and distribution of reactant and product in the three-zone reactor.

2. Kinetics of BaTiO₃ synthesis

We consider the kinetics scheme for barium titanate synthesis with BaCO₃ precursor [1,2].

**Chemical kinetics**

\[
\begin{align*}
\text{O}_2 + C \rightarrow & \text{CO}_2, \text{BaCO}_3 \rightarrow \text{BaO} + \text{TiO}_2, \text{BaO} \rightarrow \text{BaTiO}_3, \\
\text{BaO} + \text{BaTiO}_3 \rightarrow & \text{Ba}_2\text{TiO}_4, \text{TiO}_2 + \text{Ba}_2\text{TiO}_4 \rightarrow 2\text{BaTiO}_3
\end{align*}
\]

The reactions with heat release \( Q_2, Q_3 \) are endothermic ones. The volume-averaged balance of mass and energy is obtained from the averaging of the point-wise conservation equations. Rigorous derivations of volume-averaged conservation equations are obtained in [3]. The intrinsic phase-average of a scalar or vector quantity \( \psi_\alpha \) (where \( \alpha = g \) for gas and \( \alpha = s \) for solid phase) is defined as the volume average of that quantity over elementary representative region \( \Omega(x_1, x_2, x_3) \) centered at point \( B \) with coordinates \( (x_1, x_2, x_3) \). Let \( \Omega_g, \Omega_s \) be the parts of \( \Omega \) occupied by gas and solid, \( V \) be the volume of \( \Omega \) and \( V = V_g + V_S \), where \( V_g \) and \( V_S \) are the volumes of parts \( \Omega_g, \Omega_S \). The average values are defined as

\[
\langle \psi_\alpha \rangle = \frac{1}{V} \int_{\Omega_\alpha} \psi_\alpha dV, \quad \alpha = g, s; \quad \Omega = \Omega_g \cup \Omega_s, \langle \psi_\alpha \rangle^s = \frac{1}{V} \int_{\Omega_s} \psi_\alpha dV
\]

The formulas are valid \( \langle \psi_g \rangle = \chi \langle \psi_g \rangle^g, \quad \langle \psi_s \rangle = (1 - \chi) \langle \psi_s \rangle^s, \quad \chi \) is porosity. The averaged equation for gas temperature in the case of constant heat capacity at constant pressure \( C_{ps} \), reads (see [6] in details)

\[
C_{ps} \rho_s \dot{\theta} - \frac{Q}{\rho_s} \dot{T}_g^g + \nabla \cdot \left( \nabla T_g^g \right) = \langle Q_g \rangle + \nabla \cdot \left( \chi \lambda^s + D_T^s \right) \nabla \langle T_g^g \rangle - \frac{A}{V} \kappa \left( \langle T_g^g \rangle^g - \langle T_S^g \rangle^S \right)
\]

The interphase heat transfer coefficient, the other quantities are discussed below.

3. Macro dimensionless governing equations

We apply the reference time scale \( t_0, t_0 = 10(s) \), related to activation energy \( E \) and pre-exponential factor in the reaction rate expression \( k_i \), [7]. The height and radius of the porous sample are \( l_0 = 0.0007(m), r_0 = 0.07(m) \), the gas velocity \( u_0 \) related to combustion speed in CCSO is \( u_0 = 7 \cdot 10^{-4}(m \cdot s^{-1}) \) [7], \( t_0 = k_i^{-1} \exp \left( E \times R^{-1} T_0^{-1} \right) \). The dimensionless values marked by tilde for dimensional ones are presented below (the averaging symbol is omitted).

\[
\tilde{x}_i = x_i / l_0, \tilde{t} = t / t_0, \tilde{u} = u / u_0, \tilde{v} = v / u_0, \tilde{p} = p / p_0, u_0 = l_0 / t_0, \rho_g = \rho_{g0} + \rho_{g1} + \rho_{s1}, \tilde{\rho}_g = \rho_g / \rho_{g0},
\]

\[
A = \frac{k_i}{R T_0}, \chi = \frac{\rho_s}{\rho_0}, \lambda^s = \frac{\lambda^s}{T_0}, D_T^s = \frac{D_T^s}{T_0}, \kappa = \frac{\kappa}{T_0}, \langle \psi_\alpha \rangle = \frac{1}{V} \int_{\Omega_\alpha} \psi_\alpha dV
\]
\begin{align*}
\tilde{\rho}_{j} &= \rho_{j} / \rho_{0}, \quad j=1,2,3, \quad \tilde{\rho}_{s} = \rho_{s} / \rho_{0}, \quad l=1,...,6, \quad M_{0} = m_{o2} + m_{cO2}, \\
\tilde{\lambda}_{s} &= \lambda_{s} / \lambda_{0}, \quad \tilde{\lambda}_{g} = \lambda_{g} / \lambda_{0}, \quad \tilde{\varepsilon}_{s} = C_{s} / c_{p}, \quad \tilde{\varepsilon}_{pg} = C_{pg} / c_{p}, \quad D = D / D_{0}, \quad p_{0} = R_{0} T_{0} M_{0}^{-1} \\
\overline{P_{e_{r}}} &= \frac{l_{0}^{2} \rho_{0} c_{p}}{t_{0} \lambda_{0}^{2}}, \quad \overline{P_{e_{i}}} = \frac{l_{0}^{2}}{t_{0} D_{0}}, \quad \tilde{Q}_{j} = \frac{Q_{j} k_{i}}{\rho_{0} C_{pg} T_{0}}, \quad \tilde{k}_{j} = \frac{k_{j} k_{i}}{\rho_{0}} , \quad j = 1,2,3, \quad \gamma_{aw} = \gamma_{aw}^{0}, \quad Re = \frac{l_{0}^{2}}{t_{0} \nu_{aw}} \tag{3}
\end{align*}

where \( \lambda = \pi r_{0}^{2} \), \( V = l_{0} \times \lambda \), \( \rho_{0} = \rho_{aw} = 0.4 \text{kg} \cdot \text{m}^{-3}, \lambda_{aw} = \lambda_{aw} = 0.06 \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \),

\( D_{0} = 2 \cdot 10^{-5} \text{m}^{2} \cdot \text{s}^{-1} \), \( \nu_{aw} = 9.7 \cdot 10^{-5} \text{m}^{2} \cdot \text{s}^{-1} \), \( c_{p} = C_{p,aw} = 1114 \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \),

\( \rho_{S0} = \rho_{C}, \rho_{2S} = \rho_{BaCO3}, \rho_{3S} = \rho_{BaO}, \rho_{4S} = \rho_{TiO2}, \rho_{5S} = \rho_{BaTiO3}, \rho_{6S} = \rho_{Ba2TiO4}, \rho_{S0} = \rho_{O2}, \rho_{2g} = \rho_{CO2}, \rho_{3g} = \rho_{N2} \) are species densities. The temperatures of gas and solid phases \( T_{s}, T_{S} \) are found using the formulas \( T_{s} = T_{0} \left( 1 + \beta T_{s} \right) \), \( T_{S} = T_{0} \left( 1 + \beta T_{S} \right) \), \( \tilde{k}_{0} = \kappa_{0} t_{0} A / (c_{p} \rho_{0}) V \) is the dimensionless heat transfer coefficient, \( \tilde{\varepsilon}_{s}, \tilde{\varepsilon}_{pg} \) are the heat capacities, \( \tilde{\lambda}_{g}, \tilde{\lambda}_{s} \) are the heat conductivities, \( D_{0} \) is the mass diffusivity, \( Ma, Re \) are the Mach and Reynolds numbers, \( P_{e_{r}}, P_{e_{i}} \) are the thermal and diffusion Peclet numbers, subscript \( \text{air} \) is referred to the air parameters at normal condition. The main dimensionless parameters related to activation energy and combustion heat are \( \gamma = c_{p} T_{0} \beta Q_{0}^{-1} \) [7]. \( R, E, Q_{0} \) are the gas constant, activation energy and combustion heat of carbon combustion. In numerical simulation the following values are applied \( \beta \approx 0.1, \gamma \approx 0.2, k_{1} = 10, k_{2} = 0.5, k_{3} = 0.1, Q_{0} = 60, Q_{3} = 0.1, Q_{3} = 0.1 \). For the sake of brevity, we use the numbered subscripts for molar masses \( M_{1g} = m(O_{2}), M_{2g} = m(CO_{2}), M_{3g} = m(N_{2}), \quad M_{1S} = m(C), M_{2S} = m(BaCO_{3}), M_{3S} = m(BaO) \),

\( M_{5S} = m(BaTiO_{3}), M_{6S} = m(Ba_{2}TiO_{4}) \). We write down the governing equations (tilde is omitted) for variables (3) and kinetic scheme (1),(2) [1,2]. The momentum equation is the same as in [7]. The mass conservation for gas and solid reads

\begin{align*}
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) &= 0, \\
\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho h \mathbf{u}) &= \nabla \cdot \left( \chi \rho \mathbf{u} \right) = -J_{s \rightarrow g}, \quad J_{s \rightarrow g} = \chi (1 - \chi) \rho_{S} \rho_{S} k_{i} \exp \left( \frac{T_{S}}{\beta T_{S}} + 1 \right) \\
\frac{\partial \rho_{C}}{\partial t} &= \frac{\partial \rho_{S}}{\partial t} = \frac{\partial \rho_{2S}}{\partial t} = \frac{\partial \rho_{s}}{\partial t} = \frac{\partial \rho_{2g}}{\partial t} = \frac{\partial \rho_{3g}}{\partial t} = 0, \quad J_{s \rightarrow g} = \frac{M_{1S}}{M_{S}} J_{S} - \frac{M_{1S}}{M_{3S}} \left( J_{S} + J_{S} \right) J_{3S} + D_{0} \exp \left( -\beta \rho_{S} \right) \\
\frac{\partial \rho_{4S}}{\partial t} &= \frac{\partial \rho_{5S}}{\partial t} = \frac{\partial \rho_{s}}{\partial t} = \frac{M_{5S}}{M_{4S}} \left( J_{5S} - J_{S} + 2J_{3S} \right), \quad J_{3S} = \frac{M_{1S}}{M_{4S}} \left( J_{S} - J_{S} \right) \\
\rho_{S} &= \rho_{S} \mathbf{C}_{1}, \quad \rho_{CO2} = \rho_{S} \mathbf{C}_{2}, \quad \rho_{N2} = \rho_{S} \mathbf{C}_{3}, \quad D_{S0} \text{ is a coefficient accounting for the diffusion of the migrating specie } BaO, \quad D_{S0} = 0.1, \beta_{0} = 0.092 .
\end{align*}
\[
\rho_s c_m \chi \left( \frac{\partial T_g}{\partial t} + \mathbf{u} \cdot \nabla T_g \right) + c_g T_g J_{S \rightarrow g} = \nabla \cdot \left( \lambda_{s\kappa} \nabla T_g \right) - \kappa (T_g - T_s) + Q, \quad \rho_s c_p (1 - \chi) \frac{\partial T_s}{\partial t} - c_g J_{S \rightarrow g} = \nabla \left( (1 - \chi) \frac{\lambda_s}{Pe_{T_s}} \right)
\]

The mass and temperature dispersion coefficients are as follows:
\[ D_{s\kappa} = \chi (1 + b_\kappa Pe_m + b_\kappa Pe_m \ln Pe_m) \quad \text{and} \quad \lambda_{s\kappa} = 1 + (b_\kappa Pe_r + b_\kappa Pe_r \ln Pe_r). \]

The system of mass and heat balance is accomplished by momentum conservation [7] and equation for the gas pressure \( p = \rho_s (1 + \beta T_g) \). The above system of governing equations was applied with appropriate initial and boundary conditions on the lateral surface \( r = 1 \), axis of symmetry \( r = 0 \), inlet \( x = 0 \) and outlet \( x = L \). Sections of the reactor [7] along with the conjugated heat exchange on the internal boundaries \( r = R_1, r = R_2 \) of the three-zone reactor. The thermal and oxygen fluxes were given on the inlet at the prescribed time interval. The heat exchange with outer region was imposed on the lateral surface and outlet boundary.

4. Results and discussion

We present the simulation of barium titanate \( BaTiO_3 \) fine particles synthesis in the reactor region \( 0 < x < L \), \( 0 < r < 1 \) using the free heat exchange on lateral surface \( r = 1 \), \( 0 < x < L \) and on the outlet \( 0 < r < 1 \), \( x = L \) for thermal exchange coefficient \( \alpha_r = 10^3 \). The combustion is initiated by the thermal flux \( q_j(t) = Q_j \), \( 0 \leq t \leq t_{out} \); \( q_j(t) = Q_j = 100 \) on the inlet shown in figure 1. At initial instance, the species densities of reagents were given and gas velocity was zero. The results of CCSO modelling for the micron sized reagents and products were obtained for the following parameters [7]: \( \alpha_j = 0, \gamma_j = 50, t_{out} = 0.25, \chi = 0.5 \).

\[ \begin{align*}
Ma &= 0.01, \quad Q_j = 500, \quad Re = 0.1, \quad Pe_{T_g} = 0.2, \quad Pe_{T_r} = 0.4, \quad Pe_\chi = 0.72.
\end{align*} \]

The thermal and mass dispersion in barium titanate synthesis was simulated for \( b_1 = 0 \) in formulas:
\[ D_{s\kappa} = \chi (1 + b_\kappa Pe_m + b_\kappa Pe_m \ln Pe_m) \quad \text{and} \quad \lambda_{s\kappa} = 1 + (b_\kappa Pe_r + b_\kappa Pe_r \ln Pe_r), \]

particle diameter \( d_p = 3 \times 10^{-4} \) (m). The reactor region is shown schematically in figure 1. The combustion wave propagates from left to right through the porous medium consisted of gas mixture and solid particles. The product of synthesis is produced behind the combustion front. During the front movement, the \( CO_2 \) flow is generated and the \( O_2, N_2 \) and \( CO_2 \) mixture is flown out from the right boundary \( x = L \). The combustion was initiated by a heat flux supplied from the section \( x = 0 \). The result of the flow reactor modelling shown in figure 2A and 2B are in satisfactory agreement with experimental data [1, 7].

**Figure 1.** The schematic presentation of the flow reactor (A) and the three-zone reactor (B). In the flow reactor porous part of solid and gas reagent, products occupies the region: \( 0 < x < L; 0 < r < 1-d \). The porous part is shown as heated region (2a), combustion front (2c) and cold region (2b). The gas flow part is the region: \( 0 < x < L; 1-d < r < 1 \). The mixture of \( O_2, N_2 \) is supplied at the
inlet \( x = 0, 0 < r < 1 \). The gas mixture of \( O_2, N_2 \) and \( CO_2O2 \) is blown out at the outlet \( x = L, 0 < r < 1 \).

In the three-zone reactor porous part is the region \( 2: 0 < x < L; R_2 < r < R_1 \). The gas mixture of \( O_2, N_2 \) and \( CO_2 \) occupies the region \( 1: 0 < x < L; R_1 < r < 1 \) and the region \( 3: 0 < x < L, 0 < r < R_2 \).

The Oxygen and Nitrogen are supplied from the section: \( x = 0, R_2 < r < 1 \), while the mixture of Oxygen, Nitrogen and Carbon oxide is blown out from the section: \( x = L; 0 < r < R_1 \).

Figure 2. In figure 2A the gas temperature \( T(K) \) versus time at position \((0.3L, 0)\) is compared with experimental data (symbols) [7]. Figure 2B presents the comparison of product density \( \frac{BaTiO_3(t)}{\max(BaTiO_3)} \) versus time at the sample location \((2.5, 0)\) on the axis of symmetry with the experiment [1] (symbols).

Figure 3. The computations were done for \( \kappa_0 = 1200, \chi = 0.5, \alpha_{ex} = 10^3 \). Figure 3A: demonstrates the comparison of gas temperature versus time at the section \( r = 0.5, 0 < x < L \) for the three-zone reactor \( R_2 = 0.2, R_1 = 0.8 \) and the flow reactor \( d = 0.225 \) (see figure 1A). Solis lines and symbols are referred to the flow reactor and the three-zone one respectively. Curves 1,...,3 present the temperature versus time at the location \((1.25, 0.5), (2.5, 0.5), (3.75, 0.5)\) curves 1,2,3 respectively. Figure 3B shows: the result of simulation with allowance for the dispersion effect (solid curves) and no dispersion ones (points). The dispersion effect for the three-zone reactor \( R_2 = 0.4, R_1 = 0.6 \) is presented via temporal profiles of gas temperature at locations \((1.5, 0.5), (3.0, 5), (4.5, 0.5)\).

The results in figure 3A show the higher combustion speed in the three-zone reactor (symbols) as compared to ones in the flow reactor (solid curves). The data in figure 3B allows us to conclude that the thermal and concentration dispersion intensifies the heat and mass transport. The temperature (solid curves) is higher compared to ones neglecting the dispersion (symbols). Temporal temperature
profiles demonstrate the increasing thermal front propagating speed and lower rate of temperature decreasing behind the combustion wave caused by dispersion.

Figure 4. The dynamics of reagent density $\tilde{\rho}_{\text{BaO}}(t,x,r)$ (figures 4A and 4B) and the product density $\tilde{\rho}_{\text{BaTiO}_3}(t,x,r)$ (figures 4C and 4D) is presented at the time instance $t=0.5$. The densities are dimensionless (see (3)). The simulation of hot initial temperature $T_{\text{initial}} = 900(K)$ (figures 4A, 4C) and cold one $T_{\text{initial}} = 675(K)$ (figures 4B, 4D) in the three-zone reactor $R_1 = 0.8, R_2 = 0.2$ are obtained for $\chi = 0.5$, $\alpha_{\text{ex}} = 10^3$ and the heat transfer between gas and solid $\kappa = 1200$.

According to kinetics scheme (1), (2) the initial value of reagent BaO is equal to zero, the reagent BaO is produced in reaction of BaCO$_3$ decomposition and consumed in reactions of BaTiO$_3$ and Ba$_2$TiO$_4$ synthesis. These two conversion processes result in localized region of BaO nonzero density shown in figure 4. For the hot three-zone reactor the initial temperature was 900K while for cold one 675K. The high initial temperature in hot reactor results in non-zero BaO density in front of combustion front shown in figure 4A. The results presented in figure 4 demonstrate twice lower rate of barium titanate synthesis for the cold reactor as it is shown in figure 4D compared to figure 4C.

5. Conclusion
The generalization of CCSO model based on [7] with allowance for the thermal and mass dispersion (CCSOD) is presented and verified. The averaging procedure [3,6] was applied to derive two temperature model equations including the deviations of temperature and of gas species concentration from the corresponding mean values. The closure of the set of governing equations is based on [6]. The analysis of thermal non-equilibrium between gas and solid phases was made by comparison computations with dispersion and that ones for the no-dispersion model. The intensification of transfer due to the dispersion was obtained in numerical simulation of CCSOD.

The application of CCSOD model was approved for barium titanate synthesis using kinetics [1,2]. The simulation results are in satisfactory agreement with experimental data [1,7]. The thermal dispersion strongly influences on the thermal front propagation rate. We may conclude that dispersion tends to increase the heat transfer while the boundary and inertia effects tend to act contrarily. The comparison of the three-zone reactor and the flow reactor showed the higher synthesis rate and lower operating temperature for the three-zone reactor. The model developed allows us to analyze the uniformity of species distribution caused by the thermal heat exchange in reactor’s zones.

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References
[1] Brzozowski E, Sanchez J and Castro1 M S 2002 BaCO3–TiO2 Solid State Reaction: A Kinetic Study Journal of Materials Synthesis and Processing. 10 1 123-129
[2] Martirosyan K S and Luss D 2005 Carbon Combustion Synthesis of Oxides: Process Demonstration and Features AIChE J 51 10 2801-10
[3] Telles Rubens Silva and Trevisan Osvair V 1993 Dispersion in heat and mass transfer natural convection along vertical bounaries in porous media Int. Heat Mass Transfer 36 5 1357-65
[4] Chen Kai, Martirosyan K S, and Luss D 2009 Wrong-Way Behaviour of Soot Combustion in a Planar Diesel Particulate Filter Ind Eng Chem Res 48 8451–56
[5] Fatehi M and Kaviany M 1997 Role of gas-phase reaction and gas-solid thermal nonequilibrium in reverse combustion Int Heat Mass Transfer 11 2607-20
[6] Markov A A 2019 On Thermal and Mass Dispersion Effect on Barium Titanate Synthesis via CCSO Physicochemical Kinetics in Gas Dynamics 20 4 1-14
[7] Markov A A, Hobosyan M A and Martirosyan K S 2015 Simulation of heat and mass transfer in pores as applied to synthesis of magnesium–zinc and nickel–zinc ferrite nanoparticles Int J Nanomech Sci Tech 6 3 209-222