Mathematical modelling of porous materials synthesis supported by the filtration combustion of gas mixture

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Abstract. This paper proposes a mathematical model for the synthesis of porous materials from a granular low-calorie gas-free powder mixture, the reaction of which is supported by the filtration combustion of a gas mixture. The dynamics of synthesis is described by the equations that comprise the heat balance in the condensed and gas phases, the motion of the gas phase, the rate of reactions in phases, the conservation of momentum with additional relations. A numerical study was carried out using finite-difference methods. Mechanisms and modes of the propagation of reaction fronts in phases are determined depending on the characteristics of gas flow during co-current and counter filtration, the ratio of the gas-phase and solid-phase reaction constants, and the parameters of interphase heat transfer.

1. Introduction
Nomenclature of substances obtained by self-propagating high-temperature synthesis is limited by the material requirements, the main of which is high exothermicity. This circumstance does not allow many substances to be synthesized with improved physical and chemical properties. Therefore, postheating of condensed components is a perspective method for the synthesis of materials from low-calorie mixtures [1-3]. For this purpose, filtration gas combustion can be effectively used in a porous medium formed by the powder granules of condensed substances. Gas is blown through the porous permeable samples during the filtration combustion. In this case, the heat transfer and mass transfer take place, which substantially intensifies the process of chemical conversions in the solid phase and allows the structure parameters of final products to be varied in the wide range. Gas combustion in the pore medium is controlled by the gas feed rate, the composition, filtration resistance, the parameters of heat exchange with a condensed phase and the external environment. These factors determine the dynamics and efficiency of porous materials synthesis. This type of filtration combustion, covering a wide class of reacting systems, is called hybrid combustion [4, 5]. For example, the work [6] provides a two-temperature mathematical model of hybrid filtration combustion to describe chemical reactions in the gas phase and heterogeneous reactions on the surface of particles in the layer of a catalyst.

2. Mathematical model
We consider a granular powder mixture placed in a flow reactor (pipe) with an impermeable lateral surface. The mixture consists of the particles of A and B reagents with a stoichiometric composition.
The reaction gas G is filtered in the pipe in the co-current mode (figure 1). The product F is formed due to chemical reaction in the condensed phase.

![Diagram](image)

**Figure 1.** Schematic combustion of a gasless mixture in the reaction gas flow.

The mathematical formulation for the problem of synthesis of porous materials from a granular low-calorie mixture, the reaction in which is supported by the combustion of the gas mixture in pores, is given in the dimensionless form by a system of equations:

\[
\begin{align*}
\frac{\partial \theta_1}{\partial \tau} + \alpha \frac{\partial \theta_1}{\partial \xi} &= \frac{1-m}{m} \omega \frac{\partial \theta_1}{\partial \xi}, \\
\frac{\partial \theta_2}{\partial \tau} &= \frac{\partial^2 \theta_2}{\partial \xi^2} + \omega \varphi \frac{\partial \theta_1}{\partial \xi} + \frac{1}{T_d} \frac{\partial a}{\partial \tau}, \\
\frac{d q}{d \tau} &= T_d k_0 \exp \left( \frac{\sigma \theta_1}{1 + A r \theta_1} \right) f_1, \\
\frac{d a}{d \tau} &= T_d \left( 1 - \frac{a}{m} \right) \exp \left( \frac{\theta_2}{1 + A r \theta_1} \right) f_2, \\
\frac{\partial \rho_{1w}}{\partial \tau} + \frac{\partial (\omega_1 \rho_{1w})}{\partial \xi} &= - T_d \rho_{1w} \exp \left( \frac{\sigma \theta_1}{1 + A r \theta_1} \right), \\
\frac{\partial \rho_{2w}}{\partial \tau} + \frac{\partial (\omega_2 \rho_{2w})}{\partial \xi} &= - T_d \rho_{2w} \exp \left( \frac{\sigma \theta_1}{1 + A r \theta_1} \right), \\
\omega_1 &= - \left( \frac{m}{1-m} \right)^3 P e_j \frac{\partial p}{\partial \xi}, \\
p &= \rho_0 (1 + A r \theta_1). 
\end{align*}
\]

Dimensionless variables and parameters have the form as follows:

\[
\begin{align*}
\theta_1 &= \frac{E_r}{R T_r} (T_1 - T_r), \quad \theta_2 &= \frac{E_r}{R T_r} (T_2 - T_r), \quad \theta_0 &= \frac{E_r}{R T_r} (T_0 - T_r), \quad \theta_w &= \frac{E_r}{R T_r} (T_w - T_r), \quad T_d = \frac{c_r R T_r^2}{Q Q_2}, \\
\tau &= \frac{t}{t_s} \left( t_s = T_d k_2 \exp \left( - \frac{E_r}{R T_r} \right) \right), \quad \tau_w = \frac{t_w}{t_s}, \quad \xi = \frac{x}{x_s} \left( x_s = \sqrt{\lambda_o m / c_3 \rho_2} \right), \quad \Omega = \frac{3\gamma m}{\rho_2 R c_3 \rho_2}, \quad \varphi = \frac{c_r \rho_2 \rho_2}{c_3 \rho_2}, 
\end{align*}
\]
\[
q = \frac{Q_1 c_2}{Q_2 c_1}, \quad \omega_1 = \frac{v_1 l_1}{x_1}, \quad \sigma = \frac{E_1}{E_2}, \quad Ar = \frac{RT_1}{E_2}, \quad Pe_f = \frac{k_f c_2 P_0}{\lambda_0}, \quad \rho_{ia} = \frac{\rho_{ia}}{\rho}, \quad \rho_{10} = \frac{\rho_{10}}{\rho}, \quad \rho_0 = \frac{\rho_0}{\rho}
\]

\[p = \frac{P}{P_0} (P_0 = \rho RT / \psi), \quad k_0 = \frac{k_1}{k_2}, \quad l = \frac{L}{x_1}.
\]

The dimensionless quantities are written using the dimensional variables as follows: \( t, x \) are the time and spatial coordinates; \( T_0, T_1, T_2 \) are the initial temperature, and the temperature of gas (1) and condensed (2) phases; \( T_w, t_w \) are the temperature and response time of the hot surface; \( c_1, c_2, \rho_{1l}, \rho_{1a}, \rho_2 \) are the heat capacity and density of the gas mixture and the condensed substance; \( \rho_{10}, \rho_{ia} \) are the density of active and inert gas; \( T_*, \rho_* \) are the reference temperature and density; \( R_0 \) is the size of the granule; \( k_f \) is the coefficient of filtration; \( m \) is porosity; \( v_1 \) is the rate of the gas flow; \( \lambda_0 \) is the coefficient of thermal conductivity in the condensed phase; \( \chi \) is the coefficient of interphase heat exchange; \( Q_1, Q_2 \) are thermal effects of reactions; \( k_f, E_1, f_1 \) are the pre-exponential factor, activation energy, kinetic laws in the gas (\( j=1 \)) and condensed (\( j=2 \)) phases; \( R \) is the gas constant; \( P \) is the gas pressure; \( P_0^* \) is the reference pressure; \( \alpha, \eta \) are the degree of conversion in the condensed and gas phases; \( L \) is the length of the reactor.

The system of equations (1)-(9) was solved numerically using an implicit difference scheme with the dimensionless parameters: \( m=0.4, Ar=0.08, Td=0.15, \theta_0=-1/Td, q=1.5, \sigma=1, k_0=3, Pe_2=250, f_1=1, f_2=0.2, \rho_{1l}=5, \rho_{1a}=4, l=500. \) The combustion rate was calculated from the displacement of the reaction surface, when the degree of conversion was 0.5. In the calculations, the error of the mass balance did not exceed 1%. The parameters \( \Omega \) and \( \varphi \) were varied in the calculations. It is worth noting that in a real experiment, the magnitude of interphase heat transfer can be varied by changing the size of the granules of a powder mixture.

3. Discussion
Figure 2 shows the temperature profiles in the condensed (curves 1-3) and gas (curves 1'-3') phases, depending on the intensity of interphase heat transfer (a, b).

![Figure 2](image_url)

**Figure 2.** Temperature profiles in the combustion wave as a function of time (\( \tau \)) in the condensed (curves 1–3) and gas (curves 1’–3’) in the absence (a, \( \Omega=0 \)) and in the presence (b, \( \Omega=0.06 \)) of interphase heat transfer for \( \varphi=0.8 \) and \( \tau: (1, 1') – 300; (2, 2') – 600; (3, 3') – 900.

In the absence of interphase heat exchange, the combustion temperature in the condensed phase is much lower than in the gas phase (figure 2a). Analyzing the temperature profiles presented in this Figure, it can be concluded that a higher combustion rate is observed in the gas phase compared to the combustion rate in the granular mixture.

Under the conditions of interphase heat exchange, the co-current flow of the gas coolant heats the condensed substance, increasing the temperature and the rate of synthesis. Figure 2b demonstrates the limiting case of such thermal interaction between the gas and condensed phases, when the temperature
profiles in phases begin to coincide due to the intense interphase heat transfer, which leads to a single-
temperature combustion mode of the system. In this case, the influence of the filtered reaction gas on
the granular mixture is maximal. The reactivity of the granular mixture increases significantly, and the
synthesis temperature grows.

The combustion rate in the condensed phase as a function of the parameter of interphase heat
exchange is shown in figure 3. In the absence of the thermal interaction with the gas phase, the
combustion rate is slow, and the reaction front propagates in a stationary mode (line 1). The interphase
heat transfer significantly increases the combustion rate in the granular mixture and change the mode
of chemical interaction to the nonstationary one (lines 2, 3). In this case, as the filtered gas moves
through the reactor, the gas is cooled, the effect of the gas coolant decreases, and the velocity of the
combustion wave in the condensed phase becomes slower.

![Figure 3](image)

**Figure 3.** Velocity profiles of the combustion wave in the k-phase for \( \varphi=0.8 \) and different
coefficients of interphase heat transfer, \( \Omega: 1 – 0, 2 – 6 \times 10^{-5}, 3 – 6 \times 10^{-2} \).

The profiles of the function of heat release in phases for different parameters of interphase heat
transfer are shown in figure 4. The functions of heat release were set as follows: \( U_1=f_1 q k_0 \exp[\sigma \theta_1/(1+Ar \theta_1)] \) for the reaction gas and \( U_2=f_2(1-\alpha)\exp[\theta_2/(1+Ar \theta_2)]/\alpha \) for the mixture of
powders. In the absence of interphase heat transfer, the heat release in the gas phase (curve 1) is much
higher than in the condensed phase (curve 2). In this case, the separation mode takes place, when the
combustion front in the gas mixture propagates significantly faster compared to the combustion front
in the powder mixture (a).

In the presence of interphase heat transfer in the system, the gas transfers a significant amount of
heat to the granular mixture. As a consequence, there is a significant reduction in the heat release \( U_1 \),
and the heat release \( U_2 \) increases. At the same time, the rate of chemical reaction in the gas is higher
compared to the rate of reaction in the condensed substance (b).

![Figure 4](image)

**Figure 4.** Heat release profiles in the gas (curve 1) and condensed (curve 2) phases for \( \varphi=0.001 \) and
\( \tau=600 \), depending on the parameter: \( \Omega: a – 0, b – 0.006, c – 30 \).
For the high values of interphase heat transfer, when the temperatures in the phases practically coincide, only the peak of heat release $U_2$ caused by the synthesis reaction in the condensed substance (c) is observed. Under these conditions, the gas reacts at the reactor inlet, transfers heat to the condensed substance, is cooled and filtered through the reactor without noticeable chemical conversion.

4. Conclusion

- A mathematical model was constructed for the nonstationary synthesis of porous materials from a condensed powder mixture during the filtration combustion of a gas mixture and was numerically studied in the two-temperature approximation.
- The modes of propagation of combustion fronts in the condensed phase and in the flow of the filtered gas were determined depending on the parameters of interphase heat transfer. The increase in the intensity of interphase heat transfer was shown to contribute to the increase in the combustion characteristics of a granular gasless mixture.

References

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