

PROPAGATION OF TECHNOLOGICAL FILTRATION COMBUSTION WAVES IN POROUS MEDIA OF INHOMOGENEOUS COMPOSITION

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The article contains results of numerical simulation of propagation of filtration combustion waves with forced supply of gas-phase reagent into a porous medium of inhomogeneous composition. Wave "penetration" and "reflection" effects at the interface of media with different chemical compositions are found and explained.

In the technology of self-propagating high-temperature synthesis (SHS technology) [1], the properties of the resultant product are determined by the composition (qualitative and quantitative) and spatial arrangement of the initial reagent materials. If the process is organized in the filtration combustion (FC) mode, the two parameters just mentioned can be supplemented with three more characteristics (moreover, they can be controlled during the process): the velocity, composition, and initial temperature of the gas-phase reagent that is injected through the porous material (that contains the chemically active reaction component). These features of FC should markedly expand the potentialities of synthesis of materials with specified properties.

In studies of FC [2-6], porous media of a homogeneous composition were considered, as a rule. Only in [7] in numerical simulation of the "ignition" mode (initiation of FC waves), did the authors pay attention to characteristics of the behavior of the countercurrent wave (the wave that propagates toward the gas-mixture flow) at the interface of media with different compositions.

In what follows, results are presented of a more systematic study of the relations governing propagation of FC waves in porous media of inhomogeneous composition, which is not only of theoretical but also of practical interest.

In a one-dimensional approximation with familiar assumptions [5], initiation and propagation of FC waves is described by the following system of equations:

the energy equation

$$\frac{\partial}{\partial t} \left(\sum_{j=1}^4 c_j h_j \right) = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) - \frac{\partial}{\partial x} \left(v \sum_{j=1}^2 c_j h_j \right) + Qc_3^0 \Phi - \alpha^* (T - T_0); \quad (1)$$

the mass conservation equation for the gas-phase reagent

$$\frac{\partial c_1}{\partial t} = - \frac{\partial}{\partial x} (c_1 v) + \frac{\partial}{\partial x} \left(CD \frac{\partial \xi}{\partial x} \right) - \mu c_3^0 \Phi; \quad (2)$$

the continuity equation for the gas flow

$$\frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} (Cv) - \mu c_3^0 \Phi; \quad (3)$$

the kinetic equation for chemical transformation of the solid-phase reagent

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$$\frac{\partial \eta}{\partial t} = \Phi ; \quad (4)$$

the equation of state for the gas phase

$$c_1 + c_2 = C = \frac{P}{RT} ; \quad (5)$$

the form of the function Φ that determines the reaction rate is specified by the equation

$$\Phi = k_0 \exp [-E/RT] f(\eta) p_1^n, \quad f(\eta) = (1 - \eta)^2 . \quad (6)$$

The system of equations (1)-(6) is completed by the relations

$$h_4 = h_3 + \mu h_1 ; \quad h_j = \int_{T_0}^T c_{pj} dT \quad (7)$$

and the expression for $\eta = (c_3^0 - c_3)/c_3^0$, which is the extent of transformation of the solid-phase component of the reaction.

In the case of initiation of the reaction by local conductive heating of the porous medium, which is simulated by specifying a rectangular temperature profile at the initial time, the boundary and initial conditions for system (1)-(6) have the form

$$T(0, x) = \begin{cases} T_0, & x \in [0, x_1], \\ T_{\text{ign}}, & x \in [x_1, x_2], \\ T_0, & x \in [x_2, x_L], \end{cases} \quad \xi(0, x) = \begin{cases} \xi_0, & x \in [0, x_1], \\ 0, & x \in [x_1, x_L], \end{cases} \quad (8)$$

$$v(0, x) = v_0/C_0(0, x) ; \quad \eta(0, x) = \eta_0(x) ,$$

where 0 and x_L are the coordinates of the boundaries of the porous sample.

At the gas inlet interface with the porous material, use is made of the condition of balance with the chemically inert initial section, which is thermally inertialess:

$$\lambda \left. \frac{\partial T}{\partial x} \right|_{x=0} = [c_{p2}^0 + (c_{p1}^0 - c_{p2}^0) \xi_0] C_0 v_0 [T(t, 0) - T_0] ; \quad (9)$$

$$\xi(t, 0) = \xi_0 ; \quad v(t, 0) = v_0/C(t, 0) ,$$

and at the gas outlet interface, heat transfer is specified by the boundary condition of the third kind

$$\lambda \left. \frac{\partial T}{\partial x} \right|_{x=L} = -\alpha [T(t, x_L) - T_0] , \quad (10)$$

in a particular case $(\lambda \partial T / \partial x)|_{x=L} = 0$.

Results of numerical simulation are presented in the form of space-time relations of the extent of transformation of the solid-phase component of the reaction with specified controlling process parameters: $\eta = f(\tilde{x}, \tau) |_{\tilde{v}_0, \tilde{\xi}_0, \eta_0}$. Here $\tilde{x} = x/x_*$, $\tau = t/t_*$, $\tilde{v}_0 = v_0/v_*$, $\tilde{\xi}_0 = \xi_0/\xi_*$ are the dimensionless space coordinate, time, filtration velocity, and inlet relative concentration of the gas-phase reagent, respectively.

The nondimensionalization scales are specified by the following expressions:

$$x_* = \sqrt{a\gamma t_*} ,$$

where $a = \lambda_0/c_3^0 c_{p3}^0$ is the effective thermal diffusivity of the porous material in the initial state;

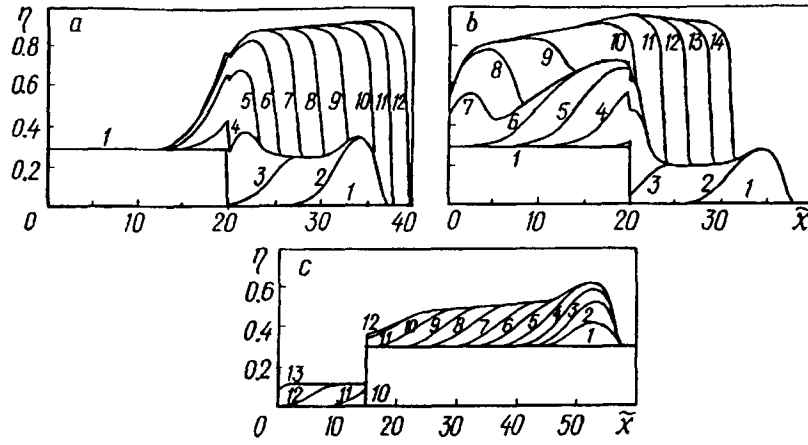


Fig. 1. Propagation of a countercurrent FC wave in an inhomogeneous porous medium ($\theta_0 = -10$; $\xi_0 = 1.2$): a) $\bar{v}_0 = 0.58$; 1) $\tau = 0$, 2) 500, 3) 1000, ..., 12) 5500; b) $\bar{v}_0 = 0.4$; 1) $t = 0$, 2) 600, 3) 1200, ..., 14) 7800 ($\eta_0 = 0.3$ at $\bar{x} < 20$, $\eta_0 = 0$ at $\bar{x} > 20$); c) $\bar{v}_0 = 0.3$; 1) $t = 0$, 2) 500, 3) 1000, ..., 13) 6000 ($\eta_0 = 0$ at $\bar{x} < 15$, $\eta_0 = 0.3$ at $\bar{x} > 15$).

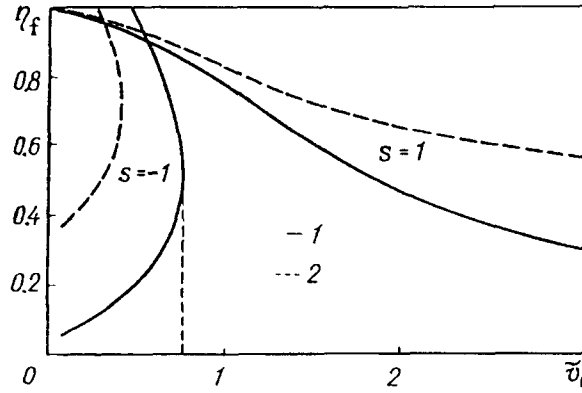


Fig. 2. Plot of the final extent of transformation of a solid-phase reagent in cocurrent ($s = 1$) and countercurrent ($s = -1$) FC waves ($\theta_0 = -10$; $\xi_0 = 1.2$): 1) $\eta_0 = 0$; 2) 0.3.

$$v_* = \sqrt{\alpha\gamma/t_*} (c_3^0 c_{p3}^0 RT_0 / Pc_{p2}^0),$$

where $\gamma = (RT_*^2/E)/(Q/c_{p3}^0)$;

$$t_* = \left\{ k_0 (P\xi_*)^n \exp[-E/RT_*] \right\}^{-1}; \quad \xi_* = \delta \left[\left(s - \frac{1}{\gamma\theta_0} + \delta \left(1 - \frac{1-s}{2} \psi \right) \right) \right]^{-1},$$

where $\delta = \mu c_{p2}^0 / c_{p3}^0$; $\psi = c_{p1}^0 / c_{p2}^0$; $\theta_0 = E(T_0 - T_*) / RT_*^2$; T_* is an arbitrarily chosen characteristic temperature, for example, the optimum one for the particular process; s is the indicator of the FC mode; $s = 1$ is the cocurrent wave and $s = -1$ is the countercurrent wave.

The inhomogeneity of the composition of the porous medium was simulated by specified the distribution of the initial extent of transformation of the solid-phase component of the reaction in the form of the step function

$$\eta_0(x) = \begin{cases} \eta_{01}, & x < x_1, \\ \eta_{02}, & x \geq x_1, \end{cases}$$

where η_{01} and η_{02} can take values from 0 to 1, and the latter value means a chemically inert composition.

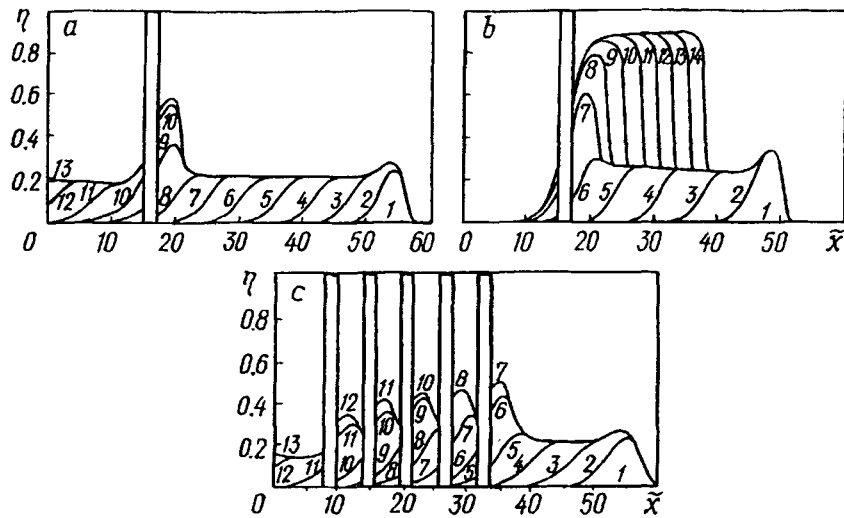


Fig. 3. Propagation of a countercurrent FC wave in a porous medium with chemically inert interlayers ($\theta_0 = -10$; $\xi_0 = 1.2$): a) $\tilde{v}_0 = 0.5$; 1) $\tau = 0$, 2) 500, 3) 1000, ..., 13) 6000, b) $\tilde{v}_0 = 0.58$; 1) $\tau = 0$, 2) 500, 3) 1000, ..., 14) 6500; c) $\tilde{v}_0 = 0.5$; 1) $\tau = 0$, 2) 500, 3) 1000, ..., 13) 6000.

The corresponding difference in thermal properties of the media, in particular, in thermal conductivities, was specified by the function $\tilde{\lambda} = f(\eta)$; the heat capacity of the condensed phase was calculated by summing the heat capacities of its components (c_{p4} of the product and c_{p3} of the reagent).

In Fig. 1 one can see results of propagation of a countercurrent FC wave in an inhomogeneous porous medium for various combinations of the initial extent of transformation in particular areas of the medium, the mutual position of the areas, and the filtration velocity of the gas mixture. The wave is initiated by heating the rear (relative to the gas injection) part of the material sample ($\tilde{x} = 30-40$, Fig. 1a and b and $\tilde{x} = 45-55$, Fig. 1c). It can be seen that some time later ($\tau > 500$), the countercurrent FC wave generated in the "ignition" zone reaches the steady-state regime (with a certain approximation, in view of the relatively short length of the areas considered) with an extent of transformation of the reagent that corresponds to the specified filtration velocity of the gas.

At the interface of zones with different compositions ($\tilde{x} = 20$, Fig. 1a and b) the FC wave that propagated at the dimensionless filtration velocity $\tilde{v}_0 = 0.58$ "stops" and, having been reflected, propagates subsequently as a cocurrent wave with a final extent of transformation η_f that corresponds to the mentioned velocity \tilde{v}_0 and to the transformation depth $\eta(\tilde{x})$ ($\tilde{x} > 20$) that became the initial one for the reflected wave. At the same time, the wave that propagated at the filtration velocity $\tilde{v}_0 = 0.4$ penetrates through the interface and reaches the boundary of the sample ($\tilde{x} = 0$), where it is transformed into a cocurrent wave (Fig. 1b).

Figure 1c is an example of propagation of the countercurrent FC wave in a porous medium with an initial extent of transformation that decreases (in the direction of the wave propagation) at the interface. It can be seen that after the wave passes through the interface, it continues to propagate with a different final extent of transformation inherent to this area.

The features of propagation of FC waves given above can be explained by the steady-state dependences of the extent of transformation on the filtration velocity $\eta_f(\tilde{v}_0)$ for the homogeneous medium (Fig. 2). It can be seen that the reflection effect of the countercurrent FC wave is related to limitation of the gas filtration velocity range within which such a wave can exist. At the same time, as follows from Fig. 2, this limitation does not exist for the cocurrent FC wave, and therefore, the wave propagates in a medium of inhomogeneous composition without hindrance. Only if this wave encounters a rather long chemically inert section, can the cocurrent wave, having been reflected from this section, not be transformed into a countercurrent one, and it is simply extinguished.

Figure 3 illustrates cases of propagation of the countercurrent FC wave in media with a chemically inert interlayer or with a "grid" structure formed by alternation of inert and active interlayers. It can be seen that depending on the filtration velocity of the gas mixture, the wave either penetrates through the inert interlayer (the

velocity is "low," Fig. 3a) or is reflected from it (the velocity is "high," Fig. 3b) and transformed into a cocurrent wave. It is evident that the penetration effect depends not only on the filtration velocity but also on the length of this interlayer; with a certain relation of these parameters the effect vanishes and the wave is reflected.

In the case of a "grid" structure of the medium considered here (Fig. 3c), the relation of the length of the interlayers, their number, and the gas filtration velocity turns out to be such that the penetration effect of the FC wave is observed. It should be noted that a decrease can be clearly seen in the growth of the extent of transformation near the boundaries of the inert interlayers as the waves propagate over the material.

Summarizing the results of the present study, it can be concluded that they confirmed the suggestion of broad possibilities for the process of controlled filtration combustion in producing new materials.

Production of electrode materials for primary chemical current sources is cited as an example. The main characteristics of these sources (voltage-current characteristics and power capacity) are determined by the electrical conductivity of the electrode and the amount of material in its composition that participates in the current-generating reaction. In polycarbonfluoride, which is used as a cathode for a type of lithium source, both of these parameters are inconsistent: carbon, used to produce polycarbonfluoride [8] has a high electrical conductivity, while the electrical conductivity of polycarbonfluoride is low. Synthesis of polycarbonfluoride by fluorination of porous carbon-graphite materials in the FC-wave mode can produce an optimum structure for the electrode.

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NOTATION

c_j , molar concentration of the j -th component of the system; c_{pj} , molar heat capacity of the j -th component of the system; E , reaction activation energy; $f(\eta)$, function of reaction suppression by the product; h_j , molar enthalpy of the j -th component of the system; n , order of the reaction in the gaseous reagent; P , pressure of the gas mixture; p_1 , partial pressure of the gas-phase reagent; Q , thermal effect of the reaction; R , universal gas constant; T , temperature; t , time; v , linear filtration velocity of the gas; x , spatial coordinate in the direction of filtration; α , heat-transfer coefficient; ξ , relative concentration; η , extent of transformation of the solid-phase reagent; λ , effective thermal conductivity of the system; μ , stoichiometric coefficient of the reaction with the gas-phase reagent; Φ , reaction rate. Subscripts: 1, 2, 3, 4, chemically active component of the gas mixture, its inert component, solid-phase reagent, and reaction product, respectively; 0, initial values of parameters (inlet values for the gas phase); ign, ignition; L , length of the sample.

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