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On the Theory of a Travelling Hybrid Wave

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A qualitative theory of hybrid waves has been developed on a basis of a mathematical model of the chemical transformation of filtrating combustible gaseous mixture in a layer of catalytically active quiescent porous solid. The constructed mathematical model of the process includes nonlinear one-dimensional equations of: heat transfer through gas and solid phases, transfer of the mass of deficient component in the gas phase, conservation of the total amount of substance in a flow, transfer of the mass of deficient component of combustible mixture on the surface of a catalyst and ideal gas state. Gas flows with negligible small pressure gradients have been considered.

Assuming a high temperature sensitivity of chemical reaction rate and isothermicity of the elements of porous medium, the ratios have been derived for combustion wave velocity, maximum gas temperature in chemical reaction zone, equilibrium temperature and other characteristics of the process.

The method of counter extrapolation has been used to estimate the structure of the hybrid wave zone. It is shown that the ratio between the specific contributions of homogeneous and heterogeneous reactions in the heat release substantially depends on the filtration velocity of the reacting gas and the coefficient of mass transfer at the interface.

INTRODUCTION

Combined homogeneous and heterogeneous reactions occurring in narrow channels and porous media have long attracted researchers for the possibility of studying the effects of their interactions (Khitrin and Solovyeva, 1959; Trimm, 1983). A deep study of this problem has led to substantial progress in the understanding of the coupled heterogeneous-homogeneous mechanism and the development of a series of applications, particularly, in the area of catalytic combustors for gas turbines, furnaces, water heaters (Kesselring, 1986; Prasad *et al.*, 1984). It appeared that on catalytic combustion, fuel mixtures can be stabi-

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lized and burned beyond the flammability limits, the NO_x emission can be substantially decreased as compared with the usual gas-phase combustion at relatively low CO/UHC emissions (Pfefferle and Pfefferle, 1986).

The problem under study displays a multiaspect character in the case of chemical reactors with granular catalyst layers. Interaction of the mechanisms of homogeneous and heterogeneous reactions can result in a change in the path of integral reaction, the development of inhomogeneous temperature fields with hot and cold spots (Boreskov *et al.*, 1981; Correa, 1995), the excitation of moving thermal waves (Babkin *et al.*, 1989), the development of accidents with increased pressure in the reactor, etc.

Recently, information on the elementary heterogeneous catalytic reactions has appeared (Deutschmann *et al.*, 1994; Veser *et al.*, 1997). This allows one to model homogeneous-heterogeneous interactions at a level of detailed kinetics and obtain more realistic data on intermediates, the role of homogeneous and heterogeneous brutto-reactions particularly, hysteresis phenomena, temperature limits of dominating reactions, etc. (Dupont and Williams, 1998; Fernandes *et al*, 1999).

The problem of the interaction of homogeneous and heterogeneous mechanisms of chemical transformation in inert and active porous media is usually considered in stationary conditions, i.e., catalytic combustors, IR-emitters, stagnation flow reactors, etc. (Pfefferle and Pfefferle, 1986). At the same time, the problem of homogeneous-heterogeneous interaction is also of interest as applied to the conditions of steady-state travelling waves (Babkin *et al*, 1989).

It is known that under filtration of reacting mixture through the granular layer of quiescent catalyst may possible formation and propagation of steady-state low-temperature (500–700 K) waves with heterogeneous reaction (K-waves)(Matros and Kiselev, 1980). The propagation of high-temperature (1500–2500 K) waves with gas-phase reaction (LVR-waves) is possible in inert porous medium in the low-velocity regime (Babkin and Laevsky, 1996; Babkin, 1993). These processes have common and at once specific features and regularities determined by the different forms of heat release. Both of the processes belong to the class of filtration combustion in which the main wave characteristics, such as: velocity, structure, equilibrium temperature, existence limit, etc., depend on the filtration velocity of reacting gas.

Until recently, the K-waves and LVR-waves have been studied in their own right. However, owing to the development of chemical wave technologies (Matros and Bunimovich, 1996; Noskov, 1997), the necessity of solving the problems of fire and explosion safety (transition from smoldering combustion to flaming combustion), deep investigation of energy problems (coal combustion in layers with output and burning of volatiles), the study of hybrid waves accompanied by homogeneous and heterogeneous reactions becomes rather urgent. In this study, we present the mathematical model of hybrid wave, the analytical solution of the problem and some physical results of the analysis of this model.

MATHEMATICAL DESCRIPTION OF THE PROCESS

A theoretical study of hybrid wave propagation is based on the system of one-dimensional equations of heat spread in gas and catalyst layer, transfer of the mass of deficient mixture component in the gas flow and on the catalyst surface, conservation of the total amount of substance in the flow, and ideal gas state. In this case, we consider the flow with the negligible small pressure gradient. It is also assumed that the fraction of a substance reacting on the catalyst surface enters reaction zone only due to the effective mass exchange with the flow.

$$\begin{aligned}
&c_T\rho_T\frac{\partial T}{\partial t}=\frac{\partial}{\partial l}\left(\lambda_T\frac{\partial T}{\partial l}\right)-c_T\rho_T v\frac{\partial T}{\partial l}-\frac{\alpha_{T,0}S}{m}(T-\Theta)+Q\rho_T W_T(\eta_T,T),\\
&c_\Theta\rho_\Theta\frac{\partial \Theta}{\partial t}=\frac{\partial}{\partial l}\left(\lambda_\Theta\frac{\partial \Theta}{\partial l}\right)+\frac{\alpha_{T,0}S}{1-m}(T-\Theta)+m_\Theta Q\rho_T W_\Theta(\eta_\Theta,\Theta),\\
&\rho_T\frac{\partial \eta_T}{\partial t}=\frac{\partial}{\partial l}\left(\rho_T D\frac{\partial \eta_T}{\partial l}\right)-\rho_T v\frac{\partial \eta_T}{\partial l}-\frac{\alpha_{\eta,0}S}{m}(\eta_T-\eta_\Theta)-\rho_T W_T(\eta_T,T),\\
&\frac{\alpha_{\eta,0}S}{1-m}(\eta_T-\eta_\Theta)=m_\Theta\rho_T W_\Theta(\eta_\Theta,\Theta), \qquad (1)\\
&\frac{\partial\rho_T}{\partial t}+\frac{\partial\rho_T v}{\partial l}=0,\quad \rho_T T=\text{const}.
\end{aligned}$$

In this case, T and Θ are the temperatures of gas and catalyst layer, η_T and η_Θ are the relative mass concentrations of the deficient component in the flow and on the catalyst surface, υ is the gas filtration velocity, ρ_i, c_i, and λ_i are the density, specific heat capacity and the thermal conductivity coefficient of gas at $i = T$ and of catalyst layer at $i = \Theta$ respectively, D is the gas diffusion coefficient, $m$and m_Θ are the porosity and fraction of reagent volume in the catalyst layer, $\alpha_{T,0}$ and $\alpha_{\eta,0}$ are the coefficients of heat and mass transfer, S is the specific catalyst layer surface, Q is the thermal effect of reaction. The irreversible chemical reactions of first order with heat release occur according to the Arrhenius law in the gas flow and the catalyst layer

$$W_T(\eta_T,T)=k_T\eta_T\exp\left(-\frac{E_T}{RT}\right),\quad W_\Theta(\eta_\Theta,\Theta)=k_\Theta\eta_\Theta\exp\left(-\frac{E_\Theta}{R\Theta}\right), \qquad (2)$$

where E_T and E_Θ are the activation energies, k_T and $k_\Theta$are preexponents, R is the universal gas constant.

The study of stationary hybrid waves is reduced to the analysis of stationary solutions of system (1) written in terms of variables t and $x = l - ut +$ *const* where u is the constant wave velocity. The stationary in specified sense equation of continuity leads to the equation

$$G \equiv \rho_T(v - u) = \text{const}. \tag{3}$$

With $x \to \pm\infty$, the following conditions are set: in the initial mixture ($x = -\infty$) $T = \Theta = T_0$, $\eta_T = 1$, $\rho_T = \rho_0$, $\upsilon = \upsilon_0$; in combustion products ($x = \infty$) $\frac{dT}{dx} = \frac{d\Theta}{dx} = 0$, $\eta_T = 0$. The values of T_0, ρ_0 and υ_0 unambiguously determine the constants in the equation of state and in (3).

Let us introduce dimensionless variables and parameters

$$\xi = \frac{x}{L},\ L = \frac{m\lambda_{T,m} + (1-m)\lambda_{\Theta,m}}{mc_T G},$$

where $\lambda_{T,m}$ and $\lambda_{\Theta,m}$ are the coefficients of thermal conductivity at the maximum gas temperature in the combustion wave, $T = T_m$. Further, we assume

$$y = \frac{T - T_0}{T_m - T_0},\quad z = \frac{\Theta - T_0}{T_m - T_0},\quad y_b = \frac{Q}{c_T(T_m - T_0)},\quad \kappa_T = \frac{\lambda_T}{c_T G L},$$

$$\kappa_\Theta = \frac{(1-m)\lambda_\Theta}{mc_T G L},\quad \kappa_\eta = \frac{\rho_T D}{GL},\quad \alpha_T = \frac{\alpha_{T,0} S L}{mc_T G},\quad \alpha_\eta = \frac{\alpha_{\eta,0} S L}{mG},$$

$$\omega = \frac{v_m - (1 + \sigma_m)u}{v_m - u},\quad \sigma_m = \frac{(1-m)c_\Theta \rho_\Theta}{mc_T \rho_{T,m}},$$

where $\rho_{T,m}$, υ_m are the values of gas density and velocity at $T = T_m$. Note that according to (3), we get

$$\omega = \frac{v_0 - (1 + \sigma_0)u}{v_0 - u},\quad \sigma_0 = \frac{(1-m)c_\Theta \rho_\Theta}{mc_T \rho_{T,0}}.$$

Further, it is assumed that

$$\tau_T = \frac{\rho_{T,m} L}{G} k_T \exp\left(-\frac{1}{\beta_T}\right),\quad \tau_\Theta = \frac{(1-m)m_\Theta \rho_{T,m} L}{mG} k_\Theta \exp\left(-\frac{1}{\beta_\Theta}\right),$$

$$\beta_T = \frac{RT_m}{E_T},\quad \beta_\Theta = \frac{R\Theta_m}{E_\Theta},\quad \gamma_T = \frac{\beta_T T_m}{T_m - T_0},\quad \gamma_\Theta = \frac{\beta_\Theta \Theta_m}{T_m - T_0},$$

where Θ_m is the maximal temperature of solid phase in the wave. The chemical reaction rates are assumed to be high temperature-sensitive

$$\gamma_T \ll 1,\quad \gamma_\Theta \ll 1, \tag{4}$$

which allows us to apply the Frank-Kamanetsky transformation to the functions of reaction rates in gas and on the surface of solid phase. In this case, instead of (2) we consider the dimensionless reaction functions in the form below

$$w_T = \eta_T \exp\left(-\frac{1-y}{\gamma_T}\right), \quad w_\Theta = \eta_\Theta \exp\left(-\frac{z_m - z}{\gamma_\Theta}\right), \tag{5}$$

where $z_m = (\Theta_m - T_0)/(T_m - T_0)$ is the dimensionless solid temperature in the wave. As a result, the dimensionless system of equations describing steady-state wave has the form

$$\begin{aligned}
&\frac{d}{d\xi}\left(\kappa_T \frac{dy}{d\xi}\right) - \frac{dy}{d\xi} - \alpha_T(y-z) + y_b \tau_T w_T = 0,\\
&\frac{d}{d\xi}\left(\kappa_\Theta \frac{dz}{d\xi}\right) - (\omega - 1)\frac{dz}{d\xi} + \alpha_T(y-z) + y_b \tau_\Theta w_\Theta = 0,\\
&\frac{d}{d\xi}\left(\kappa_\eta \frac{d\eta_T}{d\xi}\right) - \frac{d\eta_T}{d\xi} - \alpha_\eta(\eta_T - \eta_\Theta) - \tau_T w_T = 0,
\end{aligned} \tag{6}$$

where η_Θ is found from the equation below

$$\alpha_n(\eta_T - \eta_\Theta) = \tau_\Theta w_\Theta. \tag{7}$$

In this case, from (5) and (7) it follows that

$$\eta_\Theta = \left(1 + \frac{\tau_\Theta}{\alpha_\eta} \exp\left(-\frac{z_m - z}{\gamma_\Theta}\right)\right)^{-1} \eta_T. \tag{8}$$

Equations (6) is supplemented with the boundary conditions: in the initial mixture ($\xi = -\infty$)

$$y = z = 0, \quad \eta_T = 1, \tag{9}$$

in combustion products ($\xi = \infty$)

$$\frac{dy}{d\xi} = \frac{dz}{d\xi} = 0, \quad \eta_T = 0. \tag{10}$$

Equation (6) allows a decrease in order. Having multiplied equations for $\eta_T$and η_Θ by y_b, we combine all equations of systems (6) and (7). The result is integrated from $-\infty$ to ξ. Taking into account conditions (9) with $\xi = -\infty$, we get the equation

$$\kappa_T \frac{dy}{d\xi} + \kappa_\Theta \frac{dz}{d\xi} + y_b \kappa_\eta \frac{d\eta_T}{d\xi} - y - (\omega - 1)z + y_b(1 - \eta_T) = 0. \tag{11}$$

Further, as $\eta_T = 0$ at $\xi = \infty$, from (6) and (10) it follows that $y(\infty) = z(\infty) = y_e$, and according to (11) we get

$$\omega y_e = y_b. \tag{12}$$

Then we assume that the equilibrium dimensionless temperature $y_e$is higher than the dimensionless temperature of the initial mixture, i.e. $y_e > 0$. Then as it follows from Eq. (12) $\omega > 0$. Since the obvious condition $u < \upsilon_m$ holds (the wave cannot propagate coflow faster than a combustible mixture), we have

$$u < \frac{v_m}{1+\sigma_m} = \frac{v_0}{1+\sigma_0}. \tag{13}$$

Let us introduce the following designations

$$I_T = \tau_T \int_{-\infty}^{\infty} w_T d\xi, \quad I_\Theta = \tau_\Theta \int_{-\infty}^{\infty} w_\Theta d\xi, \quad I_\alpha = \alpha_T \int_{-\infty}^{\infty} (y-z) d\xi$$

and use them for reducing a series of integral balances of system (6). The sum of the third equation of (6) and equation (7) are integrated from -∞ to ∞. As a result we get

$$I_T + I_\Theta = 1. \tag{14}$$

Then we integrate the first equation of (6) from -∞ to ∞ and obtain

$$y_e + I_\alpha = y_b I_T. \tag{15}$$

Taking into account Eq. (12), we write

$$y_b \left(I_T - \frac{1}{\omega} \right) = I_\alpha. \tag{16}$$

Using balance equation (14), we transform the latter equality into

$$y_b I_\Theta + I_\alpha = \frac{\omega - 1}{\omega} y_b. \tag{17}$$

A further analysis of the mathematical model involves the approximate calculation of integrals included in balance relationships. To this end, we ascertain the behavior of the solution of (6) beyond the narrow reaction zone. In this case, as the problem is invariant with respect to the shift (arbitrary constant after introduction of variable ξ), we assume that $y(0) = 1$, i.e., $\xi = 0$ is the point near which the reaction occurs. Inequalities (4) allow us to consider the functions of reactions (5) to be nonzero only in the vicinity of this point. Therefore, in the preheat zone ($\xi < 0$), the linearized systems (6) and (11) have the form

$$\begin{aligned} \frac{dy}{d\xi} &= \frac{1}{\kappa_{T,m}} y + \frac{\omega - 1}{\kappa_{T,m}} z - \frac{1}{\kappa_{T,m}} z', \\ \frac{dz}{d\xi} &= \frac{1}{\kappa_{\Theta,m}} z', \\ \frac{dz'}{d\xi} &= -\alpha_T y + \alpha_T z + \frac{\omega - 1}{\kappa_{\Theta,m}} z', \\ \frac{d\eta_T}{d\xi} &= \frac{1}{\kappa_{\eta,m}} (\eta_T - 1). \end{aligned} \tag{18}$$

To find the general solution, we find the eigen values and vectors of the matrix of the first three equations. The characteristic equation for eigen values has the form

$$\mu^3 - \left(\frac{1}{\kappa_{T,m}} + \frac{\omega - 1}{\kappa_{\Theta,m}}\right)\mu^2 + \frac{\omega - 1 - \alpha_T}{\kappa_{T,m}\kappa_{\Theta,m}}\mu + \frac{\omega\alpha_T}{\kappa_{T,m}\kappa_{\Theta,m}} = 0. \tag{19}$$

In this case, we use the fact that $\kappa_{T,m} + \kappa_{\Theta,m} = 1$. A simple analysis shows that all three roots of Eq. (19) are real and satisfy the inequalities

$$\mu_3 < 0 < \mu_1 < \mu_2. \tag{20}$$

Since $\mu_3 < 0$, the limited solution to the problem in the preheat zone has the form

$$y_- = a_1 e^{\mu_1\xi} + a_2 e^{\mu_2\xi}, \quad z_- = r_1 a_1 e^{\mu_1\xi} + r_2 a_2 e^{\mu_2\xi}, \tag{21}$$

where the components of the eigen vector r_i have the form

$$r_i = \frac{\kappa_{T,m}\mu_i - 1}{\omega - 1 - \kappa_{\Theta,m}\mu_i}.$$

Integrating the latter equation of (18), we get

$$(\eta_T)_- = 1 - (1 - \eta_T(0))e^{\xi/\kappa_{\eta,m}}. \tag{22}$$

Let us consider the zone of thermal relaxation ($\xi > 0$) In this case, we have the system

$$\begin{aligned}
\frac{dy}{d\xi} &= \frac{1}{\kappa_{T,m}}(y - y_b) + \frac{\omega - 1}{\kappa_{T,m}}z - \frac{1}{\kappa_{T,m}}z', \\
\frac{dz}{d\xi} &= \frac{1}{\kappa_{\Theta,m}}z', \\
\frac{dz'}{d\xi} &= -\alpha_T y + \alpha_T z + \frac{\omega - 1}{\kappa_{\Theta,m}}z', \\
\frac{d\eta_T}{d\xi} &= \frac{1}{\kappa_{\eta,m}}\eta_T,
\end{aligned} \tag{23}$$

the limited solution to which has the form

$$y_+ = y_e - a_3 e^{\mu_3\xi}, \quad z_+ = y_e - r_3 a_3 e^{\mu_3\xi}, \quad (\eta_T)_+ \equiv 0. \tag{24}$$

To determine the values a_i and $\eta_T(0)$, we assume the continuity of the extrapolated into reaction zone functions y, z and η_T taking into account that $y(0) = 1$ and $z(0) = z_m$:

$$a_1 + a_2 = y_e - a_3 = 1, \quad r_1 a_1 + r_2 a_2 = y_e - r_3 a_3 = z_m, \quad \eta_T(0) = 0.$$

The latter equality and representation (22) yield directly

$$(\eta_T)_- = 1 - e^{\xi/\kappa_{\eta,m}}. \tag{25}$$

For the z_m value and a_i coefficients the following formulas are valid

$$z_m = r_3 + (1 - r_3)y_e, \tag{26}$$

$$a_1 = \frac{r_2 - z_m}{r_2 - r_1}, \quad a_2 = \frac{z_m - r_1}{r_2 - r_1}, \quad a_3 = \frac{z_m - 1}{1 - r_3}. \tag{27}$$

Now, let us calculate the approximate value of I_α. According to (21) and (24), we get

$$I_\alpha = \alpha_T \int_{-\infty}^{0} (y_- - z_-)d\xi + \alpha_T \int_{0}^{\infty} (y_+ - z_+)d\xi = \alpha_T \sum_{i=1}^{3} \frac{(1 - r_i)a_i}{\mu_i}.$$

Substituting the values of coefficients a_i into this equation according to (27), we have

$$I_\alpha = b_1 z_m - b_2, \tag{28}$$

where

$$b_1 = \alpha_T \left(\frac{1 - r_1}{(r_1 - r_2)\mu_1} + \frac{1 - r_2}{(r_2 - r_1)\mu_2} + \frac{1}{\mu_3} \right),$$
$$b_2 = \alpha_T \left(\frac{(1 - r_1)r_2}{(r_1 - r_2)\mu_1} + \frac{(1 - r_2)r_1}{(r_2 - r_1)\mu_2} + \frac{1}{\mu_3} \right).$$

The approximate calculation of integrals I_T and I_Θ is based on the method of counter extrapolation. Dimensionless temperatures and concentrations extrapolated into the reaction zone are denoted by $\tilde{y}, \tilde{z}, \tilde{\eta}_T$ and $\tilde{\eta}_\Theta$. First, we assume that $\tilde{\eta}_T = \frac{1}{2}[(\eta_T)_- + (\eta_T)_+]$. As a result, the latter of equations (24) and (25) gives

$$\tilde{\eta}_T(\xi) = \frac{1}{2}(1 - e^{\xi/\kappa_{\eta,m}}). \tag{29}$$

Since $y(0) = 1$ and $\frac{dy}{d\xi}(0) = 0$ = 0 (the point of a maximum), then $\tilde{y}(\xi) = 1+ \frac{1}{2}y'_m\xi$, where $y'_m = \frac{dy_-}{d\xi}(0) = \mu_1 a_1 + \mu_2 a_2 > 0$. Let us denote $\varepsilon_T = \gamma_T/y'_m > 0$. Then according to (5) and (29) we get

$$I_T = \frac{\tau_T}{2} \int_{-\infty}^{0} (1 - e^{\xi/\kappa_{\eta,m}})e^{\xi/2\varepsilon_T} d\xi = \frac{2\tau_T\varepsilon_T^2}{\kappa_{\eta,m} + 2\varepsilon_T}. \tag{30}$$

Note that in the absence of the catalytic process ($m_\Theta = 0$), balance relationship (14) has the form $I_T = 1$, and (30) gives the equation for wave velocities upon filtration gas combustion in inert media. Similarly, for the dimensionless temperature of the layer, we have $\tilde{z}(\xi) = z_m + \frac{1}{2} z'_m \xi$, where $z'_m = \frac{dz_-}{d\xi}(0) + \frac{dz_+}{d\xi}(0)$, and according to (21) and (24) $z'_m = r_1\mu_1 a_1 + r_2\mu_2 a_2 - r_3\mu_3 a_3 > 0$. Let us denote $\varepsilon_\Theta = \gamma_\Theta / z'_m > 0$ and $q = \tau_\Theta/\alpha_\eta$. Then, from (5), (8), and (29) it follows that

$$I_\Theta = \frac{\tau_\Theta}{2} \int\limits_{-\infty}^{0} \frac{1 - e^{\xi/\kappa_{\eta,m}}}{1 + q e^{\xi/2\varepsilon_\Theta}} e^{\xi/2\varepsilon_\Theta} \, d\xi. \tag{31}$$

Substituting variables by $p = q e^{\xi/2\varepsilon_\Theta}$, instead of (31), we have

$$I_\Theta = \frac{\tau_\Theta \varepsilon_\Theta}{q^s} \int\limits_{0}^{q} \frac{q^{s-1} - p^{s-1}}{1 + p} \, dp,$$

where $s = 1 + 2\varepsilon_\Theta/\kappa_{\eta,m}$. The latter equality can be written as

$$I_\Theta = \tau_\Theta \varepsilon_\Theta \left(\frac{1}{q} \ln(1 + q) - I_0(q, s) \right), \tag{32}$$

where $I_0(s, q)$ is the integral of the Euler type having the form

$$I_0(s, q) = \frac{1}{q^s} \int\limits_{0}^{q} \frac{p^{s-1}}{1 + p} \, dp.$$

When $q \leq 1$, this integral can be represented as the following uniformly converging series

$$I_0(s, q) = \sum_{k=0}^{\infty} (-1)^k \frac{q^k}{s + k}.$$

With small q the uniform convergence of the series $\sum_{k=0}^{\infty} (-1)^k \frac{q^k}{s + k + 2}$ gives the representation

$$I_0(s, q) = \frac{1}{s} - \frac{q}{s + 1} + O(q^2).$$

As a result, to within the terms of second-order smallness, Eq. (32) acquires the form

$$I_\Theta = \tau_\Theta \varepsilon_\Theta \left(\frac{s - 1}{s} - \frac{s}{s + 1} q \right) = \frac{2\tau_\Theta \varepsilon_\Theta^2}{\kappa_{\eta,m} + 2\varepsilon_\Theta} - \frac{\tau_\Theta \varepsilon_\Theta (\kappa_{\eta,m} + 2\varepsilon_\Theta)}{2(\kappa_{\eta,m} + \varepsilon_\Theta)} q, \tag{33}$$

which corresponds to $\alpha_\eta \gg 1$, when the catalytic reaction mainly occurs on the catalyst surface without entering the pores. The mass exchange of the deficient component on the catalyst surface with the flow is, in this case, extremely strong. In particular, with $q = 0$ ($\alpha_\eta = \infty$) we get

$$I_\Theta = \frac{2\tau_\Theta \varepsilon_\Theta^2}{\kappa_{\eta,m} + 2\varepsilon_\Theta} \tag{34}$$

(comp. with (30)).

Thus, to find three unknown variables ω, z_m and T_m we use Eqs. (14), (15), and (26) where I_α, I_T and I_Θ are determined by equalities (28), (30), and (32) (or (33) or (34)) and the $y_e$value is set by Eq. (12). Note that the former of the above variables corresponds to the dimensional values

$$u = \frac{1-\omega}{\sigma_0 + 1 - \omega} v_0, \quad \Theta_m = T_0 + (T_m - T_0) z_m.$$

Although the given equations seem rather complex, they are the algebraic relationships whose numerical realization involving simple iteration processes is simple enough.

DISCUSSION

Figure 1 shows the calculated dependencies of hybrid and LVR-waves velocities in inert porous medium. In both cases, we take the same values of parameters except for $\alpha_{\eta,0} = m_\Theta = 0$ for the LVR-wave. In calculations, the following values are assumed $\rho_{T,0} = 0.5$, $\rho_\theta = 1500$ *kg/m*^{3}, $c_{pT} = 2500$ *J/kgK*, $c_{p\theta} = 1000$ *J/kgK*, $\lambda_T = 0.1$ *W/mK*, $\lambda_\theta = 1$ *W/mK*, $Le = 1$, $m = 0{,}5$, $\alpha_{T,0} = 10^4$ *W/m*^{2}*K*, $\alpha_{\eta,0} = 4$ *kg/m*^{2}*s*, $S = 3000$ *1/m*, $T_0 = 300$ *K*, $Q/c_{pT} = 1100$ *K*, $E_T/R = 2\cdot 10^4 K$, $E_\theta/R = 7500$ *K*, $k_T = 10^{12} 1/s$, $k_\theta = 5\cdot 10^6$ *1/s*. It is seen that for the hybrid wave, the $u(v)$ dependencies are U-shaped with a minimum which is typical of the LVR-wave. However, the difference in the velocities of hybrid and LVR-waves is most significant in the region of the low values of filtration velocity υ. In this case, the heterogeneous catalytic reaction considerably increases the velocity of hybrid wave which is opposite in direction to the reacting gas flow. At great filtration velocities, the velocities of hybrid and LVR waves are almost the same. The fact of realization of the catalytic, gas-phase, or hybrid waves with changing parameters of chemical reactions in Eq. (1) is quite obvious. However, the result of the parallel occurrence of catalytic and gas-phase reactions in terms of the hybrid wave velocity is not so clear. In Fig. 1, the realization of the parallel catalytic reaction mainly increases the wave velocity with respect to porous medium. However, from general considerations, we do not exclude the possibility of a hybrid wave with the negative interaction of two brutto-reactions.

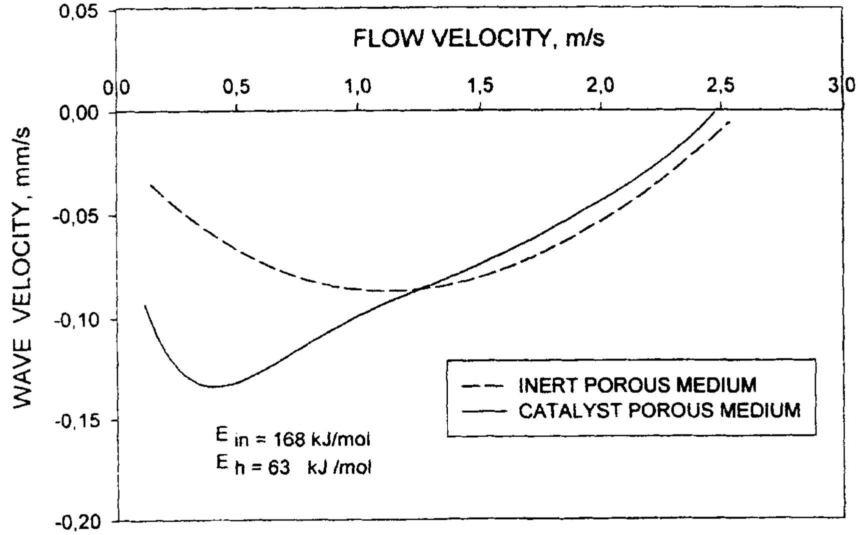

FIGURE 1 The dependence of wave velocity in inert (u_{in}) and catalytic active (u_h) porous media on filtration velocity of combustible gas. Combustible gas mixture is 65% H_2+air

Figure 2 shows the calculated dependencies of the maximum temperatures in gas, T_m, and solid phase, Θ_m. It is seen that at small υ, the maximum temperatures of gas and solid in the hybrid wave coincide. As the filtration velocity increases, the maximum temperatures of the phases in the wave front become different. Thus, the catalytic source of heat release is followed by the volumetric source determined by a competitive change in the ratio between the rates of the brutto-stages of chemical reactions. Indeed, if the characteristic diameter of pore channels is not too small, the LVR-wave structure displays the temperature peak in the gas, $T_{max} > \Theta_{max}$. This is caused, on the one hand, by excess enthalpy in the reacting gas due to its heating by a carcass in front of the chemical reaction zone, and on the other hand, by the ratio between the characteristic times of the gas-phase chemical reaction, t_c, and the time of internal thermal relaxation, t_h, when $t_h \gg t_c$ (Babkin, 1993). As a result, the temperature peak in the chemical reaction zone may serve as indicator of the existence of the gas-phase reaction. In low-disperse porous medium, the ratio between the times can be inverse. In this case, the thermal equilibrium is realized in the chemical reaction zone. For the given values of parameters for the LVR-wave, the difference $T_m - \Theta_m > 0$ is observed over the entire range of combustion wave existence with respect to υ.

Transition from the K-wave to LVR-wave regime with increasing filtration velocity confirms also the ratio between the integral fractions of heat release, I_T

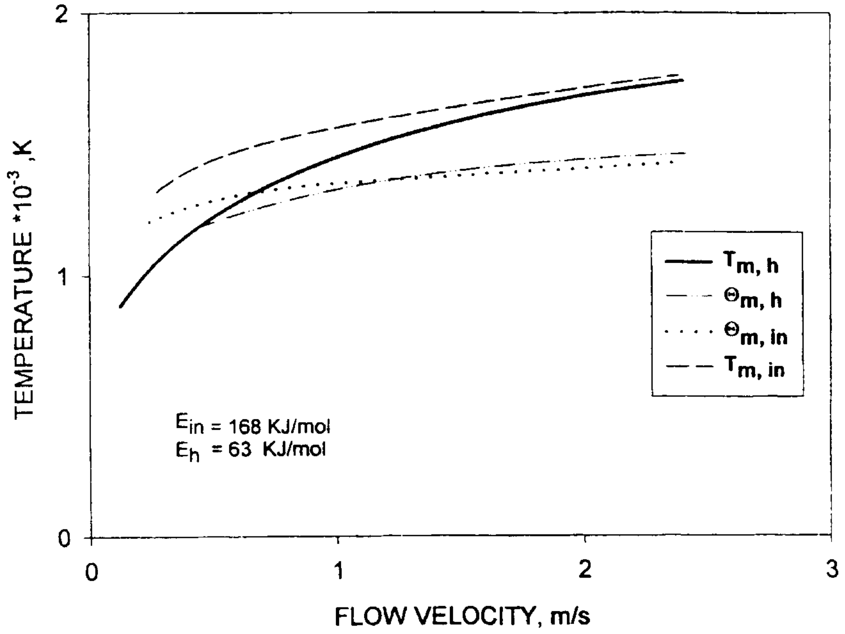

FIGURE 2 The dependencies of maximum gas and porous medium temperatures in the waves with homogeneous – heterogeneous (*h*) and homogeneous (*in*) reactions on filtration velocity of gas

and I_Θ, characterizing the contribution of volumetric and catalytic combustions to the total process of hybrid wave propagation (Fig. 3). Theoretically, T_m and Θ_m increase with increasing υ. At increased temperatures, the gas-phase reaction with a high activation energy becomes more competitive with respect to the catalytic one.

It may be assumed that the effects of interaction of two brutto-reactions substantially depend on the temperature nonequilibrium of phases $T \neq \Theta$. Usually, in the chemical reaction zone, $T_m/\Theta_m > 1$. This favours the passing of the gas-phase reaction. As mentioned above, the $T_m/\Theta_m > 1$ value is determined by the parameters of both chemical reaction and interphase heat transfer.

Another important fact is strong temperature gradients under which the chemical transformation occurs. Indeed, in both stabilized and travelling thermal waves there are conditions under which the catalytic reaction is preferable in the initial stage of chemical transformation and the gas-phase reaction occurs at higher temperatures in final stages. This transformation of the dominating reaction from the catalytic to gas-phase one during the process can be accompanied by a change of the regimes of heterogeneous reaction (kinetic, diffusional). This

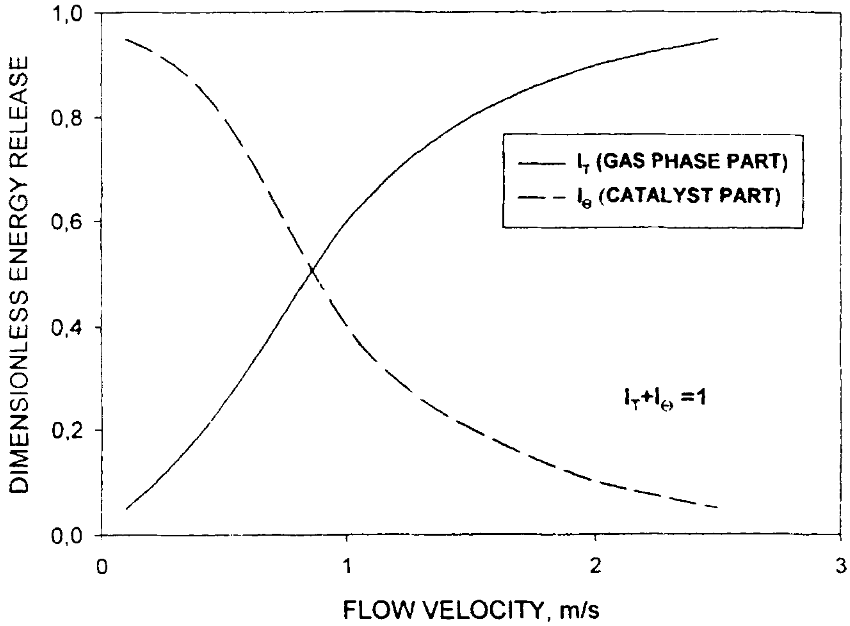

FIGURE 3 The dependencies of dimensionless parts of heat release in the volume (I_T) and on catalytic surface (I_Θ) on filtration velocity of combustible gas

aspect of the combined homogeneous-heterogeneous chemical transformation is highly essential in practice for catalytic combustors. The catalytic combustor is actually divided into two sections. In the first, low-temperature section the catalytic reaction dominates, and in the second, down flow high-temperature section, the gas-phase reaction runs. The catalyst is thus protected from high-temperature deactivation (Kesselring, 1986).

We should determine another peculiarity of the hybrid wave. Additional with respect to the wave in the inert porous medium, catalytic reaction in the hybrid wave, leads at low υ to an increase in wave velocity and thus, to a decrease in the maximum phase temperatures. Thus, a change in the type of the dominating reaction at constant mixture composition and filtration velocity causes a change in the thermal state of a combustion wave. This fact related to wave travelling may be useful in technological aspect, e.g., for the problem of decreasing NO_x emission. A similar effect but of a different origin was observed by Schlegel et al., (1996). Experiments on methane combustion were performed in a tabular adiabatic flow reactor with catalytically active or inactive honeycomb structures. In order to study the effect of catalytic combustion on NO_x formation, the fraction of fuel converted within the catalytic was varied within the range of 0% (corresponding to noncatalytic combustion) to 100%. It has been shown the higher this fraction, the lower are the NO_x emission.

CONCLUDING REMARKS

This paper develops a qualitative theory of a hybrid wave reflecting the main regularities of the process and allowing one to readily obtain the velocity, structural and other wave characteristics over relatively wide ranges of parameters.

This paper takes into account two sources of heat release localized in gas and on the surface of a porous medium. In this regard, the model is a generalization of the model of gas-phase combustion in inert porous medium (LVR-waves) and heterogeneous-catalytic combustion in quiescent catalyst layer (K-waves). The model makes it possible to analyze the effects of a change in the dominating reaction path upon chemical transformation (spatial-time changes) with changing reactivity of porous medium and gas and changing filtration velocity and other parameters. These aspects are urgent for design catalytic combustors, solving the problems of fire and explosion safety of chemical reactors, developing the general theory of filtration combustion.

The present paper considers the problems of a steady-state hybrid wave. In prospect it is of interest also the nonstationary phenomena such as the dynamics of initiation of high-temperature hybrid waves by low-temperature thermal sources, transient processes upon spatial-time changes of system parameters. Of interest are the problems of autostabilization near and far from the boundaries of porous media in the cases of tubular and spherical symmetries of waves. Finally, we need the systematic experimental data to compare theory with experiment. We are going to obtained such data in the nearest future.

NOMENCLATURE

T, Θ	gas and porous medium temperature
S	specific surface area
Q	heat release of chemical reaction
W	rate of chemical reaction
D	diffusion coefficient of the gas
E	activation energy

R	universal gas constant
k	pre-exponential factor
c	specific heat capacity
v	gas velocity
m	porosity
u	wave velocity
ρ	density
λ	thermal conductivity
$\alpha_{T,0}$; $\alpha_{\eta,0}$	coefficients of heat and mass transfer
η	mole fraction of deficient component

Subscripts

T	gas phase
Θ	solid phase
0	initial condition
m	maximum value

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