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THERMAL RECOVERY OF SORBENTS BY FILTRATION COMBUSTION

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Thermal Recovery of Sorbents by Filtration Combustion

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Abstract: We have investigated theoretically and experimentally the process of filtration combustion with hydrocarbon desorption from a porous skeleton realized, in particular, in heat cleaning of porous media out of residues of organic impurities. Two basic configurations were considered: fixed and moving beds. The problem of the combustion wave propagation in a system with three phases—gaseous, liquid, and inert solid—has been solved analytically. The specific features of this process as compared to the conventional filtration combustion of gases have been revealed. The dependences of the basic characteristics of the waves on the content of methane in the gas mixture as well as of absorbed oil and water in a porous medium have been obtained. A comparison with the experimental data has been made. Recommendations for optimizing the operation of decontamination plants on the basis of the process considered are given.

Keywords: Decontamination, Desorption, Filtration combustion, Porous media, Recovering technology, Sorbents, Thermal wave

INTRODUCTION

Nowadays, problems connected with controlling hazardous pollutant emissions and industrial waste recycling are becoming increasingly urgent. An important class of such problems is safe decontamination

of adsorbents and other porous media containing the phase of liquid hydrocarbons or other combustible substances bound on their surface, in particular, the problem of regeneration of zeolite sorbents from residues of transformer or machine oil. The same problem exists, e.g., in choosing efficient and clean recovery technology of diesel oil and naphtha contaminated soils.

The conventional thermovacuum method of recovery of the sorption properties of zeolite does not permit getting rid of solid-phase contaminants. Attempts to burn off organic impurities were unsuccessful because of the release into the atmosphere of large amounts of unoxidized organic matter.

The regeneration of sorbents in the filtration combustion (FC) wave is a promising alternative method, since it makes it possible to fairly completely burn evaporated organic matter and use the heat of its combustion to maintain the process, which considerably reduces expenditures of energy.

Filtration combustion with oxidizer being filtered through porous media is proved to be useful to a variety of applications, ranging from waste incineration, catalyst regeneration, agglomeration of ores, smoldering and high-temperature synthesis of solid materials to fuel reforming, in situ combustion for the recovery of oil and coal gasification.

The advantages of combustion in porous media, such as low NO_x, CO emissions, high energy efficiency, power turndown ratio and compactness can be fully implemented in such technologies. Organic fuel desorption in the preheating zone of the combustion wave gives the process interesting physical peculiarity—wave propagation velocity couples with additional fuel generation rate—which require theoretical and experimental studies and leads to specific effects, as it shown below.

Filtration combustion with evaporation of additional fuel from the condensed phase is a little-studied process (see, e.g., review by Babkin (1993)), which has good prospects for industrial use. Works in this field are mainly focused on the investigation of the combustion of aerosols (Martynenko et al., 1993; Kaplan and Hall, 1995; Tseng and Howell, 1995) and liquid, in particular, monofuel (Kakutkina et al., 1995; Koshkin et al., 1995). In recent work by Koshkin et al. (1995) the FC of a monofuel—hydrazine—was investigated and dynamic characteristics of the combustion wave were obtained.

For instance, a liquid fueled porous ceramic burner was reported by Kaplan and Hall (1995) with stable complete combustion achieved for heptane at equivalence ratios 0.57–0.67. Very low emissions of CO (3–7 ppm), NO_x (15–20 ppm) were measured. In experiments conducted by Itaya et al. (1995) kerosene and air was supplied to ceramic porous burner to study emissions and blowoff limit in dependence of equivalence ratio. Heptane fuel was used by Tseng and Howell (1995, 1996) to measure emissions of NO_x and CO, temperature profiles, flame speeds and

extinction limits. Hall and Petroutka (1995) tested a methanol fueled burner in which fuel was directly impringed on upstream surface of porous ceramic burner due to poor vaporization of methanol.

Theoretical considerations of liquid fuel combustion in porous media burners are generally assume that atomization of the fuel takes place upstream of the burner inlet and the mixture of fuel droplets and air then enters the porous body (see, e.g., Haack (1993)). Further improvements were introduced by Tseng and Howell (1994) and Tseng (1995) by accounting for effects of droplet vaporization in the entrance region of a porous medium burner.

In the paper by Pedersen-Mjaanes et al. (2005) experimental study on filtration combustion of rich fuel-air mixtures of methanol, octane and automotive-grade petrol inside inert porous media was performed to examine the suitability of the concept for hydrogen production. It was noted that the high conversion efficiencies, quick startup times and compact size make filtration combustion burner suitable for consideration as part of a reformer in a fuel cell powered automobile.

Results on filtration combustion of rich liquid fuels (up to kerosene) with particular emphasis on syngas production applications are presented in recent reviews by Zhdanok (2003) and Futko and Zhdanok (2004).

The possibility of FC control with participation of liquid (in absorbed phase) are poorly studied (see, e.g., Rabinovich and Gurevich, 1995) and can be considered as actual task.

In the present paper, theoretical and experimental studies of the filtration combustion of gases at hydrocarbon desorption from a porous medium have been made. The basic features of the thermal regime and dynamics of FC waves have been revealed. The influence of water additives on the heat-wave characteristics has been analyzed. Recommendations on the realization of the practically important process—removal of organic contaminants from a zeolite sorbent—have been given.

Concept of Thermal Recovery of Sorbents by Filtration Combustion

Adsorption involves the physical adhesion of molecules to adsorbent surface. During a typical adsorption process, organic molecules collect onto adsorbent surfaces as the gas stream passes through the adsorbent bed. Eventually, the bed reaches its sorbtion capacity and must be regenerated or replaced with new sorbent.

Typical thermal regeneration process consists of passing preheated gas through the sorbent bed. The contaminated regeneration gas is then vented to atmosphere or treated in another process. If sorbent cannot be regenerated, it must be disposed, often as a hazardous waste.
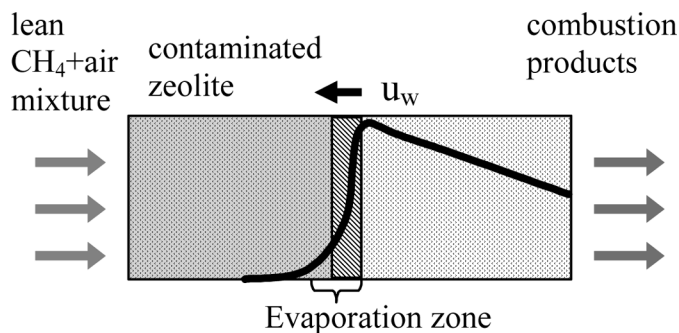
Figure 1.   Scheme of the zeolite cleaning in the counter-running FC wave regime.

To reduce the costs of sorbents regeneration filtration combustion can be applied, when the high temperature combustion wave travels relative to the packed bed. The main advantages of the technology are: hazardous air pollutants are oxidized to nonhazardous chemicals, such as carbon dioxide and water; no contaminated liquids or residues are produced and operating costs are relatively low. Most adsorbed organics can be oxidized, however, the process must be controlled to prevent formation of products of incomplete combustion—in particular, enough oxygen must be present.

In the case of a cocurrent combustion wave, organic vapors freely go out into the atmosphere, which requires inclusion in the system of an additional device for waste gas cleaning and increases the process cost. In the counter-current combustion wave, adsorbed organics is vaporized by reaction zone forming volatile organic compounds (VOCs) that subsequently moving downstream with a gas flow and finally destroyed in a reaction zone, serving as an additional fuel. Figure 1 illustrates this concept.

Moreover, the technology is utilizing very attractive intrinsic features of filtration combustion processes: low NO_x generation and high energy efficiency due to internal heat recuperation.

EXPERIMENT

Two major setup configurations were considered based on transient filtration combustion and stabilized one respectively.

The first is unconfined counter-flow combustion wave moving in a fixed bed of contaminated zeolite, representing transient filtration combustion and forming the basis of this type of sorbents recovering technologies.

The second experimental setup is based on filtration combustion stabilized by moving bed of zeolite particles and was proposed to overcome
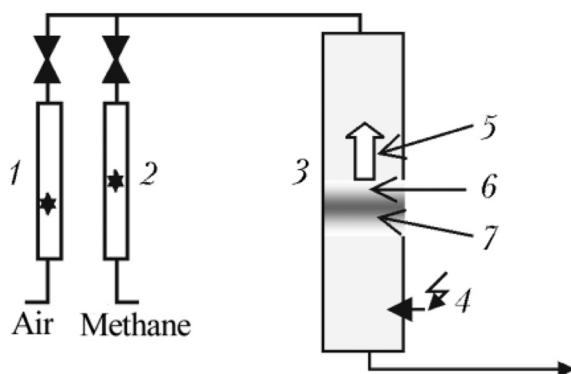
Figure 2. Scheme of the zeolite cleaner in a fixed bed configuration: 1, 2) rotameters with regulating valves; 3) reactor; 4) spark ignition; 5) direction of combustion-front movement; 6) oil evaporation front; 7) combustion zone.

some drawbacks of the first one (particularly, overheating of zeolite). The approach is based on spatial separation of VOCs oxidation zone and treated zeolite material.

Fixed Bed

The experimental facility designed to maintain and measure temperature time profiles of upstream filtration combustion waves in a packed bed of contaminated zeolite particles is shown schematically in Figure 2. Quartz cylinder of 0.07 m in diameter and 0.4 m height was used as reactor.

The reactor fill was formed from three alternating layers: Al_2O_3 balls (where the combustion wave was initiated and formed) — zeolite—Al_2O_3 balls. The fill porosity was $\varepsilon = 0.4$. Combustion was initiated by a spark device in the Al_2O_3 balls with a stoichiometric composition of the combustible mixture. A quartz capillary, into which a movable thermocouple was introduced, was placed inside the cylinder.

The combustion-front velocity was determined visually by means of a ruler and a timing device. The experimental results are given in Table 1. The mass fractions of oil and water (of the filling mass of zeolite) were estimated, respectively, as $\chi_m \cong 0.1$ and $\psi \cong 0.054$.

In experiment 3, despite the much smaller discharge of methane than in the other series of measurements, the wave-front velocity and, consequently, the capacity of the cleaning process are much higher. Note that in experiments 1, 2, and 4 the combustion wave experienced pulsing movement. When the combustion front reached the nonannealed layer of zeolite it began to die out and slow down, the wave-front temperature

Table 1. Experimental data for fixed bed (for an air flow rate of 1000 liters/h)

Exp. number	Methane flow rate, liters/h	Φ	u_w, m/sec	$T_{s,m}$, K
1	75	0.73	$-2.8 \cdot 10^{-5}$	1300
2	50	0.45	$-3.3 \cdot 10^{-5}$	1380
3	23	0.18	$-5.0 \cdot 10^{-5}$	1400
4	80	0.75	$-2.8 \cdot 10^{-5}$	1220

thereby remained fairly high (>1100 K). But when the layer was annealed, the wave front flared up again and its propagation velocity increased. When the wave reached the nonannealed zeolite layer, the cycle was repeated.

Since gaseous combustion products completely oxidize, to provide a possibly lower temperature in the wave front (to save zeolite from destruction and corrosion), it is expedient to wet the porous medium with water. Optimization of the system parameters can make the process relatively cheap. This method can also be used to clean other sorbents (catalyses) out of organic contaminants.

Moving Bed

One of the major drawbacks of the experimental configuration considered is rather high temperatures of porous media ($T_s = 900 - 1100°C$) that in some cases may lead to zeolite particles deactivation, sintering and destruction. To decrease working temperatures dramatically another concept of the installation was proposed and tested (Fig. 3). Main idea is to organize VOC oxidation outside zeolite material but in a close vicinity of evaporation zone. Process stabilization in this scheme is achieved by moving bed of particulates: contaminated zeolite particles are inserted from above and annealed ones released from the bottom. The rate of particles supply can be optimized to obtain desired quality of zeolite cleaning and, simultaneously, very low concentration of volatiles in exhaust gases.

Another favorite feature of this setup is enhanced combustion products heat utilization achieved by imbedded counter-flow heat exchanger (Fig. 3). The reactor is imbedded into the counter flow exchanger and consists of two concentric quartz tubes filled with a uniform packed bed (porosity $\varepsilon \cong 0.4$) of alumina pellets (5 mm diameter). An inner ceramic tube (40 mm diameter) is filled by contaminated zeolite particles from above and annealed zeolite particles are allowed to drop from reactor bottom at a prescribed rate. The inner tube was made from two parts (25 and 80 mm respectively), connected by metallic mesh (length 50 mm), placed at 20 mm from reactor bottom. Forced suction ventilation is used for air supply.
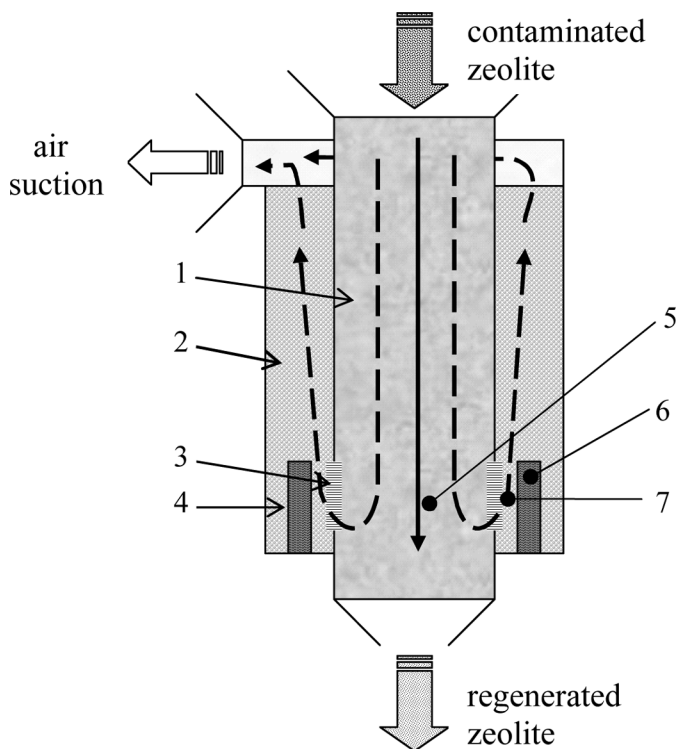
Figure 3. Scheme of the zeolite cleaner in a moving bed configuration: 1) zeolite, 2) inert porous media Al_2O_3, 3) internal mesh, 4) electrical heater 5) thermocouple TC1, 6) thermocouple TC2, 7) thermocouple TC3.

Air flow directs VOCs formed in a vaporization zone (in an inner tube) to the combustion zone near metallic mesh (in an outer tube). Combustion products flow through the insulated outer tube (70 mm diameter) transferring heat to the fresh zeolite particles. This counter-flow arrangement has a heat exchange efficiency of approximately 40%. An electric heater is placed near metallic mesh and used to initiate and maintain (if needed) combustion.

Typical temperature histories of the cleaning process as written from three thermocouples (TC1-TC3, Fig. 3) are collected in the Table 2 and presented in Figure 4. In the case the power of electric heater supply was 560 W. Zeolite supply was performed in discrete portions in definite moments of time (shown by figures in the Table 2 and Fig. 4). Average rate of contaminated zeolite particles supply was approximately $4.7 \cdot 10^{-6}$ m^3/c and was chosen to obtain complete desorption of organics from untreated material and, simultaneously, to conserve zeolite so that its temperature was not exceed $600°C$.

Table 2. Experimental data for moving bed of zeolite particles

| Time, min	Zeolite temperature, °C (TC1)	Inert Al_2O_3 temperature, °C (TC2)	Electric heater temperature, °C (TC3)	Contaminated zeolite supply:
0	10	18	20	
10	30	246	486	
20	160	447	557	
30	256	500	637	
40	380	562	678	
50	477	603	704	
60	543	636	724	
70	590	658	737	
80	622	683	755	
90	652	701	765	
100	673	713	773	
108	665	715	776	(1) Start: 1 cm zeolite layer is inserted (and withdrawn from below)
118	463	705	767	(2) withdrawal of 3 cm zeolite layer
123	515	720	780	(3) withdrawal of 1 cm zeolite layer
124	550	726	788	
127	484	730	790	
130	560	740	799	
135	480	749	806	(4) withdrawal of 3 cm zeolite layer
139	564	758	811	(5) withdrawal of 1.5 cm zeolite layer
141	517	758	812	
142	557	761	814	
144	497	761	814	(6) withdrawal of 1.5 cm zeolite layer
147	558	766	818	
149	463	762	817	(7) withdrawal of 3 cm zeolite layer
153	553	767	820	
155	478	763	818	(8) withdrawal of 3 cm zeolite layer
158	552	768	820	
162	600	776	829	
164	483	774	826	(9) withdrawal of 3 cm zeolite layer
171	604	781	830	
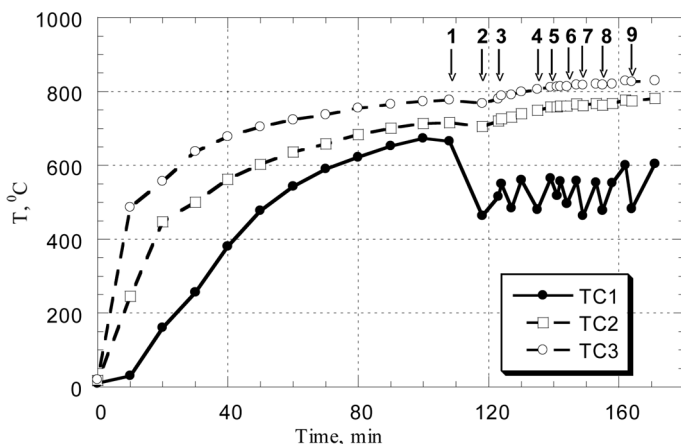
Figure 4. Temporal temperature evolution of treated zeolite particles (TC1), inert alumina layer (TC2) and electrical heater (TC3). Figures correspond to the data in Table 2.

An electric heater can be switched off completely after combustion process initiation given sufficient external thermal insulation. Furthermore, this device can be connected (or imbedded into) to the additional unit (radiation burner or boiler) to utilize heat, deliberating in the self-sustained combustion process.

THEORETICAL ANALYSIS

To elucidate the temperature and dynamic features of this kind of filtration combustion and choose an optimum regime of the process, a theoretical study has been performed.

The model chosen is a combustion wave moving at a constant speed in a porous bed. The reaction front is assumed to be small relative to the width of the preheated zone. The thermal conductivity of the porous media is considered to be large relative to that of the gas mixture.

The one-dimensional equations describing the FC wave propagation in a porous medium with a liquid phase, neglecting diffusion and thermal conductivity of the gas, can be written as:

$$\rho_g \frac{\partial T_g}{\partial t} + c_{pg} G \frac{\partial T_g}{\partial x} = \varepsilon \rho_g H_1 K Y_1 \exp(-E/(RT_g)) + \frac{\partial}{\partial t} Q_2 + \frac{\partial}{\partial t} Q_3 + \alpha_v (T_s - T_g) \tag{1}$$

$$(1 - \varepsilon) c_s \rho_s \frac{\partial T_s}{\partial t} = (1 - \varepsilon) \frac{\partial}{\partial x} \lambda_s \frac{\partial T_s}{\partial x} - \alpha_v (T_s - T_g) \tag{2}$$

$$G\frac{\partial Y_i}{\partial x} = \varepsilon\rho_g K Y_i \exp(-E/(RT_g)) \quad i = 1, 2 \tag{3}$$

Further details about general assumptions used can be found, e.g., in Zhdanok et al. (1995) and Foutko et al. (1997). Here we apply the equations for filtration combustion of gases (FCG) to which we added source terms of the form $\partial Q_k/\partial t, k = 2, 3$, that are due to the presence of the liquid phase and correspond to the heat released in oil vapor combustion (Q_2) or the heat absorbed in water evaporation (Q_3). Since the chief aim of this model is to determine the summed energy balance in the wave, the additional sources are assigned to the gas phase. The mixture enters the system with a constant mass flow rate $G = \varepsilon\rho_g u_g$.

We assume that with the approach of the wave combustion front all the liquid contained in the porous medium is evaporated and combustion proceeds in the gas-phase reactions. Such a simplified representation of the process, in particular, excludes the possibility of cycling: evaporation→condensation→evaporation, and so on. It is also assumed that the water present in the porous medium always evaporates completely and does not participate in the reactions (is chemically inert).

Similarly to recent works (Zhdanok et al., 1995; Foutko et al., 1997) in Eqs. (1)–(3) the transition to a coordinate system moving together with the wave front at a constant velocity u_w has been made, and using the boundary conditions

$$
\begin{aligned}
&T_s|_{-\infty} = T_g|_{-\infty} = T_o, &&\partial T_s/\partial x|_{\pm\infty} = \partial T_g/\partial x|_{\pm\infty} = 0 \\
&T_g|_{-0} = T_{g,i}, &&T_g|_{+0} - T_g|_{-0} = \Delta\tilde{T}_a \\
&T_s|_{-0} = T_s|_{+0}, &&\partial T_s/\partial x|_{-0} = \partial T_s/\partial x|_{+0}
\end{aligned}
\tag{4}
$$

and integrating (1)–(3) with respect to x from $-\infty$ to $+\infty$, we can obtain the FC wave balance equation:

$$T_{s,m} = T_0 + \frac{\Delta T_{1a} + |u|\Delta T_{2a}}{1 - u} \tag{5}$$

Here $\Delta T_{1a} = H_1/c_{pg}$, $|u|\Delta T_{2a}$ is the adiabatic temperature rise of the methane-air mixture and oil vapors, respectively; $u = u_w/u_{th}$ is the dimensionless velocity of wave-front propagation, and $u_{th} = c_{pg}G/[(1 - \varepsilon)c_s\rho_s]$ is the heat wave velocity.

It should be emphasized that the balance equation (5) includes the resulting adiabatic heat built-up of the system $\Delta\tilde{T}_a(u) = \Delta T_{1a} + |u|\Delta T_{2a}$, which, unlike the FCG wave (see Zhdanok et al. 1995), is an explicit function of the front velocity, the liquid-phase combustion heat, and other parameters of the porous medium.

An important element of the model is the account of the oxygen consumption in the system. Depending on the presence of an oxidizer,

complete burn-out (CB) and incomplete burn-out (IB) of organic matter is possible. In the latter case, unwanted release of hydrocarbons from the system into the atmosphere is possible. Introducing the mass flow of oil vapor G_2

$$G_2 \equiv |u_w|\rho_s(1-\varepsilon)\chi = \frac{|u|c_{pg}G\chi}{c_s} \tag{6}$$

We give the condition of oxygen deficiency for oxidation of oil entering the wave front with the rate of flow G_2 in the form

$$\frac{G_2}{C_2}\left(\frac{F}{A}\right)_{2st}^{-1} > \frac{G(1-\Phi)}{v_n\rho_{g,o}} \tag{7}$$

Here $(F/A)_{st}$ is the stoichiometric fuel to air ratio, Φ is the equivalence ratio for the methane-air mixture, C_2 is the molar mass of condensed organic matter, and v_n is the molar volume of gas under normal conditions.

Inequality (7) can be rewritten as the condition of excess over some critical flow of oil vapor G_2.

$$G_2 > G_2^* \qquad G_2^* = \frac{GC_2(1-\Phi)}{v_n\rho_{g,o}}\left(\frac{F}{A}\right)_{2st} \tag{8}$$

Relation (8) defines the boundary between the CB and IB regimes for the FC wave. For practical estimations, it is convenient to represent the critical condition (8) in the equivalent form

$$|u_w| > |u_w^*| \qquad |u_w^*| = \frac{GC_2(1-\Phi)}{v_n\rho_{g,o}\rho_s(1-\varepsilon)\chi}\left(\frac{F}{A}\right)_{2st} \tag{9}$$

or

$$|u| > |u^*| \qquad |u^*| = \frac{c_sC_2(1-\Phi)}{v_n\rho_{g,o}c_{pg}\chi_m}\left(\frac{F}{A}\right)_{2st} \tag{10}$$

Let us introduce the degree of burn-out of condensed organic matter χ':

$$\chi' \equiv \frac{G_2^*}{|u_w|\rho_s(1-\varepsilon)\chi} \tag{11}$$

Thus, to the CB regime there corresponds $\chi' = 1$, and in the case of incomplete burn-out $\chi' < 1$. Accordingly, the total heat build-up, $\Delta\widetilde{T}_a$ a will be determined as

$$\Delta\widetilde{T}_a(u) \cong \Delta T_{1a} + \frac{|u|}{c_s}(\chi H_2 - \psi H_3) \tag{12}$$

in the CB regime ($G_2 \leq G_2^*$) and

$$\Delta\widetilde{T}_a(u) \cong \Delta T_{1a} + \frac{C_2 H_2 (1 - \Phi)}{v_n \rho_{g,o} c_{pg}} \left(\frac{F}{A}\right)_{2st} - |u| \frac{\psi H_3}{c_s} \qquad (13)$$

in the IB regime ($G_2 > G_2^*$)

From the point of view of this model and the above assumption for certain characteristics of the FC wave one can use the known solutions for filtration combustion waves of gases. In particular, we shall use the analytical expression from Dobrego and Zhdanok (1998) obtained in the approximation of a narrow reaction zone:

$$T_{s,m} \cong \frac{\Delta\widetilde{T}_a}{1 + a} + \frac{E}{R \ln \frac{\varepsilon c_{pg} \rho_{g,o} T_o K (1 + a)}{\alpha_v \Delta\widetilde{T}_a}} \qquad (14)$$

where $a = (1 - \varepsilon)\lambda_s \alpha_v / (c_{pg} G)^2$ is the dimensionless parameter.

RESULTS AND DISCUSSION

To calculate the maximum temperature and velocity of the FC wave front, the system of equations (5), (12)–(14) was solved for the following values of parameters: $\varepsilon = 0.49$, $c_s = 794 \, \text{J/(kg·K)}$, $\rho_s = 3.15 \cdot 10^3 \, \text{kg/m}^3$, $c_{pg} = 1.3 \cdot 10^3 \, \text{K/(kg·K)}$, $\lambda_{s,o} = 1.0 \, \text{W/(m·K)}$, $d = 6 \, \text{mm}$, $(F/A)_{1st} = 0.11$, $E = 1.3 \cdot 10^5 \, \text{J/(mole·K)}$, and $K = 2.6 \cdot 10^8 \, \text{c}^{-1}$ (according to Yoshizawa et al., 1988). The heat conductivity and interphase heat-transfer coefficients were determined in accordance with Wakao et al. (1979):

$$\lambda_s = \lambda_{s,o} + \frac{32 \varepsilon \sigma d}{9(1 - \varepsilon)} T_s^3 \qquad (15)$$

$$\alpha_v = \frac{\pi \lambda_g}{d^2} (2 + 1.1 Re^{0.6} Pr^{1/3}) \qquad (16)$$

assuming that in the reaction zone $T_s \cong T_{s,m}$.

The data for ΔT_{1a} used in the calculations are given in Table 3. It is considered that machine oil (in the liquid phase) consists of light fractions and is mainly represented by tetradecane ($C_{14}H_{30}$), for which the brutto-reaction of complete oxidation is of the form

$$C_{14}H_{30} + 21.5 O_2 + 80.84 N_2 \rightarrow 15 H_2O + 14 CO_2 + 80.84 N_2 \qquad (17)$$

It is also assumed that the global kinetic combustion coefficients of oil vapor are close to the respective data of the methane-air mixture and in the first approximation they can be considered to be equal. To model

the tetradecane oxidation, we used the following values of the parameters: $(F/A)_{2st} = 1.0 \cdot 10^{-2}$; $H_2 = 5.1 \cdot 10^7\,J/kg$; $C_2 = 198 \cdot 10^{-3}\,kg/mole$. The water evaporation heat (taking into account the heating from ambient temperature to 100°C) was estimated as $H_3 \cong 2.55 \cdot 10^6\,J/kg$. The heat of oil desorption from zeolite H_{2d} was neglected ($H_{2d} \ll H_2$), since according to the estimates from Belinskii and Fursenko (1992): $H_{2d}/H_2 \cong 0.024$.

Let us analyze the influence of the most important parameters of the process—methane, oil, and water concentrations—on the FC wave characteristics.

Dependence on Methane Content

Figure 5 shows the calculated dependences of the wave-front velocity u_w, the maximum temperature of the porous skeleton $T_{s,m}$, and the degree of burn-out χ' on the gas flow for various concentrations of methane and oil.

Consider the behavior of the system with decreasing gas flow beginning with the moment the wave goes from the cocurrent regime
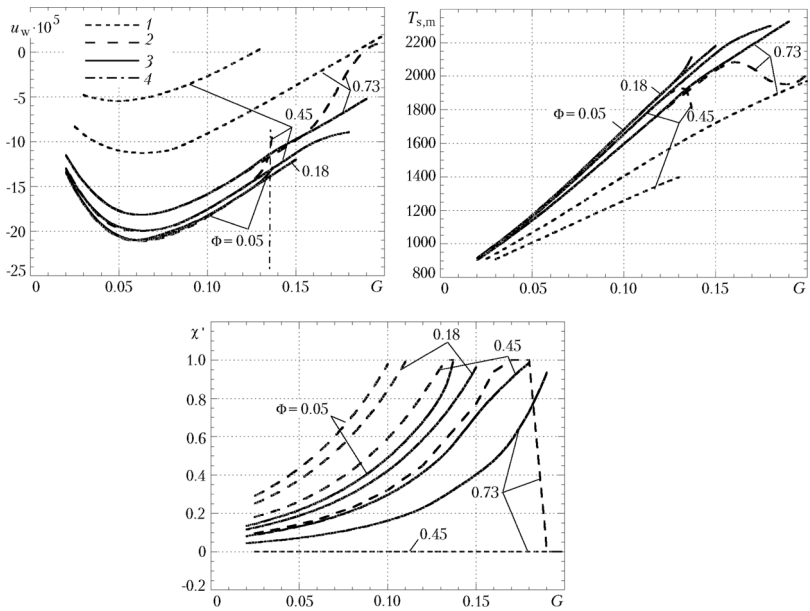

Figure 5. Wave-front velocity u_w, skeleton maximum temperature $T_{s,m}$, and degree of burn-out χ' as a function of the gas flow rate for various concentrations of methane and the mass fraction of oil: 1) $\chi = 0$; 2) 0.05; 3) 0.1; 4) transition point of CB to IB for $\chi = 0$. u_w, m/sec; $T_{s,m}$, K; G, kg/(m²·sec).

of propagation to the counter propagation one. It is seen from Figure 5 that as oil vapor enters the reaction zone, the front velocity and the maximum temperature of the skeleton sharply increase, which shows up as a "kink" on the $u_w(G)$ curve distorting the U-shaped front-velocity-flow curve characteristic of FCG waves (see, e.g., Babkin, 1993). Such "kinks" and their respective nonmonotonic regions (i.e., regions where the maximum temperature of the skeleton decreases with increasing flow) of the $T_{s,m}(G)$ dependence are distinguishing attributes of the filtration waves with evaporation and combustion of the liquid phase (compared to the FCG waves).

In the system under investigation, considerably larger values of $|u_w|$ and $T_{s,m}$ compared to the FCG waves with the same concentration of methane in the mixture (see, e.g., the family of curves for $\Phi = 0.73$ in Fig. 5) are attained. The above properties of the system explain the experimentally observed effects of extinction and deceleration of the wave front upon the warming-up of the next layer of zeolite (since oil and water evaporation requires additional expenditures of energy), as well as of "acceleration" and "burning-up" of the front as oil vapor enters the reaction zone.

Complete oxidation of complex organic matter requires large consumptions of oxygen (≈ 20 moles per tetradecane mole); therefore, the critical condition (7)–(10) for the beginning of the IB regime is reached fairly fast. As a result, the degree of burn-out χ' has a maximum and rapidly decreases with decreasing gas flow (see Fig. 5). As a consequence of this, the regime of complete burn-out takes place only in a rather narrow range of parameters. The value of the gas flow corresponding to the change-over from the CB to the IB regime strongly depends on the methane concentration and shifts towards smaller values with decreasing Φ.

In practice, even in the regime of considerably "incomplete" burn-out there will be no marked releases of non-oxidized organic matter from the system, since the gas phase will pass through the wave-annealed region of zeolite with recovered sorption properties and will be reabsorbed with a high probability. From the ecological point of view, such a "safety factor" of the process under consideration is an additional advantage of this cleaning technology.

It is interesting to note that in the IB regime (on the side of "small" expenditures) the shape of the u_w, $T_{s,m}(G)$ curves is similar to the analogous curves for the filtration combustion of gases, which is due to the fulfillment of the condition $\Delta \widetilde{T}_a(u) \cong$ const. In this case, an increase in the mass content of oil χ in a porous medium does not affect the wave characteristics (see Fig. 5). But the portion of the sharp "kink" of the $u_w(G)$ curve is due to the greatly varying function of the overall adiabatic heating of the system ($\Delta \widetilde{T}_a(u) \neq$ const).

Dependence on Condensed Oil Concentration

The features of the behavior of the FC waves in the regime of complete burn-out can be considered in more detail by "extending" the CB existence zone to a wider region of expenditures, which is achieved by decreasing the oil content χ in the system and/or increasing the methane concentration (see Fig. 6). It is seen from Figure 6 that a specific feature of the $T_{s,m}(G)$ curve (distinguishing this type of filtration combustion from FCG) is the nonmonotony of the $T_{s,m}(G)$ curve which shows up as the fact that the skeleton temperature may increase with decreasing gas flow. It is important to note the nontrivial fact that this portion of the growth of the $T_{s,m}(G)$ dependence coincides with the portion of the "kink" of the $u_w(G)$ curve and corresponds to the region of the CB regime, which can be used in practice to choose optimum (in terms of purity of sorbent cleaning) operating conditions of the system. Taking into account that on the limit of the appearance of such a nonmonotony the function $T_{s,m}(G) \cong$ const (see, e.g., the data for $\Phi = 0.45$, Fig. 6) and varying (5), we obtain the following condition needed for the maximum in the $T_{s,m}(G)$ to exist:
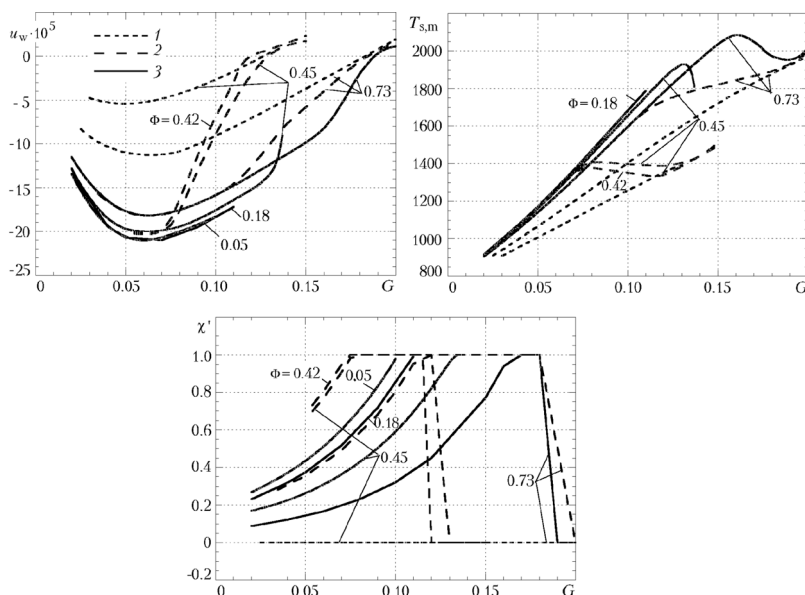

Figure 6. Wave-front velocity u_w, skeleton maximum temperature $T_{s,m}$, and degree of burn-out χ' versus the gas flow rate for small values of the mass fraction of oil: 1) $\chi = 0$; 2) 0.02; 3) 0.05. u_w, m/sec; $T_{s,m}$, K; G, kg/(m^2·sec).

$$\Delta T_{1a} < \Delta T_{2a} \equiv \frac{\chi H_2 - \psi H_3}{c_s} \tag{18}$$

which, in particular, is attained in the case of fairly low-calorific-value (low Φ values) methane-air mixtures.

Note one more feature of the system in the CB regime, which is unusual for the filtration combustion of gases: a practically linear dependence of the wave-front velocity on the gas flow rate (see Fig. 6). Indeed, from the condition $T_{s,m}(G) \cong$ const, in view of balance (5), one can obtain the expression

$$u_w \cong \frac{\Delta T_{s,m} - \Delta T_{1a}}{\Delta T_{2a} - \Delta T_{s,m}} u_{th} \sim G \tag{19}$$

From the form of function (19) the conclusion also follows that with decreasing methane concentration the tilt of the "kink" in the $u_w(G)$ dependence increases:

$$\partial u_w / \partial \Delta T_{1a} \cong -u_{th}/(\Delta T_{2a} - \Delta T_{s,m}) \tag{20}$$

which also agrees with the calculated dependences (see Fig. 6).

In the limit of small concentrations of methane ($\Phi \to 0$), where $\Delta T_{1a} \ll \Delta T_{2a}$, the tilt of the "kink" tends to $\pi/2$, and the region of the CB regime shrinks up to a point ($\Phi < 0.18$, Fig. 5). And vice versa, when the calorific values of the methane-air mixture and oil vapor become equal ($\Delta T_{1a} \sim \Delta T_{2a}$), the "kink" in the $u_w(G)$ dependence becomes "gently sloping" and the region of expenditures corresponding to the regime of complete burn-out expands and becomes comparable in size to the region of incomplete burn-out ($\Phi = 0.73$, Fig. 5).

Dependence on Water Addition

A practically important method for controlling this process is the addition of water to the porous medium. This makes it possible to lower the temperature in the wave reaction zone and, consequently, preserve the zeolite. The calculated dependence of the wave characteristics on the mass content of water ψ in a porous medium is shown in Figure 7.

From the data given in Figure 7 it is seen that the addition of water leads to a decrease in $T_{s,m}$ by 70–150 K and a considerable decrease in the front velocity depending on the flow rate and concentration of methane, which is explained by the reduction of the heat release in the system as a result of the heat expenditures in water evaporation.

In this case, an interesting feature of the process is also a marked increase in the completeness of oil burn-out, which increases the capacity of the sorbent cleaning process (see Fig. 7).
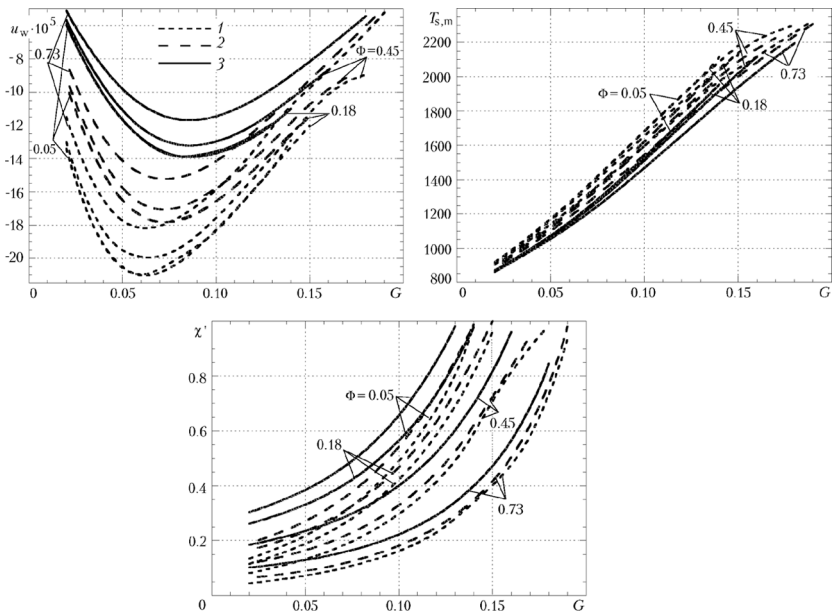
Figure 7. Wave-front velocity u_w, skeleton maximum temperature $T_{s,m}$, and degree of burn-out χ' versus the gas flow rate for various concentrations of methane and water content ($\chi = 0.1$): 1) $\psi = 0$; 2) 0.1; 3) 0.3. u_w, m/sec; $T_{s,m}$, K; G, kg/(m^2·sec).

Dependence on Heat Content of Methane and Adsorbed Organic Vapor Ratio

An important parameter of the proposed system is the relation between the heat content of the methane-air mixture and the adsorbed organic vapor. Figure 8 shows how the shape of the calculated $T_{s,m}$ and u_w (Φ) curves change depending on the oil combustion heat H_2. The same figure also gives the experimental data from Table 1. It is seen that the experimentally observed monotonic decrease in $T_{s,m}$ and u_w is only achieved at fairly high values of $H_2 \geq 5.1 \cdot 10^7$ J/kg, which is explained by the respective decrease in the total adiabatic temperature rise $\Delta \widetilde{T}_a$ with increasing Φ in this case. These considerations have determined the choice of the value of $H_2 = 5.1 \cdot 10^7$ J/kg for parametric calculations.

Cleaning Process Optimization Trends

In the general case, the choice of parameters of the process of thermal regeneration of zeolite is directed towards optimizing the following basic
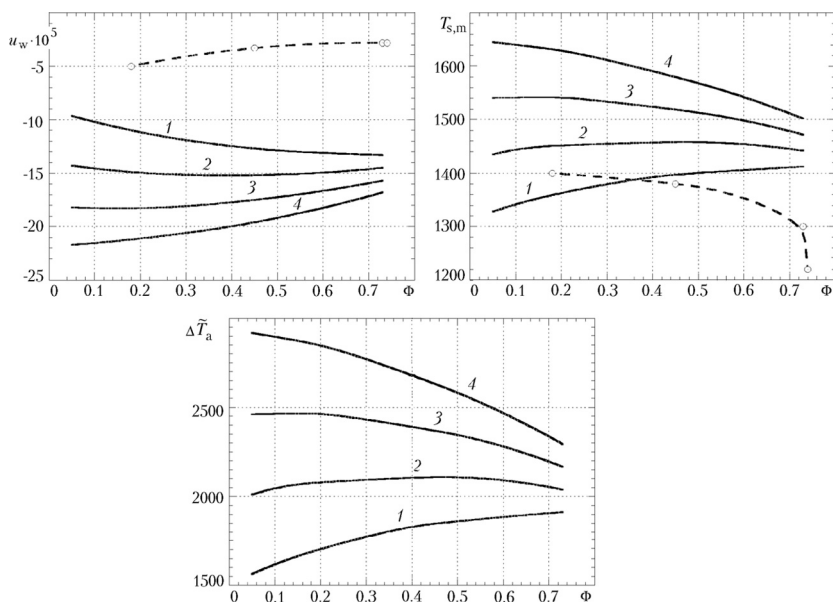
Figure 8. Wave-front velocity u_w, skeleton maximum temperature $T_{s,m}$, and resulting adiabatic temperature rise $\Delta \widetilde{T}_a$ versus the methane content for various values of the combustion heat of adsorbed organic matter: 1) $H_2 = 31\,MJ/kg$; 2) 41; 3) 51; 4) 61; $\chi = 0.1$; $\psi = 0.054$; $G = 0.1\ kg/(m^2 \cdot sec)$; dots, experiment (according to Table 1). u_w, m/sec; $T_{s,m}$, K; G, $kg/(m^2 \cdot sec)$; $\Delta \widetilde{T}_a$, K.

factors: increase in χ' and u_w (this factor increases the capacity of the cleaning process), decrease in $T_{s,m}$ (preserves zeolite) and Φ (decreases the cost of the process), expansion of the region of existence of the CB regime (which facilitates the realization of high degrees of cleaning in the case of fluctuation of the outer parameters of the system).

From the data given in Figures 5–8 it is seen that the typical choices are: "rate" or "purity" of cleaning of the porous medium; "CB region width" or "cleaning rate," etc. For example, a decrease in the concentration of methane is energetically advantageous and increases the cleaning rate of zeolite, but at the same time it sharply narrows the region of the CB regime, which makes it difficult to provide stability of the process characteristics.

In general, the addition of water is very desirable, since this decreases the skeleton temperature, increases the degree of burn-out, and widens the region of the CB regime, but at the same time it noticeably decreases the cleaning rate. The latter lowers the total capacity of the process. Therefore, the optimum choice of the system parameters should be based on concrete technological limitations of the process and the sorbent properties.

CONCLUSIONS

The possibility of realizing a controlled process of oxidation of organic matter adsorbed in a porous medium in the filtration combustion wave has been proved. The relation between the temperature and dynamic parameters of the wave and other characteristics of the system, in particular, the amount of adsorbed organic matter and the air and fuel gas (in the case under consideration—methane) flow rate has been shown. The proposed model permits optimizing practical systems of cleaning porous and free-flowing media. The results of the investigation have a fairly wide field of application and can be used for qualitative description of the properties of three-phase systems with a different state of the organic matter in a porous medium (in the liquid or solid phase)—in the form of a binding component of composite materials, gasifying solid-fuel additives, etc.

NOMENCLATURE

c	specific heat, $J/(kg \cdot K)$
d	fill grain diameter, m
E	activation energy, $J/(mole)$
H	combustion heat, $J/(kg)$
G	mass flow rate, $kg/(m^2 \cdot sec)$
K	pre-exponential factor, sec^{-1}
Pr	Prandtl number
Q	heat release, W/m^3
R	universal constant, $J/(mole \cdot K)$
Re	Reynolds number
t	time coordinate, sec
T	temperature, K
u_w	wave-front velocity, m/sec
u_g	speed of filtration, m/sec
x	space coordinate, m
y	dimensionless concentration of fuel

Greek

σ	Stefan-Boltzmann constant, $W/(m^2 \cdot K^4)$
α_v	interphase heat-transfer coefficient, $W/(m^3 \cdot K)$
ρ	density, kg/m^3
ε	porosity
Φ	equivalence ratio of the methane-air mixture
λ_s	heat-conductivity coefficient $W/(m \cdot K)$
χ	mass fractions of organic matter

ψ	mass fractions of water
χ'	degree of burn-out

Subscripts

a	adiabatic
d	desorption
n	normal conditions
p	pressure
v	volume
g	gas
s	solid
en	environment
m	maximum
th	thermal
st	stoichiometric
w	wave
1	methane
2	oil
3	water

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