Filtration combustion of solid fuel in countercurrent reactors

G. B. Manelis, S. V. Glazov,** *D. B. Lempert, and E. A. Salgansky

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 522 3507. E-mail: glazov@icp.ac.ru

The works studying filtration combustion of solid fuels in the countercurrent mode are reviewed. The phenomenon of superadiabatic overheating is described. The data of experimental and theoretical studies and some results of the development of technological processes of production of thermal or electric energy from substandard raw materials and extraction of valuable components (for example, rare metals) from unconventional sources (industrial wastes, poor ores, burrows, *etc.*) are presented. The processes of safe treatment of problematic wastes are considered.

Key words: filtration combustion, countercurrent reactor, macrokinetics, gasification, pyrolysis, heat exchange, mass transfer, superadiabatic overheating, solid fuel.

1. Introduction

Wave combustion is one of the frequently met modes of chemical reactions in a medium with enthalpy excess. Waves of filtration combustion (FC) in a porous medium have several features that make it possible to group them as a special type of combustion processes. The process of solid fuel oxidation during the filtration of gaseous oxidant is usually understood as FC. Processes of FC are rather attractive for industrial use due to some their peculiarities.

An important role in wave combustion processes belongs to modes with thermal energy accumulation, whose typical example is the combustion of a layer of the solid lump fuel during the filtration of the gaseous oxidant, when the direction of motion of the combustion front coincides with the direction of the gas flow.[1—5] In the system of coordinates related to the combustion front (zone of exothermic conversion), this process can be considered as an interaction of counter flows of the gas and condensed phases passing through the zone of chemical reactions and transforming in this zone with a change in the composition and physicochemical properties (Fig. 1).

The presence of the high-temperature region with intense processes of interphase heat and mass exchange during countercurrent of the phases can result in the formation of the zone structure. The physicochemical processes corresponding to the conditions (temperature, properties of the medium, concentrations of reactants, and others) occur in each zone. Spatial separation of the zones provides localization of these or other substances in certain

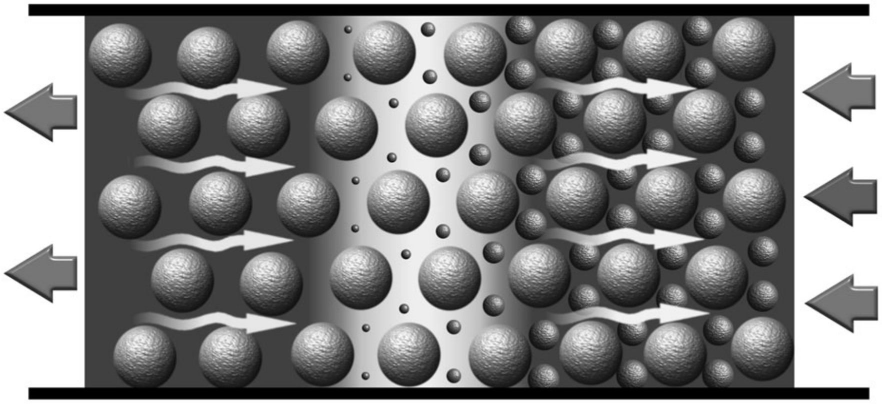

Fig. 1. Scheme of the combustion wave with superadiabatic overheating. Solid combustible and inert materials are designated by small and large balls, respectively. The solid material flow is shown from the right to the left, and the gas flow goes from the left to the right. The high-temperature combustion zone is shown by a lighter color of the background.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1278—1294, July, 2011.

zones with allowance for their physicochemical properties. These features make it possible to perform some industrial processes in the very efficient low-expense mode based on thermal efficiency of the combustion wave. Examples for the accomplishment of processes of superadiabatic FC modes are described in the literature. These are the efficient gasification of solid fuels and waste treatment by the superadiabatic combustion method,[6] intraformational gasification of oil,[7] agglomeration of the metallurgical charge,[8—10] oxidative regeneration of catalysts,[11,12] self-propagating high-temperature synthesis,[13,14] *etc.* The processes considered are typical examples of FC with countercurrent, where superadiabatic overheatings are observed.

The heat released in chemical reactions is intensely transferred to the initial reactants due to the countercurrent of phases without using external heat-exchange devices only due to very efficient direct interphase heat exchange during filtration. Because of rather considerable heat accumulation the temperature of the front of the combustion wave can multiply exceed the adiabatic burning temperature of the mixture calculated assuming that the initial temperature of the reactants is equal to the temperature of the environment. Due to this, the terms "superadiabatic overheating," "superadiabatic filtration combustion mode," or simply "superadiabatic heating" are used for the description of the process.[15]

The term "superadiabatic" seem disputable at the first glance; however, any recuperation of heat from combustion products to the initial reactants leads to the possibility of exceeding the temperature, which is considered adiabatic for this mixture, assuming that the initial temperature is equal to the temperature of the environment. Actually, due to the intensive interphase heat exchange, in this system the temperature of the initial components entering the reaction considerably exceeds the temperature of the environment and, possibly, approaches the temperature of the combustion front.

Just in the superadiabatic mode the efficiency of recuperation can be maximally high, and this is observed in the case of a rather large amount of an inert material in the solid fuel and a rather high content of the inert component in the gaseous oxidant.[16] This is caused by the fact that for this organization of the process the inert components of the system are represent a very efficient heat carrier, due to which both the fuel and oxidant can be warmed with the maximum efficiency before they get into the zone of chemical reactions. The solid fuel is heated from gaseous combustion products, whereas the gaseous oxidant is heated from the ash residue and solid inert component.

In the systems considered, the most interesting feature of combustion waves is the nonlinear dependence of the burning temperature of the established combustion wave on the heat effect of the reaction (if this effect is positive). After ignition the temperature in the combustion front reaches the established level when the heat entry from exothermic reactions becomes equal to the value of lateral heat losses. When the lateral heat losses are minimized, this equilibrium is achieved only at very high temperatures sufficient for chemical reactions to occur with high intensity. The temperature profile of the combustion wave of the solid fuel in the countercurrent of the gaseous oxidant is schematically shown in Fig. 2.

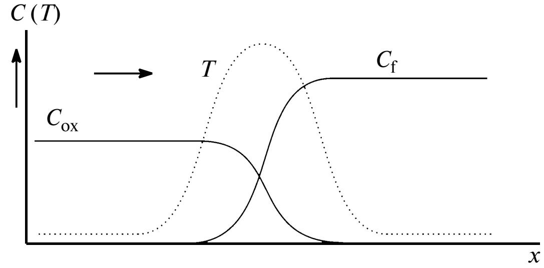

Fig. 2. Temperature (T) and concentration profiles (C_{ox} is the gaseous oxidant, and C_f is the solid fuel) of the FC wave in the case of equality of the heat capacity of the countercurrents of the solid and gas phases. The gas flow direction is shown by arrow.

For the countercurrents of the oxidant and fuel and high temperature, such an important characteristic as the combustion rate is determined by the coming of reactants to the reaction zone only (filtration rate) rather than the heat transfer rate. In addition, the reduction zone with a large amount of fuel and rather high temperature is usually present in front of the combustion zone (in Figs 1 and 2, the reduction zone occurs to the right from the high-temperature region of the most efficient occurrence of the main reactions responsible for the thermal regime of the process), which favors the more complete consumption of the gaseous oxidant, while behind the combustion zone (to the left from the high-temperature region), on the contrary, there is a zone with a high content of the oxidant, which at high temperatures provides the completeness of combustion of the material.

All this makes the FC process very stable and attractive for practice, especially in the cases where it is necessary to

— burn the fuel with a small combustible content expending minor energy,

— obtain high burning temperatures,

— attain the maximum completeness (purity) of combustion of the solid fuel, and

— perform the spatial separation of zones (zones of heating, pyrolysis, vaporization, oxidation, condensation, cooling, *etc.*) in the reactor.

In this case, the energy expenditures can be reduced to minimum due to efficient heat recuperation in the FC wave.

2. Features of the physical and chemical structure of filtration combustion waves

The principal scheme of the FC of the solid fuel in open systems is presented in Fig. 1. Since nearly any fuel initially contains chemically inert impurities (*e.g.*, ash), the porous medium in front of the reaction zone represents, in the general case, a mixture of the condensed fuel with an inert material. The porous residue containing a ballast and condensed combustion products remains behind the combustion front. The heat released in the reaction is transferred to unreacted layers of the substance having a lower temperature and initiates intrinsic heat release in them, due to which the self-sustaining process of reaction wave propagation occurs. As a result of the heterogeneous interaction of the solid fuel with the gaseous oxidant in the FC wave, both condensed and gaseous products can be formed in the FC wave. The overall scheme of the reaction has the form

$$\text{Fuel(s)} + \text{Ox(g)} + \text{IC(s, g)} = \text{P(s, g)} + \text{IC(s, g)},$$

where Fuel is the fuel, Ox is the oxidant, IC is the inert component, P are products, and s and g are the solid and gaseous states, respectively.

Here the inert component designates gases and condensed substances that are not involved in the oxidation and gasification reactions. These are air nitrogen, ash of the solid fuel, *etc.*

Two phases, intense heat and mass exchange between them, and constant countercurrent of the solid and gaseous phases considerably impede both the theoretical description of the FC wave and interpretation of the experimental results.[17] Not only thermal and concentration fields but also the dynamics of the gas flow and features of heterogeneous reactions should be taken into account in similar systems. In addition, a huge difference in densities of the components of the system causes the necessity of combined consideration of processes with substantially different characteristic rates.

2.1. Simplest case of filtration combustion with countercurrent. The simplest case of FC with countercurrent in the one-dimensional approximation is the chemical interaction of counter flows of the solid fuel with the gaseous oxidant filtration through the fuel to form the single reaction product. The fuel is assumed to include both the solid inert substance and the gaseous component that is not involved in the reaction. Depending on the state of the reaction product (in the gaseous state, as, *e.g.*, during carbon oxidation, or in the solid state as for the oxidation of aluminum), the reaction product is added to the corresponding substance flow through the reaction zone. Then the interphase mass transfer of any solid fuel to the gaseous product occurs or the gaseous oxidant is transferred to the solid product. In the both cases, the all oxidation process with heat release is localized in the narrow reaction zone.

For the heterogeneous process, the width of the chemical reaction zone is mainly determined by the particle size. In addition, for countercurrent the width of the chemical reaction zone depends not only on the temperature but also on the concentration of reactants. Thus, even for a broad high-temperature region, the width of the reaction zone can be small compared to the width of the heat zone of the combustion wave. The higher the temperature of the combustion wave, the narrower the reaction zone. In particular, in the FC processes of the carbon systems during air filtration the temperature of the front exceeds, as a rule, 1000 °C, which suggests that the approximation of narrow combustion front is valid.

Depending on the conditions of the process (the concentration of the fuel in the loaded mixture and the concentration of oxygen in the gaseous oxidant), the heat structure of the FC wave can be analogous to that presented in Fig. 3, *a* (at $\delta < 1$) or 3, *b* (at $\delta > 1$). The type of heat structure is determined by the value of δ equal to the ratio of the heat capacity of countercurrents of the gas and solid phases through the reaction front.[5,18] The heat released in the combustion front is removed, in the case of $\delta > 1$, from the high-temperature zone with the gas flow, whereas in the case of $\delta < 1$ the removal is performed by the solid substance flow, which determines the type of the temperature profile of the combustion wave. Perhaps, the heat capacity currents are equal, *i.e.*, $\delta \approx 1$, which results in the symmetric temperature profile of the FC wave and the maximum heat concentration in the combustion wave. In this case, the heat released in the chemical reaction is removed by both the solid residue and gaseous products.[19,20]

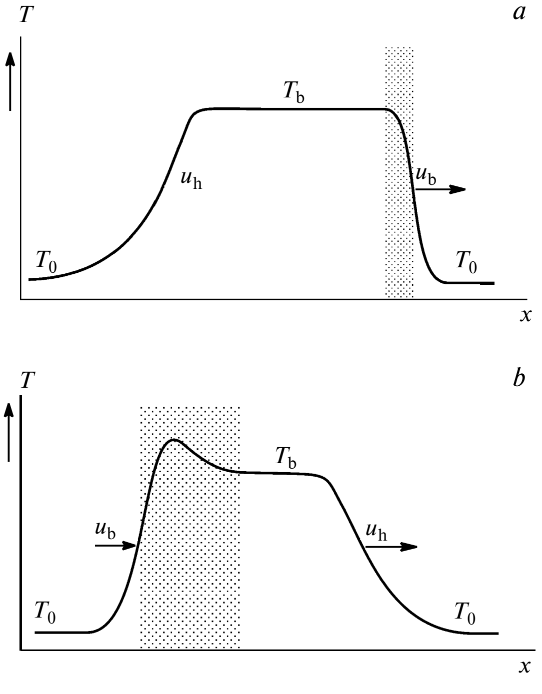

Fig. 3. Dynamics of the temperature profiles of the combustion wave in the absence of lateral heat losses at $\delta < 1$ (*a*) and $\delta > 1$ (*b*). The hatched area is the chemical reaction zone; u_b and u_h are the zones of the burning and heating waves, respectively.

Zones of interphase filtration heat exchange are formed at the both sides from the combustion front. On the one hand, the gaseous oxidant is heated upon filtration through the solid ash residue; on the other hand, gaseous products emerging from the combustion zone transfer heat to the solid fuel. The optimization of these heat exchange processes results in the maximum localization of the released thermal energy near the combustion front.

The heat exchange ceases in a rather long reactor, and all substances are removed from the reactor at the initial temperature. The continuous accumulation of the thermal energy results in the expansion of the heated zone towards the gas flow or solid phase flow according to the type of thermal structure of the FC wave. The high-temperature zone expands until the lateral heat losses of the combustion wave become equal with the level of heat release in the front. Thus, the steady-state mode of the FC wave is formed. If lateral heat losses are absent, the steady-state is possible only at non-ceased heat exchange. Then either gas or solid is removed from the reactor being hot.

Due to the effect of heat concentrating in the combustion zone, the region of existence of self-sustaining regimes of gasification propagates far to small contents of the fuel in the initial mixture. Stable gasification processes occur upon the supply of air even at carbon content 2% only.[21,22] Combustion of such poor mixtures is interesting for the processes of ore agglomeration or catalyst regeneration.

The general dependence of the maximum temperature in the combustion wave on the carbon content in the mixture is non-monotonic (Fig. 4). When air is used as a gasifying agent, this dependence has a maximum in region of the carbon content 17—25%.[23] The maximum corresponds to the optimum concordance of the heat capacity of countercurrents of the solid and gas in the heat exchange zones, providing the maximum heat recuperation from the products to the initial reactants. In the region of smaller carbon contents (to the left from the maximum), the combustion wave has the thermal structure determined by the condition $\delta < 1$ (see Fig. 3), and in the region of high contents, on the contrary, $\delta > 1$. Numerous experiments and numerical calculation data confirm the character of the dependence and the temperature maximum in this region.[5,8,18] A similar maximum is observed in the case of the dependence of the temperature on the oxygen content in the gasifying agent.

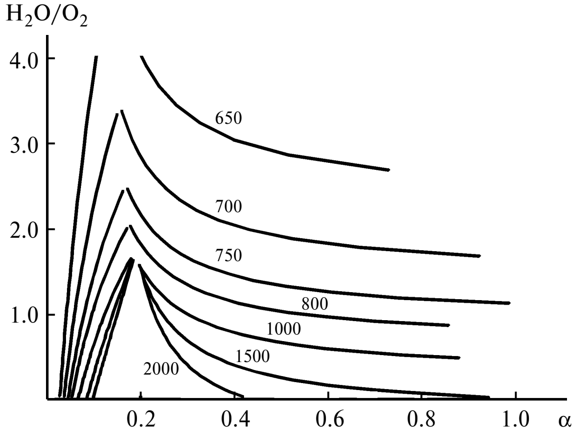

Fig. 4. Temperature in the combustion front (*T*/°C, indicated near curves) *vs* mass fraction of carbon (α) in the mixture.

For the vapor—air gasification of carbon, the general type of the temperature dependence in the combustion front on the fuel content in the mixture is retained; however, the maximum in the curve is less pronounced due to endothermic reactions that occur. The calculated and experimental data on the temperature of the front of the FC wave at various contents of carbon in the initial mixture and of water vapor in the gasifying agent[5] are presented in Fig. 5. The experimental data were obtained on small-scale laboratory devices in which relative heat losses are high. Nevertheless, in the systems with carbon content 5—10% the stable process of wave propagation is observed during the filtration of air and vapor—air mixtures.

This or another effect on the combustion wave is ambiguous because of the non-monotonic dependence of the parameters on the carbon content, since the behavior of the wave characteristics depends strongly on the type of the structure. The behavior of the combustion wave of the thermal structure with $\delta < 1$ differs significantly from that at $\delta > 1$. For instance, the temperature decreases with the dilution of the solid fuel with an inert material in the case of this first type of the combustion wave. On the contrary, the temperature increases for the wave of the second type. Sharp changes in the composition of the fuel or oxidant

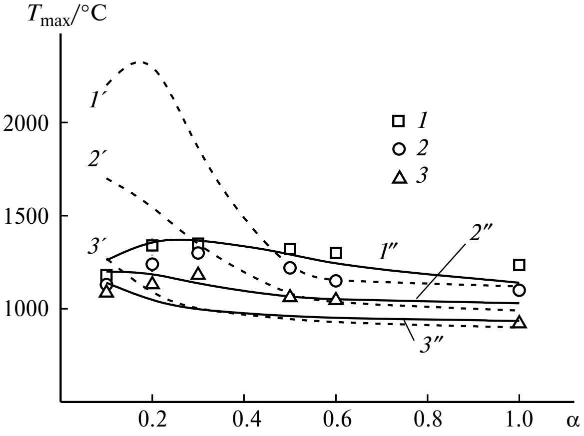

Fig. 5. Comparison of the experimental and calculated temperature data at various carbon contents (α) in the initial mixture and for various mole ratios vapor/oxygen: H_2O/O_2 = 1.0 (*1*, *1*′, *1*″), 2.5 (*2*, *2*′, *2*″), 4.5 (*3*, *3*′, *3*″). The maximum temperature of the gas is shown by dashed line (*1*′—*3*′), the maximum temperature of the solid phase is shown by the solid line (*1*″—*3*″), and points are experiment (*1*—*3*).

during combustion wave propagation will be accompanied by the change in the type of the structure.[24]

2.2. Accompanying processes of vaporization and condensation. The thermal structure of the FC wave determines the conditions of heating of substances during the combustion wave propagation, as well as all accompanying physical and chemical processes. For instance, an additional evaporated component in the solid fuel (along with the combustible and solid inert substances) determines the localization of the evaporated component in the region of fuel heating (Fig. 6, *a*). The main heat release providing the existence of the whole wave structure occurs in the combustion front. The vaporization process occurs due to the convective heat flow from the combustion front. The mass transfer of the evaporated component with the gas flow occurs before the condensation region. In the absence of heat losses, when the convective heat flow from the combustion front exceeds the heat expenses to vaporization, the concentration region of the evaporated component in the gas flow expands. In the case of lateral heat losses, the expansion of the concentration region ceases sooner or later, and then all the structure of the combustion wave propagates stationary as a single whole.

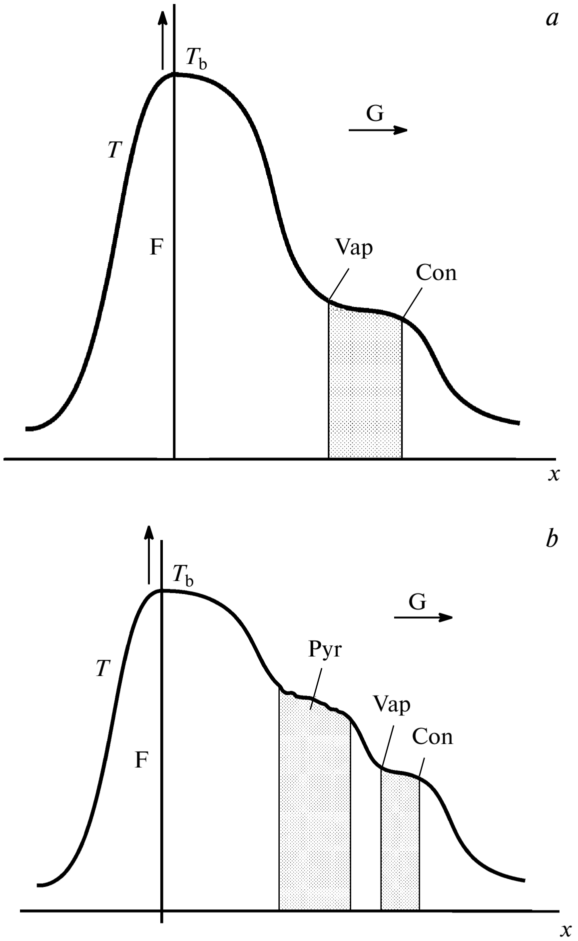

Fig. 6. Thermal structure of the combustion wave propagating in the solid porous fuel with an evaporated component (*a*) and of a pyrolyzed (organic) fuel with an evaporated component (*b*); G is the gas flow, Vap is the vaporization, Con is the condensation, Pyr is the pyrolysis zone, and F is the FC front.

In the case of the thermal structure of the combustion wave with $\delta < 1$, the vaporization zone is situated close to the combustion front, which determines and provides the existence of the whole wave structure. Therefore, considerable heat expenditures to evaporation can decrease the temperature of the front, which would necessarily affect all characteristics of the FC wave. In the case of the thermal structure with $\delta > 1$, heat expenditures to the evaporation of the component decrease the temperature in the heating zone rather than in the combustion front. Therefore, these losses exert no noticeable effect on the process of heat release of the front, which is a remarkable feature of such FC modes. The condensation zone of the evaporated component is arranged a little further along the gas flow. The condensation process is accompanied by some heat release. Therefore, in this case, not only mass transfer occurs, but also the transfer of the heat energy from one zone to another takes place. The typical example for the evaporated component is the moisture of the fuel. Due to superadiabatic overheatings, such FC modes are possible where the high moisture content (up to 70%) does not prevent the propagation of the stable combustion wave.[25]

Condensation of the evaporated component does not always result in its concentrating in a certain zone of the reactor. For instance, moisture condensation results in the formation of aerosol. The larger the size of the liquid droplets, the easier their precipitation on the initial solid substance upon filtration. The temperature gradients in the FC wave can be very high. In this case, the high rate of gas cooling will lead to the formation of very small droplets (smaller than 10^{-6} m), which precipitate poorly during filtration and can be removed from the reactor with the gas as a fog. Thus, the extraction of the evaporated component, which is present in the initial solid, can rather simply be organized.

2.3. Filtration combustion of the pyrolyzed fuel. The typical case of the combustion wave accompanied by thermal decomposition processes is the FC of fuel of organic origin. As a rule, on heating such fuels undergo pyrolysis to form liquid and gaseous products and a coke residue. A striking example are fuels of organic origin: wood, peat, natural coals, *etc.* In this case, the thermal structure of the wave will be impeded by the appearance of the thermal decomposition zone arranged before the combustion front (see Fig. 6, *b*). Pyrolysis will occur in the oxygen-free region of heating of the solid fuel. Usually the heat effect of pyrolysis is low compared to the heat release of the combustion front.

The solid coke residue is formed, as a rule, due to pyrolysis and then gets into the combustion zone and burns there, as well as pyrolysis resins and gaseous destruction products. At relatively high temperature, pyrolysis resins exist in the gaseous state and, like gaseous products, are transferred with the gas flow from the pyrolysis zone to the region of lower temperatures. Pyrolysis resins, being various hydrocarbons, are condensed in this region. Due to this, the zone of accumulation of liquid pyrolysis products, which is similar to the zone of accumulation of the evaporated component but with the different origin of concentrated substances, is formed in front of the pyrolysis zone.

The composition of pyrolysis resins is very complicated and changes depending on the character and properties of the material subjected to pyrolysis and on the heating rate and intensity. The resins contain, as a rule, thousands of different organic compounds, among which there are rather toxic substances. The value of these resins themselves is low, because complex processes of chemical conversion should be organized for the production of any commercial product (for example, motor fuel) from them. At this stage, it is much more simpler to organize their combustion with the production of the thermal or electric energy. However, it should be kept in mind that technologies of liquid fuel production from non-petroleum raw materials can be developed, the more so, the cost of this raw materials can be even negative (in the case of utilization of any varieties of organic wastes).

The experiments on the FC of pyrolyzed fuels showed[26] that pyrolysis resins condensed in the gas flow upon its cooling are transformed into aerosol as the evaporated component. The pyrolysis resins can also be removed from the reactor along with the gas flow as fine fog droplets. Unlike moisture and other incombustible components, the pyrolysis resins are combustible and can be burned after supplying a gaseous oxidant.

It was established that during the FC of the pyrolyzed fuel the combustion rate increases with an increase in the fuel fraction in the initial mixture. This is due to the fact that the yield of the pyrolysis products changes depending on the pyrolysis conditions. As a result, the fraction of the fuel burned in the oxidation zone decreases to some value with an increase in the fuel content in the initial mixture and then remains almost unchanged.

The data on the yield of liquid products of pyrolysis of solid organic fuels in percents of the initial mass for various methods (oxygen-free pyrolysis, gasification, and FC with superadiabatic overheatings)[26] are presented in Table 1. In experiments on FC, the maximum yield of pyrolysis resins for the fuels studied reaches 65% of the fuel mass, which is close in amount to that obtained by oxygen-free pyrolysis, but the energy efficiency of the process is higher in this case, because requires no additional energy supply.

The combustible gas formed in the process contains CO and H_2, as for oxygen-free pyrolysis. The initial fuel is dried in the combustion wave due to internal heat exchange, which is much more efficient than the drying of the fuel in a particular device.

Table 1. Yield of liquid products upon the thermal treatment (%)

Fuel type	Gasification	Pyrolysis	FC
Wood	20	75	65
Cellulose	No data	~100	30
Peat	10	10—12	12—14
Brown coal	7—9	5—15	8—10
Rubber	No data	20—45	40—50

The mathematical model of steady-state combustion of a mixture of particles of the pyrolyzed solid fuel with an inert material in the countercurrent of gaseous oxidant was developed for the theoretical study of the influence of the stage of pyrolysis of organic fuels on the characteristics of combustion.[27] The chemical scheme of the model includes the following reactions:

— pyrolysis of the initial fuel with the formation of the coke residue and gaseous products (pyrolysis resin),

— oxidation of the pyrolysis resin, and

— oxidation of the coke residue.

The process was considered in an endless non-adiabatic reactor. The one-model steady-state one-temperature model included the equations of conservation of the energy of the system and the mass of each component. The initial system of equations was solved for each case of the thermal structure of the combustion wave by the asymptotic method using the approximation of narrow combustion zone. The analytical expressions relating the main macrokinetic parameters of the process were obtained.

The calculations were performed for the air gasification of a mixture of wood with an inert material. The thermophysical characteristics of the initial fuel were assumed to be equal to the characteristics of birch wood, those of the coke residue were assumed to be equal to the characteristics of wood coal, and those of the inert material were accepted to be the same as the characteristics of firebrick. The parameters of the oxidant were chosen according to the characteristics of air.

The dependences of the burning temperature (T), oxygen content in the gaseous product ($\rho_x{}^*$), mass rate of fuel combustion (U_m), and fraction of the fuel oxidized in the combustion zone (η) on the fuel content in the initial mixture are presented in Fig. 7. It was assumed in the calculations that the ultimate yield of coke was 15%. The dashed lines show the tentative values of parameters in the region where no calculations were performed.

The dependence of the burning temperature on the content of the fuel in the initial mixture is non-monotonic with the maximum value in the region of $C = 45—50\%$. The oxygen content in the gaseous products decreases lin-

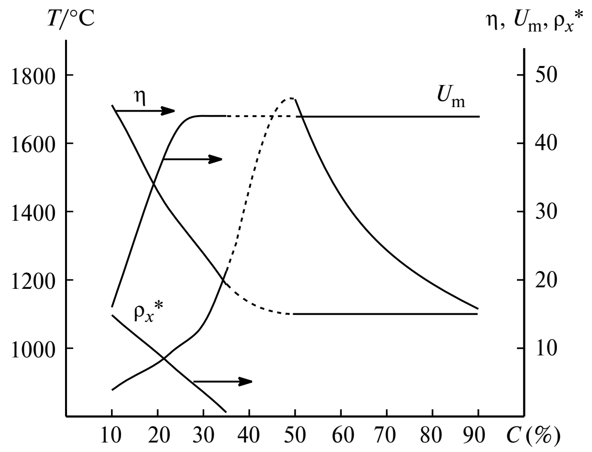

Fig. 7. Dependences of the burning temperature (T), oxygen content in the gaseous product (ρ_x* (%)), mass combustion rate ($U_m \cdot 10^3$/kg m^{-2} s^{-1}), and fraction of the fuel oxidized in the combustion zone (η (%)) on the initial fuel content (C).

early from 15 to 0% with an increase in the fuel content from 10 to 35%. The mass combustion rate increases from 0.016 to 0.044 kg m^{-2} s^{-1} with an increase in the fuel content from 10 to 30% and remains unchanged with the further increase in C. The increase in the mass combustion rate at a low fuel content in the mixture is explained by the more complete consumption of oxygen, and the constant character of the combustion rate in the region of high fuel contents is due to the complete consumption of the reactants and constant stoichiometry of the process.

The fraction of the fuel oxidized in the combustion zone remains unchanged and equal to 0.15 at the fuel content in the initial mixture 50% and more. In this case, pyrolysis of the fuel is complete in a separately situated zone, and only the coke residue gets into the combustion zone. At the same time, pyrolysis resins are removed from the reactor by gas flow and are not involved in oxidation. At the fuel content in the initial mixture smaller than 50% the ratio of heat capacities of the gas and solid phase flows becomes lower than 1 and the fuel has no time to be completely pyrolyzed. A portion of pyrolysis resins is oxidized along with the coke part of the fuel in the combustion zone. In this case, with a decrease in the fuel content from 50 to 10% the amount of oxidized resins increases and, accordingly, the completeness of fuel consumption in the combustion zone increases from 15 to 45%.

The calculations in terms of the indicated model showed that at a small content of the solid inert component (in the parametric region $\delta > 1$) autolocalization of the conversion zones takes place (spatial separation of the pyrolysis and combustion stages) and the wave structure with the complete pyrolysis in the zone separated from the combustion front is observed. No spatial separation of stages occurs in the region with $\delta > 1$. The pyrolysis resins are partially oxidized in the combustion front.

3. Prospects of industrial use of filtration combustion with countercurrent

The use of the countercurrent gasification scheme makes it possible to achieve a high energy efficiency of the process. This becomes possible due to some features of the process, namely:

— intensive internal heat exchange between products and reactants occurs without the use of additional devices in the case of the countercurrent of the solid fuel and gaseous oxidant;

— the heat released in chemical reactions is concentrated in a relatively narrow combustion zone, and the products emerged from the reactor have a relatively low temperature;

— the autolocalization of zones occurs in the reactor. Physicochemical processes occur in each zone according to the conditions (temperature, properties of the medium, concentrations of the reactants, and others). This makes it possible to easily organize processes of extraction of valuable components and efficiently perform several technological processes in one device (reactor).

The solid fuel is gasified in the countercurrent mode in a reactor-gasifier of the shaft type with superadiabatic overheatings in the "compact" layer. A specific feature of this process is such its organization when the heat released during combustion would not removed from the reactor (solid and gaseous products emerge from the reactor at relatively low temperatures) but was concentrated in the gasification zone.

The processed raw material is loaded in the reactor from the top through a lock chamber. Air and water vapor are supplied from the bottom. The gaseous product is taken in the upper part of the reactor, while the ash residue is discharged in the bottom part. The working mixture moves in the reaction under the action of its weight. Several characteristic zones are arranged along the gasifier height. In the upper layers the temperature remains within 100—200 °C. Here the newly supplied raw material blown with the gaseous product is dried. As a result, the raw material is saturated to some extent with water vapor. The zone with predominant processes of pyrolysis and sublimation of organic substances is arranged lower. The thermal decomposition and coking of the organic mixture occur in the oxygen-free medium. Here gaseous products are enriched with volatile pyrolysis products. The gasification zone is situated in the medium part of the reactor, where the reaction of the coke residue with oxygen, water vapor, and carbon dioxide occurs at 1000—1200 °C to form CO and H_2. Some portion of carbon is burned to form carbon dioxide, due to which the necessary temperature is maintained in the gasification zone. The zone, where the solid residue consisting mainly of mineral compounds is gradually cooled in the gasifying agent flow rich with oxygen, is arranged lower. Here residues of carbon and organic compounds undergo afterburning, and combustible materials are completely transformed into ash. The zone of final cooling of the solid residue is situated in the lowest part of the reactor.

Thus, the fuel is treated by the two-stage scheme. At the first stage, the fuel is gasified in the FC mode with superadiabatic overheating. At the second stage, combustible gaseous products are burned in a standard device with energy production. The two-stage of processing provides a decrease in the formation harmful wastes due to the following factors.

— Low linear rates of the gas flow in the reactor and its filtration through the layer of the initial processed material provide a very low emergence of dust particles with the gaseous product; the conditions favoring the capture of dust particles from the gaseous flow due to the adhesion of pieces of the initial material to the surface are created in the upper part of the reactor; and favorable conditions appear for the neutralization of acidic impurities (HF, HCl) with mineral components of the charge, which makes it possible to strongly reduce capital expenses to gas-cleaning and energy equipment.

— In some cases, where gaseous wastes should be purified from sulfur-, chlorine- or fluorine-containing compounds, dust, and mercury vapor, the purification of the gaseous product is simpler than smoke fumes due to lower temperature, substantially smaller volume, and higher concentration of contaminators; in addition, sulfur is present in the product in the reduced forms (H_2S, COS), which can more easily be adsorbed than SO_2; and chlorine-containing organic compounds are at least partially dehydrochlorinated to form HCl rather than Cl_2 under the pyrolysis conditions in the reductive hydrogen-containing atmosphere.

— Nitrogen-containing organic compounds partially decompose in the oxygen-free medium during gasification, due to which the content of nitrogen oxides in smoke fumes decreases.

— Gas combustion in modern gas burners is the purest combustion method of all known methods: due to the high completeness of combustion, smoke fumes contain very small amounts of CO and residual hydrocarbons, including cancerogenic polyaromatics.

— The formation of dioxines (polychlorinated dibenzodioxines and dibenzofurans) decreases sharply, because the appearance of soot particles and aromatic compounds (dioxine precursors) is suppressed and the low content of dust particles (catalyst for dioxine formation in smoke fumes) is provided even in the presence of chlorine in prestirred flame.

— The ash discharged from the reactor has a low temperature and contains almost no incompletely burned carbon and organic substances.

Commercial materials for subsequent processing (for instance, oil and others) can be extracted from the gaseous product during the utilization of some types of wastes. The choice of equipment for heat utilization during product combustion is not restricted by a steam or water boiler. Gas turbines or energy Diesel engines can be applied in future: the scheme proposed can easily be incorporated into available industrial infrastructure (for example, the product can be fed to the available fire-chamber to replace a part of the conditional fuel).

3.1. Energy efficiency of the process. As already mentioned above, the most favorable conditions for heat exchange processes between hot products of chemical reactions and relatively cold initial reactants are created in the reactor in the countercurrent motion of the gaseous oxidant and solid fuel. The solid fuel is heated from gaseous combustion products, and the gaseous oxidant is heated from the ash residue. The possibility appears to optimize this heat exchange in such a way that the initial reactants would be at a maximum heated still before getting into the zone of chemical interactions. The optimization of heat exchange by equalizing the heat capacity of the countercurrent flows of the gas and solid phases makes it possible to organize efficient processes of gasification of substandard, particularly, high-ash or high-moisture fuels. Thus, requirements imposed on the fuel quality decrease sharply.

The study of combustion of a mixture wet wood coal—inert material showed that a gasification process in the countercurrent mode occurred in the whole range of changing the moisture content (up to 70%) even in a small-scale laboratory device with a diameter of 46 mm (in spite of the high level of heat losses).[25] It was revealed that the moisture content exerted almost no effect on the characteristics of the process. The combustion wave is self-controlled over the temperature by an increase in the thermal effect of the reaction.

The main influence of the moisture content of the fuel on the process is the heat consumption to the evaporation of water. The heat consumed to evaporation affects the temperature in the consumption wave and, hence, stoichiometry of carbon oxidation. The change in the stoichiometry of the process towards the greater formation of CO_2 increases the thermal effect of the reaction in the combustion zone and thus compensates, to a considerable extent, the influence of losses to evaporation. In all cases, the temperature and mass rate of gasification are poorly sensitive to a change in the moisture content of the fuel.

The efficient conversion of the energy of the solid fuel to the energy of the gaseous product implies the minimum heat release in the gasification zone, because it is a loss of net energy in this case. In the countercurrent modes, high temperatures necessary for the process to occur can be attained due to the efficiency of internal heat exchange between the products and initial reactants. Even in the case of a low overall thermal effect of the reaction, a thermal energy sufficient for intensive gasification can be accumulated.

For the air gasification of a simple carbon solid fuel, the efficiency of gasification cannot exceed 72% (complete conversion of all carbon to CO). However, if the gaseous oxidant includes waver vapor, at a high temperature (above 800 °C) vapors can react with the carbon surface. The product is enriched in hydrogen and carbon monoxide, and the restriction of the efficiency is eliminated.[23] The addition of carbon dioxide to the gaseous oxidant works similarly. Moreover, these endothermic reactions occur most efficiently in the hottest points, which decreases the thermal strain of the construction.

The efficiency of gasification approaches 100% by nulling of the overall thermal effect in the zone of chemical reactions (at the complete heat exchange and without heat losses).

The results of thermodynamic calculations of the energy efficiency of the vapor—air gasification of mixtures of carbon with an inert material, depending on the fraction of carbon in the mixture and the volume ratio water/oxygen in the gasifying agent, are presented in Fig. 8. The calculated value of efficiency is the ratio of the calorific value of the gaseous products formed by the reaction of carbon with oxygen and water vapor under the FC wave conditions to the heat of combustion of the initial mixture (with allowance for expenditures to vapor formation). It is seen that for the gasification of pure carbon, an increase in the vapor/oxygen ratio in the gasifying agent first results in some increase in the efficiency; however, then the efficiency decreases again. The content of water vapor exerts a considerably stronger effect on the gasification of mixtures containing a noticeable amount of an inert admixture. In particular, as can be seen from Fig. 8, for mixtures containing ~80% of an inert material, the increase in the vapor/oxygen ratio to ~1.7 makes it possible to increase the efficiency of gasification to almost 0.95. Thus, the substandard fuel (with a high ash content) can be gasified in the superadiabatic mode more efficiently than the high-quality fuel.

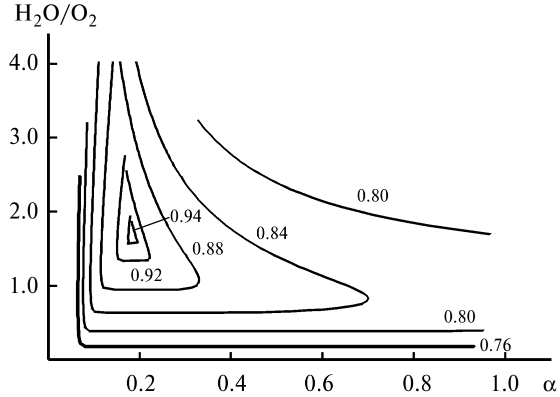

Fig. 8. Calculated values of the energy efficiency (digits near curves) for the vapor—air gasification of mixtures of carbon with an inert material; α is the fraction of carbon.

The concentrating of heat in the combustion zone and the efficient heat transfer from hot products to the initial reactants make it possible to gasify low-sort types of fuel, such as poor high-ash coals, coal burrows, peat, shale oils, biomass of various origin (wastes from wood and wood processing economy, agricultural wastes, *etc.*) and any combustible domestic and industrial wastes without special efforts. In this case, the term "combustible wastes" means the presence of at least several percents of combustible components.

One of the promising alternative energy sources is the biomass, because it is widely abundant, accessible, and reproducible (renewable) resource with a minimum amount of ecologically dangerous contaminators. The main obstacle in the way of wide use of the biomass as an energy source is the necessity to develop modern ecologically safe technologies that make it possible to obtain the thermal or electrical energy from substandard fuels (high moisture content and relatively low heat of combustion). The method for gasification of solid fuels in the FC modes with countercurrent developed at the Institute of Problems of Chemical Physics (Russian Academy of Sciences) has not only high efficiency but also allows one to substantially decrease requirements imposed on the processed material, in particular, to expand the range of appropriate moisture content.

The studies performed confirmed that an efficient thermal treatment of some types of biomass, including those, whose treatment by other methods is difficult, is possible in the superadiabatic FC modes.[28] This gives the energy gaseous product containing a large amount of pyrolysis resins in the form of fog. The admissible moisture content in the material during gasification in the superadiabatic FC modes is noticeably higher than that when other known methods are used. Materials with a large amount of the solid inert substance can also be processed without substantial worsening of parameters of the process.

3.2. Extraction of valuable components. Owing to the fact that in the combustion wave with countercurrent the heat released in chemical reactions is concentrated in a relatively narrow zone, and the temperature in this zone can achieve very high values. The motion of solid phase through the FC wave is accompanied by intense mass transfer processes. In this connection, it was assumed that this process can be fruitful for the extraction of some metals, namely, those that can form relatively volatile products (both oxidation and reduction products), since they are transferred along with the gas phase, shifting the chemical equilibrium towards the needed side, even at their low equilibrium content in the gas phase in the presence of the gas flow.[29] The FC process in the superadiabatic mode should be especially interesting for the extraction of rare metals from unconventional sources, namely, from industrial wastes, poor ores, burrows, *etc.*[30] Several types of nonferrous metal sources are described, and the applicability of the method under study was shown using these examples.

The mass transfer of various metal compounds in the FC wave can successfully be performed, because the pressure of saturated vapors of some metals and their compounds at temperatures characteristic of real FC processes (approximately from 800 to 1200 °C) is quite sufficient for their efficient mass transfer from the initial reaction mixture along with the gas flow. The objects of mass transfer can be both some free metals (for example, zinc, cadmium, mercury, arsenic, selenium, tellurium, and tantalum) and their oxidized forms (*e.g.*, molybdenum and rhenium trioxides, arsenic, selenium, tellurium, and tantalum oxides, as well as tungsten hydroxides). The possibility appears for the development of efficient technologies for extraction of valuable components from poor ores or from burrows and others. Since the mass transfer of relatively volatile substances from the reaction mixture is accompanied by permanent processes of vaporization and condensation, in the case of mass transfer of several products from the initial mixture, they are spatially separated depending on the degree of their volatility, adsorption coefficients, *etc.*

It is very helpful for providing the mass transfer of metal compounds in FC processes that the reaction space is nonuniform not only by temperature but also by the nature of the gas medium surrounding the condensed phase. In the zone to the left from the combustion front (see Fig. 2) the gas medium possesses the properties of an oxidant (the presence of oxygen), and in the zone to the right it has the reducing properties (the gas phase contains almost no oxygen but a large amount of carbon oxides). This property can be used for the optimization of extraction of compounds of this or another metal from the mixture. Thus, the process considered can become selective, when only one of the metals present in the charge is extracted from a mixture of compounds of diverse metals.

We have shown[31] that for the combustion of a molybdenite (MoS_2) concentrate the combustion process can successfully be performed even without an additional fuel, but adding only an inert component to provide the intrinsic mode of superadiabatic combustion. To burn systems containing small amounts of molybdenum sulfide (wastes of mining-concentrating industry from the production of molybdenite), it is necessary to add a solid fuel. The regularities of the FC process and mass transfer of molybdenum-containing products for the MoS_2—carbon systems during air filtration were experimentally studied. The results showed that molybdenite can be burned in the superadiabatic mode with the formation of molybdenum trioxide of high-purity. The conditions for the nearly complete extraction of molybdenum from systems with a low content of molybdenum sulfide in the FC mode were found.

In addition, we studied the methods for molybdenum extraction from spent aluminosilicate catalysts alloyed with nickel (these are large-tonnage wastes from petrochemical synthesis containing 11—12% MoO_3).[32] For stable propagation of the combustion wave in this system, it is necessary to add some amount of a fuel to the charge, for example, coal, because the catalysts themselves contain no combustible components. The stable combustion modes are observed at coal content in the charge 3—10%.

A residue was formed on "cold" walls of the reactor during experiments on laboratory equipment. The optical microscopic studies in transmitted and polarized light showed that the residue collected from the reactor walls was a transparent crystalline powder consisting of needle-like particles with the length from 50—100 μm to 1—2 mm and a thickness of 10—20 μm. According to the analysis, the concentration of MoO_3 in the crystals is >95%. The maximum yield of molybdenum trioxide in the sublimate (up to 80%) was achieved at carbon content 5—6%. The temperature of the combustion front was 850—950 °C. The increase in the carbon fraction in the charge to 8—10% and, accordingly, in the temperature of the front to 1000—1340 °C resulted in a sharp decrease in the yield of MoO_3. This is related, most likely, to the fact that with an increase in the carbon fraction the thermal structure of the combustion wave changes and the heated zone gains more reductive properties. Another possible reason for the decrease in the yield of MoO_3 can be a change in the structure of aluminosilicate frame of the matrix at 1000—1340 °C and, as a consequence, in worsening of the conditions of molybdenum mass transfer.

If we speak about such metals, whose reduced form is more volatile (for example, zinc), the FC should be organized in the combustion wave mode with $\delta > 1$ (see Fig. 3, *b*). Then the zinc compounds will be reduced in front of the combustion front in the heated reduction zone and will move as zinc vapor ahead of the FC front.

What combustion mode should be chosen for the mass transfer of this or another metal? This can preliminarily be determined by the results of calculation of the equilibrium concentrations of the reaction products. As an example, we present the results of the thermodynamic analysis of the system containing a metallurgical slime with a large amount of iron and zinc.

The possibility of extracting useful metals from the products, which were accumulated in Russia in an amount of many millions of tons, was studied.[33] However, economically reasonable processing methods have not yet been developed. One of the samples of real wastes containing (%): Fe (28.4), Zn (12.05), Ca (5), Si (2.65), Mn (1.26), Pb (1.07), Mg (0.86), Al (0.2), Cr (0.16), Cu (0.11), and P (0.037) was studied. The analysis was carried out for the isothermal system at atmospheric pressure varying the temperature (from 500 to 1300 °C) and the mass fraction of oxygen. The major conversion products under specified conditions were determined by the calculation results. Zinc and lead give the most volatile compounds that can be extracted from the mixture. In the oxidation zone all the zinc exists in the form of condensed ZnO and, therefore, the possibility of its extraction from the mixture is very low. However, in the reductive medium, beginning from a certain temperature, zinc compounds are reduced to free metal, which is transferred to the gas phase (the vapor pressure at 927 °C is 0.00002 MPa and that at 1027 °C is 0.0001 MPa). The enhancement of the reductive properties of the medium substantially decreases the temperature at which a large portion of zinc already exists in the gaseous state (*cf.* Fig. 9, *b* and *c*) and, therefore, facilitates the process of zinc extraction.

As for lead,[33] a considerable amount of volatile oxides is formed in the oxidation zone and at ~1000 °C almost 50% lead are transferred to the gas phase (below ~1400 °C these are mainly Pb_2O(g) and PbO(g), see Fig. 9, *a*). Gaseous lead appears in the reductive medium beginning from ~800 °C, and at temperatures higher than 1200 °C it becomes almost the only gaseous lead-containing product (the pressure vapor at 927 °C is 0.00016 MPa, and at 1027 °C is 0.0028 MPa). It should be mentioned that, unlike zinc, the system with lead remains almost unchanged with an increase in the reduction potential of the medium (the curves in Fig. 9, *b* and *c* are very similar).

Thus, it was theoretically shown that zinc and lead can be extracted from the indicated type of metallurgical slime by the FC wave. Zinc can be extracted using the high-temperature reduction zone, which exhibits the structure with $\delta > 1$ during FC wave propagation. Zinc can be extracted by the combustion wave of both the first and second type. In the first case, gaseous oxides undergo mass transfer. In the second case, the mass transfer of gaseous lead occurs. The thermodynamic analysis shows that other metals, which are present in the product under study, form nearly no gaseous products.

It was experimentally shown on laboratory devices for the zinc-containing systems that the degree of extraction of ZnO to the sublimate depends on the initial zinc content in granules of the zinc-containing component of the charge.[34—36] The change in the zinc content at various heights of the charge in the course of combustion was observed for the FC of systems with a high zinc content (10—30% ZnO). At small gas flow rates (<0.1 m s^{-1}) the ZnO content in the charge decreases in the direction of the oxidant flow, whereas at high flow rates (0.4—1.7 s^{-1}), on the contrary, the ZnO content increased, which confirms the mass transfer process of the zinc-containing combustion products. The degree of extraction of zinc-containing products to the sublimate increases with an increase in the maximum temperature in the combustion wave and can range from 3.0 to 34%.

For the zinc-containing systems with a small amount of zinc in the charge (2—4%), the degree of extraction of the zinc-containing combustion products to the sublimate depends on the flow rate of the oxidant and the fuel content and, in several cases, can reach 100% at low flow rates of the oxidant.

The mathematical simulation of the influence of the gas flow on the mass transfer of solid volatiles in the heterogeneous systems was performed for the zinc-containing compounds.[37] The formation of the solid and gas phases for the sublimation ZnO(s) ↔ Zn(g) with allowance for the transfer of the volatile product with the flow was calculated by mathematical simulation (the program package in the MATLAB language in the Windows medium). The mathematical description of the model contains the system of the following equations: equations of state of the gas phase, equations of mass conservation of the components, and equations of the temperature dependences of the heat capacity and diffusion of the phases. The three-dimensional *x*,*t*-characteristics of the content of components in the gas and solid phases were obtained.

Up to now we considered only the systems containing small amounts of metal compounds along with a mixture of a fuel (for instance, coal) with an inert material and air,

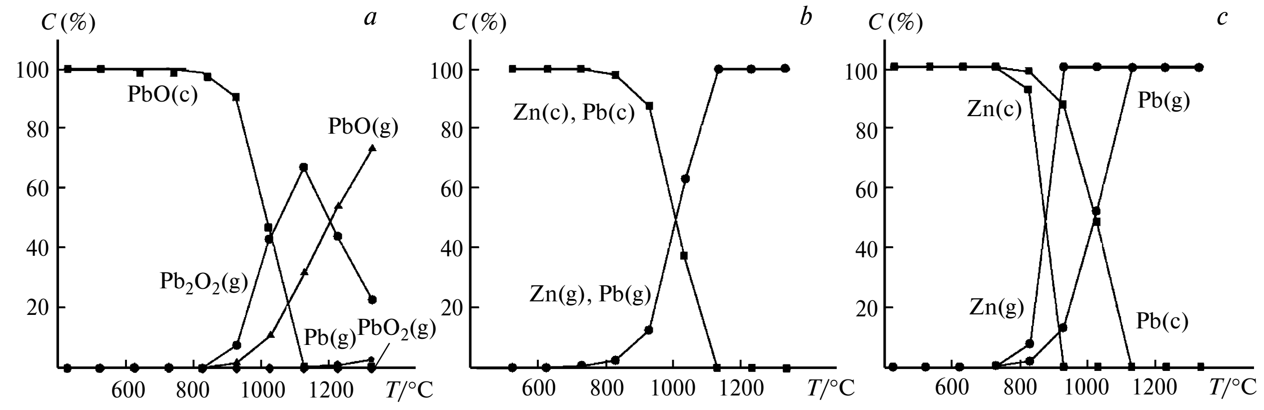

Fig. 9. Main compounds containing Zn and Pb in diverse media: in the oxidizing medium with an oxygen excess (*a*) and in the reducing medium where the most part of carbon exists as CO (*b*) and free carbon (*c*).

i.e., the thermodynamic system C—N—H—O—M. However, there are few metals with a relatively high pressure of saturated vapor at temperatures below 1200—1300 °C (*i.e.*, economically reasonable for an industrial technological process). For the case of free metals or their oxides, these are nearly only Zn, Cd, Hg, Te, Tl, Se, As, W, and Re. The list of metals capable of being extracted from complicated mixtures during FC can be multiply expanded if chlorine or fluorine would be introduced into the system, *i.e.*, if we assume the formation of chlorides or fluorides, the most part of which are very volatile at temperatures below 1200 °C. However, along with the extension of potential possibilities of the FC in the solution of the problem of metal extraction, the presence of chlorine, the more so fluorine, creates additional problems for providing purity of the environment. In addition, a question arises about the corrosion resistance of the apparatus to hydrogen chloride at high temperatures.

We only recently started to study the FC processes in the systems simultaneously containing metals and chlorine[38] and, hence, this problem is not discussed in detail in this paper.

It should only be emphasized that all processes described above can be carried out in a standard furnace mode heating all the reaction mixture in a medium of the corresponding gas (depending on the type of extracted metal and the nature of a metal-containing compound extracted from the charge, this gas can be air, carbon monoxide, hydrogen, *etc.*). However, the energy amount consumed in this case will be multiply greater than that for the same processes to occur in the superadiabatic FC modes, because the permanent heat recuperation in the FC wave and the fact that only a small portion of the reaction mixture is heated determine the high energy efficiency. Thus, the mass transfer of the evaporated component distributed in the initial fuel to the gas followed by its extraction by known method can be performed due to the FC wave using blowing with a large volume of the gas flow. Energy expenses to the mass transfer in the wave process are considerably lower than those to heating of all the fuel mixture, which provides the economically reasonable development of extraction technologies on the basis of mass transfer in the FC wave.

3.3. Waste treatment. All created by the mankind is transformed into combustion products by these or other routes. In past epochs, the most part of materials produced by people was biodegradable. The situation changes when a larger amount of chemical industry products, plastics, and other synthetic materials, which decompose many times more slowly and upon decomposition sometimes yield very toxic compounds, begin to enter wastes. Dealing with wastes inevitably becomes more and more expensive. It is necessary to prevent contamination of subsoil waters and soil with products of uncontrolled decomposition of wastes.

Waste accumulation in dumps (or in equipped grounds) for a very long period withdraws considerable territories from natural and economical turnover. The number of half-legal and completely unauthorized dumps grows everywhere. Ecological danger of the release of the "dump gas" (methane and carbon dioxide) appeared during dump putrefaction has been realized in the recent years. In addition, dumps undergo periodical self-ignition even if security measures are thoroughly fulfilled, and huge amounts of extremely toxic contaminants are released in conflagrations.

Waste burning, especially for the uncontrolled combustion of dumps, emerges a huge amount of toxic substances in atmosphere. Polychlorinated dibenzodioxines and dibenzofurans (dioxines), which possess powerful mutagenic, immunodepressive, cancerogenic, teratogenic, and embryotoxic effect, are presently considered to be most dangerous.[39]

However, the thermal treatment of wastes remains very attractive, in spite of considerable expenses associated with the multistage treatment of wastes to a normative level. Waste combustion is attractive due to a multiple decrease in the volume of wastes, decomposition of hydrocarbons, including toxic, and the possibility of producing a considerable amount of energy released upon the combustion of the carbon residue.

Numerous technologies for thermal waste treatment were developed to the present time. The technology based on FC in the countercurrent modes is one of the most promising direction, because it combines the efficient solution of both energy and ecological problems.[6] This technology can be used even for the processing of some types of radioactive wastes.[40]

Dealing with solid municipal wastes (SMW) is a very urgent problem of the modern civilization. For the purpose of studying the possibility of using the superadiabatic combustion method for SMW treatment, we carried out the experimental study on compositions modeling this type of wastes. Four model compositions imitating different types SMW were proposed on the basis of analysis of the data on the SMW composition. The characteristics of these model compositions are given in Table 2. An enlarged laboratory reactor with a diameter of 160 mm was used for the study of gasification and afterburning processes. In all experiments, the temperature of the process was continuously measured and samples of the gaseous product were periodically taken for the subsequent determination of its composition. The carbon content in the ash residue was analyzed after burning. The elemental analysis of pyrolysis resins was carried out by the combustion method in specially pure oxygen followed by the absorption of H_2O, CO_2, SO_2, HCl, and unreacted O_2 and by the measurement of the N_2 volume.

The experimental results showed that all studied types of model wastes can successfully be gasified in the superadiabatic FC mode. The high productivity by SMW and the

Table 2. Characteristics of compositions modeling SMW for burning in the enlarged laboratory reactor

SMW	Composition/g kg^{-1}								Moisture content	Sol content	Elemental composition (%)[a]					ΔH_c[b]
	Paper	Food waste	Textile	Plastics	Wood	Metals	Ceramic	Water	%		C	H	O	N	S	
1	372	70[a]	3	59	5	71	23	398	47.3	16.62	19.32	2.76	13.89	0.28	0.09	6700
2	248	586	12	85	8	10	14	38	55.0	8.58	20.74	3.05	11.97	0.50	0.11	7490
3	328	338	25	106	10	13	31	150	48.4	11.14	23.13	3.39	13.42	0.36	0.11	8650
4	311	462	36	111	24	11	45	0	42.8	12.66	25.52	3.72	14.57	0.51	0.14	9820

[a] Wastes dried to a moisture content of 30%.

[b] Heat of combustion/kJ kg^{-1}.

high chemical efficiency of gasification can be attained already in the scale of a laboratory reactor. A considerable fraction of the calorie content of the gaseous product falls on the calorie content of pyrolysis resins. The high quality of burning of organic components from the ash residue is provided in all cases.

In was confirmed in full accord with the earlier established facts that the process is most efficient for more high-calorie and dry wastes. The intrinsic ash content exerts no substantial effect on the occurrence of the process. The high moisture content of the treated material affects the productivity of the reactor with respect to SMW and, in addition, high vapor content in the gaseous product impedes its burning at the stage of energy production.

The performed study of the influence of the change in the gaseous oxidant consumption on the gasification parameters also confirmed that the efficiency of the process with respect to SMW is nearly linear with respect to the gaseous oxidant consumption. Therefore, the process is reliably controlled by the supply of air and vapor to the reactor. It should specially be mentioned that the gasification process only stops for a while even at the complete cessation of the gaseous oxidant supply. If the reactor has no time to cool down within the time of stopping, the combustion wave is formed again with the renewal of air supply. In this sense, this technology is maximum resistant to various types of extraordinary situations.

In addition to SMW, the treatment of many types of industrial wastes is a serious problem.

The development of the technology for combined treatment of wastes typical of the industry of city economy and being ecologically dangerous to some extent was demonstrated using as an example a series of particular problematic industrial wastes of some enterprises of the Moscow region. The list of presented wastes included greasy sawdust, thickened oil-slimes from walls of sedimentation tanks of sewage disposal plants, worked-out filtration load of purification of rain waters and automobile washing, filtration load and precipitate of hydrofilters of chambers of automobile coloring, oiled rags, and overdue paintwork materials in the dry and paste states.

The results of determination of the physicochemical properties (thermogravimetric, chromatographic, mass-spectrometric, qualitative, and quantitative analyses) showed that, in some cases, it is unreasonable to neutralize particular types of wastes separately by the proposed method. The samples of industrial wastes presented in this example can efficiently be neutralized by their combined treatment in various combination. When choosing combinations and ratios of components, it is necessary to take into account their properties and volumes formed in industrial enterprises of the region. As a rule, a set of wastes appropriate for similar treatment can always be found both in one enterprise and in several adjacent plants.

It was shown for this example that the proposed method provides high purity of wastes of gaseous consumption products to atmosphere during the neutralization of wastes. Thus, the method described allows one not only to get rid of harmful, ecologically dangerous wastes but to use them for the production of thermal or electric energy.

The FC mode with superadiabatic overheatings can be used for the treatment of solid fuels and for the combustion of combustible liquids. In this case, an inert material plays the role of the porous frame and the liquid fuel can get into the zone of chemical reactions with the solid inert material impregnated or covered with a fuel layer. As the combustion wave approaches, the solid material is gradually heated and the liquid is evaporated. When rather large pieces of the porous solid material are impregnated with a considerable amount of the combustible liquid, on fast heating a portion of the liquid has no time to evaporate until the piece gets into the oxygen zone. This liquid evaporated in the high-temperature oxygen zone will immediately be oxidized maintaining the temperature in the combustion wave. The rest portion of the combustible liquid will be removed with the gas flow to the cold zone and condensed into aerosol in the same way as the pyrolysis products formed by the FC of the pyrolyzed fuel.

We proposed efficient and ecologically pure treatment of oil wastes and oil-slimes by the FC method with superadiabatic overheatings.[41] The method proposed is predominantly designed for processing of slimes containing heavy liquid or solid hydrocarbons, solid incombustible substances, water, *etc*. These can be wastes of industrial oils formed upon the thermal or mechanical treatment of metals and unsuitable for regeneration, including worked-out and partially decomposed, containing asphaltoresinous substances along with oils, cinder, other mechanical admixtures, and water, as well as crude oil spills mixed with mineral particles, oil-slimes and slimes of oil storages, bituminous sands, *etc*.

Ecologically and economically appropriate methods for utilization of similar wastes are presently absent. Their utilization is usually aimed at either burning hydrocarbons composing these wastes (in the case where they have no other practical value except for the use of the heat of their combustion) or separating hydrocarbons from mineral admixtures for the subsequent use.

Direct burning of these wastes is usually impeded by the fact that the high viscosity and mechanical admixtures in the composition do not allow one to use the known technical solutions, in particular, sputtering on sprayers and torch burning. Hydrocarbons cannot be mixed well with oxygen because of a low volatility and the presence of a considerable amount of mechanical admixtures, which results in the appearance in the flame of oxygen-deficient zones, where soot and other products of incomplete combustion are abundantly formed. The possible high moisture content creates additional difficulties, because it decreases the burning temperature. In addition, the most nonvolatile hydrocarbons cannot completely be removed, as a rule from the solid residue of the treatment and, hence, the problem of further neutralization or burial of solid treatment products.

The method based on the superadiabatic FC mode makes it possible, depending on the purpose of performing the process, to provide either ecologically pure and complete combustion of wastes, which cannot be regenerated, with the utilization of the released heat or separation of liquid hydrocarbons from mineral admixtures almost without additional energy expenses, and the solid treatment products formed (sand, stones, cinder, *etc*.) contain no organics, including cancerogens.[42]

This method of treatment approved on the laboratory devices of the Institute of Problems of Chemical Physics (Russian Academy of Sciences) was accomplished in the pilot scale at the EZTM public corporation (Elektrostal, Moscow Region) for processing of oil wastes of an engineering production. The structure was developed and a pilot installation was created with the tight cooperation with experts of the EZTM public corporation. A series of debugging launchings was performed on this plant, then this installation has successfully been used for the regular treatment of thermal production oil wastes formed at the EZTM public corporation.

The possibility of the treatment of liquid combustible wastes by the FC method in the superadiabatic mode was shown for oil wastes of the engineering production. The pilot installation for the ecologically safe processing of combustible wastes from the engineering production is the first example of successful manufacturing application of the developed technologies based on FC in the superadiabatic modes.

In recent years, plastic wastes form a considerable fraction of the overall waste flow. According to the estimates, in Europe 7 mln tons of plastic wastes annually get into the city garbage. If such "long-term" wastes as old automobiles, domestic and office equipment are taken into account, the total amount of plastic wastes is ~15 mln tons annually. If paper and cardboard are rather rapidly mixed with ground and decompose under the effect of bacteria, then plastic is nearly eternal. Many plastics are dangerous when using for food purposes and upon combustion. During combustion polyvinylchloride from which many widely consuming goods are produced (linoleum, leather-substitutes, plastic bottles, wire insulation, and others) forms many very toxic compounds.

The gasification method in the filtration mode with superadiabatic overheatings developed at the Institute of Problems of Chemical Physics (Russian Academy of Sciences) for the utilization of various types of wastes and substandard fuels can successfully be used for the treatment of polymer materials, which cannot be reused. The experimental data obtained are necessary for the scientific substantiation of polymer treatment by the FC technology.

Polyethylene is the most part of plastic wastes. We showed that the method of treatment in the FC wave can successfully be used even for compositions with non-coking polymer (for example, polyethylene) without an additional fuel.[43] The thermal structure of the wave with the steep front edge ($\delta < 1$) is observed in this case. The behavior of plastic in the combustion wave with the thermal structure at $\delta \sim 1$ and $\delta > 1$ can be studied introducing an additional fuel into the composition.

For the FC of the mixture polyethylene—coal—inert material, the characteristics of the process depend on the type of the thermal structure of the wave. For the case of FC waves with $\delta > 1$ (coal content 30% and more), the polymer was completely pyrolyzed and removed with the gas flow without getting into the oxidation zone and exerting no effect on the characteristics of the FC process (burning temperature and composition of gaseous products). At a small coal content (10%), a noticeable portion of the polymer (~10%) got into the oxidation zone. The fraction of burned polyethylene was independent of its content in the initial composition and increased with a decrease in the coal content.

For the FC of mixtures with polyurethanes, the characteristics of the process also depend on the type of the wave structure, but the influence of the amount of plastic on the characteristics of the combustion process is considerably stronger, because the thermal destruction of polyurethane always results in the formation of coke residue increasing heat release in the combustion wave. Experiments on the FC of a mixture of plastics with a solid inert material confirmed the stability of the combustion wave at the polymer content up to 40%.

Automobile tires, as well as other rubber technical units, are a well combustible material with a high heat of combustion. As other polymer materials, they undergo thermal destruction on heating. Among the materials present in automobile tires, the polymer itself, whose wastes can find use, is of the main value. The metallic cord, tires, and mineral additives, in particular, zinc oxide, which is present in rubber, have considerably lower cost.

The utilization of automobile tires by burning with the formation of the thermal or electric energy remains reasonable if ecological norms and rules are fulfilled. In this respect, the FC with superadiabatic overheatings has a considerable advantage over other thermal methods of treatment. The completeness of combustion and purity of wastes are due to the two-stage process (gasification followed by the combustion of the gaseous product formed). To perform the process, it is not necessary to divide the material, separate the cord, and use other methods of raw materials preparation. It is enough to cut the tire into pieces, which can conveniently be loaded into the gasifier. The efficiency of thermal energy utilization is caused by the energy device used, which is, as a rule, a standard serial equipment.

Under laboratory conditions, we checked the possibility of application of the FC method to processing of automobile tires. The results of the studies suggest that the production on tire processing by the FC method can be a simple and efficient solution distinguished by low expenses and fulfillment of all ecological norms.

The thermal treatment of slime deposits is being developed actively in the recent years. The main difficulty appeared during the thermal treatment of slimes from the filtration fields consists in large energy expenses to drying and heating of a material with high moisture content. The improvement of thermal treatment methods can be performed using the two-stage scheme of combustion of the slime deposit by gasification followed by burning of the obtained gaseous product under standard devices of a boiler working on natural gas. The use of the gasification method in the superadiabatic consumption mode with a high energy efficiency makes it possible to eliminate the main drawbacks of the thermal treatment methods used. All advantages of the thermal treatment methods are retained, namely:

— the process is transformed from energy-consuming into energy-producing with energy delivery to consumers;

— the absence (or a sharp decrease in the content) of dust particle during combustion in fire-chambers of boilers diminishes requirements imposed on the gas treatment system (for example, excluding or decreasing the parameters of electric filters) and impedes the formation of dioxines, which also substantially simplifies the purification of smoke fumes;

— the requirements imposed on the preparation of the initial raw materials to provide the stable work of the gasifier; and

— prolonged residence times of solid combustion products in the high-temperature zone in oxygen excess almost exclude the appearance of unburned carbon and organics in ash.

It seems reasonable to process thus the slime deposit preliminarily released to a moisture content of ~60%. At present industries of various countries produce special mechanisms for mechanical dehydration of slime deposits. The gasification process in the superadiabatic mode should be carried out in a dense layer in reactor of the vertical shaft furnace type, where the treated material and a mixture of air with steam are fed in the countercurrent. Since the process is carried out at relatively low linear gas flow rates, the gaseous product contains almost no priming ash.

The possibility of using the FC method in superadiabatic modes for the combustion of slimes from filtration fields was experimentally checked on pilot installations of various scales. Based on the data obtained, we calculated several variants of technological complexes for processing of slime deposits from filtration fields. The technological and economical estimate of the proposed production were performed, and the mass and energy flows were calculated.

The countercurrent FC gasifier of the industrial scale were developed and produced by the results of works of the Institute of Problems of Chemical Physics (Russian Academy of Sciences) in cooperation of the engineering enterprises. The photograph of the pilot installation at the Salyut plant (Moscow) is presented in Fig. 10. The productivity of the gasifier is 2 t h^{-1} based on processed raw materials, which corresponds to a heat power of 5—6 MW when a gaseous product is burned. The sizes of the work-

Fig. 10. Pilot installation at the Salyut plant (Moscow).

ing zone of the gasifier: diameter 1.5 m, height 7.3 m. The characteristics of ejected gas were experimentally measured and confirmed the high ecological purity of the process during SMW combustion. The concentration of dioxines in smoke fumes did not exceed $2 \cdot 10^{-10}$ g m^{-3} even without their treatment.

Conclusion

The phenomenon of spatial separation of zones of physicochemical conversion of the solid fuel analogous to the spatial separation of diverse substances in chromatography was observed in the studies of the mechanisms and regularities of the FC systems in which several reactions can occur. The separation in the space of processes of oxidation, pyrolysis, extraction of valuable products, vaporization, and condensation was established for solid organic fuels and metal-containing mixtures used as examples. These processes were found to proceed kinetically independently, and their mutual influence is determined by the concordance of mass flows.

It was shown that the main advantages of gasification in superadiabatic modes (high energy efficiency approaching 90%, the possibility of stable occurrence of the process at any ash and moisture contents of the fuel, a sharp decrease in the formation of toxic products, the absence of organics in the ash residue, *etc.*) were retained for the use of pyrolyzed fuels. The possibility to perform efficiently the following processes within one process (reactor) appears: (1) oxidation of the coke residue with oxygen with the formation of CO in combination with the endothermic reactions with water vapor affording CO and H_2, (2) pyrolysis of organic raw materials without energy feeding from the outside with the formation of liquid hydrocarbons, (3) selective extraction of valuable products; and (4) drying.

Filtration combustion in the countercurrent mode can successfully be applied to a very broad range of raw materials, mainly (and most efficiently) to various types of waste, or to substandard sources of useful chemical products, whose processing using available technologies is poorly efficient.

Based on the FC method with countercurrent, at the Institute of Problems of Chemical Physics (Russian Academy of Sciences) we developed a whole series of technologies for processing combustible wastes with both high and very low caloric value and technologies for the extraction of valuable metal compounds from unconventional sources. This provides ecological purity of the process, and the possibility of efficient use of the thermal energy of combustion of wastes appears.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 09-03-00623a), the Presidium of the Russian Academy of Sciences (Program No. 3 "Chemical Aspects of Power Engineering"), and the Council on Grants at the President of the Russian Federation (program for State Support of Young Scientists PhDs, Grant MK-3125.2011.3).

References

1. A. P. Aldushin, A. G. Merzhanov, in *Rasprostranenie teplovykh voln v geterogennykh sredakh* [*Heating Wave Propagation in Heterogeneous Media*], Ed. Yu. Sh. Matros, Nauka, Novosibirsk, 1988, p. 9 (in Russian).
2. V. S. Babkin, V. P. Drobyshevich, Yu. M. Laevskii, S. I. Potytnyakov, *Dokl. Akad. Nauk SSSR*, 1982, **265**, 1157 [*Dokl. Chem.* (*Engl. Transl.*), 1982].
3. V. S. Babkin, I. Vezhba, G. A. Karim, *Fiz. Goren. Vzryva* [*Combustion, Explosion and Shock Waves*], 2002, **38**, No. 1, 3 (in Russian).
4. A. P. Aldushin, B. S. Seplyarskii, *Dokl. Akad. Nauk SSSR*, 1979, **249**, 585 [*Dokl. Chem.* (*Engl. Transl.*), 1979, **249**].
5. E. A. Salgansky, V. M. Kislov, S. V. Glazov, A. F. Zholudev, G. B. Manelis, *Fiz. Goren. Vzryva*, 2008, **44**, No. 3, 30 [*Combustion, Explosion and Shock Waves* (*Engl. Transl.*), 2008, **44**, No. 3, 273].
6. G. B. Manelis, E. V. Polianchik, V. P. Fursov, *Khimiya v interesakh ustoichivogo razvitiya* [*Chemistry in Interests of Stable Development*], 2000, **8**, 537 (in Russian).
7. A. B. Sheinman, K. K. Dubrovai, P. A. Sorokin, M. M. Charygin, S. L. Zaks, K. B. Zinchenko, *Neftyanoe khozyaistvo* [*Petroleum Economy*], 1935, No. 4, 21 (in Russian).
8. E. W. Voice, R. Wild, *Iron Coal Trade Review*, 1957, **175**, 841.
9. N. M. Babushkin, V. N. Timofeev, *Sb. Nauch. Trudov VNIIMT* [*Collection of Scientific Works of VNIIMT*], Sverdlovsk, 1962, **7**, 3 (in Russian).
10. N. M. Babushkin, V. N. Timofeev, *Sb. Nauch. Trudov VNIIMT* [*Collection of Scientific Works of VNIIMT*], Sverdlovsk, 1962, **7**, 16 (in Russian).
11. O. V. Kiselev, Yu. Sh. Matros, N. A. Chumakova, in *Rasprostranenie teplovykh voln v geterogennykh sredakh* [*Heating Wave Propagation in Heterogeneous Media*], Ed. Yu. Sh. Matros, Nauka, Novosibirsk, 1988, p. 145 (in Russian).
12. A. A. Bezdenezhnykh, A. P. Orlov, N. V. Timofeev, V. E. Mungalov, Yu. A. Grigor´ev, *Teoreticheskie osnovy khimicheskoi tekhnologii* [*Theoretical Foundations of Chemical Technology*], 1976, **10**, 219 (in Russian).
13. A. G. Merzhanov, *Vest. Akad. Nauk SSSR* [*Bulletin of the Academy of Sciences of the USSR*], 1976, **10**, 76 (in Russian).
14. A. G. Merzhanov, A. K. Filonenko, I. P. Borovinskaya, *Dokl. Akad. Nauk SSSR*, 1979, **228**, 892 [*Dokl. Chem.* (*Engl. Transl.*), 1979, **228**].
15. G. B. Manelis, *Priroda* [*Nature*], 1996, **3—4**, 43 (in Russian).
16. E. A. Salgansky, V. P. Fursov, S. V. Glazov, M. V. Salganskaya, G. B. Manelis, *Fiz. Goren. Vzryva*, 2003, **39**, No. 1, 44 [*Combustion, Explosion and Shock Waves* (*Engl. Transl.*), 2003, **39**, No. 1].
17. D. Lempert, S. Glazov, G. Manelis, in *Mass Transfer in Multiphase Systems and its Applications*, InTech, 2011, p. 483.
18. A. P. Aldushin, I. E. Rumanov, B. J. Matkowsky, *Combustion and Flame*, 1999, **118**, 76.
19. E. A. Salgansky, *Ezhegodnik IPKhF RAN* [*Year-Book of the Institute of Problems of Chemical Physics, Russian Academy of Sciences*], 2004, **1**, 132 (in Russian).

20. G. B. Manelis, E. A. Salgansky, V. P. Fursov, S. V. Glazov, M. V. Salganskaya, *Nauka — Proizvodstvu* [*Science for Industry*], 2001, **8**, 28 (in Russian).
21. I. I. Amelin, N. N. Volkova, A. A. Zhirnov, A. P. Alekseev, A. F. Zholudev, E. V. Polianchik, G. B. Manelis, *Khim. Fiz.*, 2010, **29**, No. 3, 76 [*Russ. J. Phys. Chem. B* (*Engl. Transl.*), 2010, **4**, 265].
22. I. I. Amelin, N. N. Volkova, A. A. Zhirnov, A. P. Alekseev, E. V. Polianchik, G. B. Manelis, *Dokl. Akad. Nauk*, 2008, **421**, 65 [*Dokl. Chem.* (*Engl. Transl.*), 2008, **421**].
23. E. A. Salgansky, V. P. Fursov, S. V. Glazov, M. V. Salganskaya, G. B. Manelis, *Fiz. Goren. Vzryva*, 2006, **42**, No. 1, 65 [*Combustion, Explosion and Shock Waves* (*Engl. Transl.*), 2006, **42**, No. 1, 1].
24. S. V. Glazov, E. A. Salgansky, V. M. Kislov, M. V. Salganskaya, A. F. Zholudev, *Fiz. Goren. Vzryva,* 2010, **46**, No. 3, 52 [*Combustion, Explosion and Shock Waves* (*Engl. Transl.*), 2010, **46**, No. 3, 286].
25. M. V. Salganskaya, S. V. Glazov, E. A. Salgansky, V. M. Kislov, A. F. Zholudev, G. B. Manelis, *Khim. Fiz.*, 2008, **27**, 20 [*Russ. J. Phys. Chem. B* (*Engl. Transl.*), 2008, **2**, 71].
26. E. A. Salgansky, V. M. Kislov, S. V. Glazov, A. F. Zholudev, G. B. Manelis, *Fiz. Goren. Vzryva*, 2010, **46**, No. 5, 42 [*Combustion, Explosion and Shock Waves* (*Engl. Transl.*), 2010, **46**, No. 5, 528].
27. E. A. Salgansky, E. V. Polianchik, G. B. Manelis, *Tez. dokl. V Mezhdunar. simp. "Gorenie i plazmokhimiya"* [*Proc. V International Symposium "Combustion and Plasmochemistry"*] *(Kazakhstan, Almaty, September 16—18, 2009)*, Almaty, 2009, p. 142 (in Russian).
28. V. M. Kislov, S. V. Glazov, N. A. Chervonnaya, L. I. Patronova, M. V. Salganskaya, G. B. Manelis, *Khim. Tverd. Topliva* [*Solid Fuel Chemistry*], 2008, No. 3, 9 (in Russian).
29. Pat. RF 2 278 185; *Byul. Izobr.* [*Invention Bulletin*], 2006, No. 17 (in Russian).
30. A. S. Rozenberg, D. B. Lempert, L. A. Grigoryan, A. S. Medvedev, G. B. Manelis, *Dokl. Akad. Nauk*, 2005, **405**, 493 [*Dokl. Chem.* (*Engl. Transl.*), 2005, **405**].
31. A. S. Rozenberg, D. B. Lempert, A. S. Medvedev, L. A. Grigoryan, I. Yu. Gudkova, L. G. Zemlyakova, G. B. Manelis, *Khim. Fiz.*, 2006, **25**, No. 2, 50 (in Russian).
32. A. S. Rozenberg, L. A. Grigoryan, I. Yu. Gudkova, L. G. Zemlyakova, D. B. Lempert, A. S. Medvedev, G. B. Manelis, *Khim. Fiz.*, 2006, **25**, No. 5, 39 (in Russian).
33. I. Yu. Gudkova, D. B. Lempert, A. S. Berestov, V. G. Dyubanov, *Tez. dokl. 2-oi konf. po fil´tratsionnomu goreniyu* [*Proc. 2nd Conference on Filtration Combustion*] *(Chernogolovka, Moscow Region, October 20—25, 2010)*, Chernogolovka, 2010, 146 (in Russian).
34. S. I. Soglasnova, A. S. Rozenberg, D. B. Lempert, *Khim. Fiz.* [*Chemical Physics*], 2009, **28**, No. 7, 60 (in Russian).
35. A. S. Rozenberg, L. A. Grigoryan, I. Yu. Gudkova, D. B. Lempert, G. B. Manelis, *Khim. Fiz.* [*Chemical Physics*], 2009, **28**, No. 9, 62 (in Russian).
36. A. S. Rozenberg, L. A. Grigoryan, I. Yu. Gudkova, D. B. Lempert, G. B. Manelis, *Khim. Fiz.* [*Chemical Physics*], 2009, **28**, No. 10, 52 (in Russian).
37. A. C. Rozenberg, D. B. Lempert, *Tez. dokl. XVIII Simp. "Sovremennaya khimicheskaya fizika"* [*Proc. XVIII Symposium "Modern Chemical Physics*] *(Tuapse, September 25—October 2, 2006)*, Tuapse, 2006, 228 (in Russian).
38. E. M. Balabaeva, L. A. Korshunova, G. B. Manelis, E. V. Polianchik, M. V. Tsvetkov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2009, **76**, No. 8, 190 (in Russian).
39. L. A. Fedorov, in *Dioksiny kak ekologicheskaya opasnost´: retrospektiva i perspektiva* [*Dioxines As Ecological Danger: Retrospective and Perspective*], Nauka, Moscow, 1993, p. 126 (in Russian).
40. A. A. Semenov, B. V. Safronov, A. P. Chukanov, E. V. Polianczyk, G. B. Manelis, S. V. Glazov, I. A. Revelsky, E. S. Brodsky, E. N. Kapinus, *Fusion Science and Technology*, 2010, **58**, 625.
41. Pat. RF 2 116 570; *Byul. Izobr.* [*Invention Bulletin*], 1998, No. 7 (in Russian).
42. S. V. Glazov, G. B. Manelis, L. N. Stesik, V. P. Fursov, G. S. Yakovleva, *Mashinostroitel´* [*Mechanician*], 1996, **1**, 26 (in Russian).
43. M. V. Salganskaya, S. V. Glazov, E. A. Salgansky, A. F. Zholudev, *Khim. Fiz.* [*Chemical Physics*], 2010, **29**, No. 11, 63 [*Russ. J. Phys. Chem. B* (*Engl. Transl.*), 2010, **4**, 928].

Received March 4, 2011