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Autowave processes in the filtration combustion in counterflow systems

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Abstract. The review presents the results of studies on autowave processes of filtration combustion in counterflow systems. Specific features of these processes are described. Considerable attention is paid to mathematical modelling of combustion waves in counterflow systems and to stability analysis of filtration combustion waves. Accompanying processes including pyrolysis, evaporation and condensation of both the initial components and combustion products are considered. The applicability of filtration combustion in counterflow systems in the technologies for energy production from low-grade fuels and various kinds of waste and for extraction of metals from nontraditional sources is discussed. The bibliography includes 129 references.

I. Introduction

Autowave processes in non-isothermal conditions are interesting objects from the standpoint of both basic research and practical application. A typical example of such processes is provided by filtration combustion with accumulation of thermal energy. Here, filtration combustion means oxidation of a layer of a solid fuel during filtration of a gaseous oxidant through the fuel. This is the most widespread case of wave combustion in a heterophase system. Filtration combustion in the counterflow regimes occurs if in a system of coordinates related to the combustion front (exothermic reaction zone), counterflows of the solid fuel and gaseous oxidant interact while passing through the reaction zone and being converted in that zone with changes in the chemical composition and physicochemical properties.[1–5] Counterflow of the gas and condensed phases through the reaction zone is responsible for accumulation of energy released owing to highly intense interphase heat exchange during filtration.

The combustion temperature can be increased using heat transfer from the combustion products to initial reactants, thus making efficient combustion of even low-calorie systems possible.[6] This can be done using heat exchangers. However, industrial heat exchangers have complex design, are expensive, require regular maintenance, but the efficiency of heat exchange in them is low. It is much more convenient to carry out the process with internal heat recuperation, as in the case of filtration combustion in the counterflow regime. Owing to the counterflow of the phases, heat released in the chemical reactions is rapidly transferred to the initial reactants through highly efficient direct interphase heat exchange during filtration and there is no need for using external heat exchangers. In the case of counterflow of two phases, intense interphase heat and mass transfer in the high-temperature zone leads to the formation of a zone-type structure. Each zone corresponds to physicochemical processes determined by the steady temperature, by the properties of the medium, by reactant concentrations and other parameters.

Self-localization of conversion zones in heterogeneous reacting systems with counterflow is similar to the processes occurring in the operation of a chromatographic column except that one deals with evaporation and condensation in the former case and with sorption and desorption in the latter case. Anyway, there is an analogy between the

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mathematical descriptions of these processes of different physicochemical nature. Propagation of filtration combustion waves is accompanied by concentration of particular processes and compounds (initial reactants and products) in some part of the reactor due to different vapour tension and different behaviour of the initial reactants and intermediates in the oxidative and reductive media. The same also occurs in a chromatographic column, *viz*., each component present in the initial solution is concentrated in a narrow zone because the component–sorbent binding energies of all components are different. Also, autowave filtration combustion is characterized by automatic establishment of rigorous localization with respect to the physical (temperature profile of combustion wave) and chemical (separation of the reaction space into the oxidative and reductive zones with different products) parameters.

Pioneering scientific observations of the thermal energy concentration in a autowave non-isothermal process with the counterflow regime were reported in studies on the optimization of agglomeration† of metallurgic charge.[7] The accumulation of heat in a relatively narrow burning zone can be so high that the temperature in the combustion wave front can much exceed the adiabatic combustion temperature of the mixture calculated assuming that the initial reactant temperature equals the temperature of the environment and that the thermal effect of the oxidation of the whole mass of fuel is distributed over the entire volume of the reactor. The phenomenon of heat concentration is due to the fact that in the counterflow regime, inert components of the system are efficient heat transfer agents; consequently, the fuel and oxidant can be heated before arriving at the reaction zone. Heat from gaseous combustion products is transferred to the solid fuel while heat from the ash residue and solid combustion products is transferred to the gaseous oxidant. Therefore, such processes are often described (see, *e.g*., Refs 8 and 9) using the terms 'superadiabatic heating',‡ 'superadiabatic regime of filtration combustion' or simply 'superadiabatic combustion'.

The most interesting feature of autowave combustion processes in such systems is the nonlinear dependence of the temperature of the steady combustion wave on the thermal effect of the reaction. The temperature profile of a combustion wave of the solid fuel moving in counterflow with the gaseous oxidant is schematically shown in Fig. 1.

The rate of filtration combustion with the counterflow regime is governed by the supply rate of the reactants to the combustion zone (filtration velocity) and by the stoichiometry of the process rather than by the heat transfer rate. Also, a high-temperature zone with a high content of fuel usually appears in front of the combustion zone (on the right of the high-temperature region in Fig. 1); this favours a complete consumption of the gaseous oxidant. Behind the combustion zone (on the left of the high-temperature region) there is a zone with high content of the oxidant; this ensures completeness of combustion of the material at

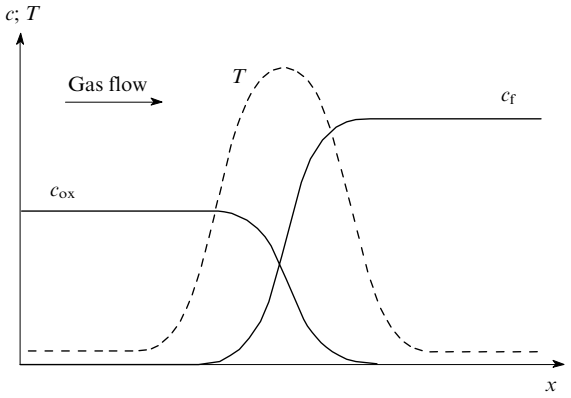


Figure 1. The temperature (T) and concentration profiles (c_{ox} is the gaseous oxidant and c_f is the solid fuel) of a filtration combustion wave for equal heat capacities of the counterflows of the solid and gas phases.

high temperatures. A steady combustion regime of carbon-containing systems in counterflow reactors usually involves the release of gaseous products of incomplete oxidation, *i.e*., the format of a combustible gas containing CO and hydrogen which can be used for both energy production and as raw materials for chemical industry. In this connection, some processes can be carried out in highly efficient and cheap regimes. This is quite attractive from the practical standpoint, especially if there is a need for combustion of low-grade fuels without additional energy expenditures or for providing high temperatures and complete combustion.

From the aforesaid it follows that autowave processes in counterflow systems are not only of scientific interest, but also promising for elaboration of various processes for efficient processing low-calorie components and energy production. Studies on the title subject are mainly carried out by researchers from the scientific school headed by Academician N N Semenov. They work in domestic institutes including the Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences (ICKC SB RAS) in Novosibirsk; the Institute of Problems of Chemical Physics, Russian Academy of Sciences (IPCP RAS) and the Institute of Structural Macrokinetics, Russian Academy of Sciences (ISMAN) in Chernogolovka, Moscow Region. Also, there is research activity at the A V Lykov Institute of Heat and Mass Transfer, National Academy of Sciences of Belarus, in Minsk.

Interesting theoretical and experimental studies have been reported to date. In this connection, publication of a review with thorough analysis and generalization of the results obtained seems to be topical.

II. Peculiarities of filtration combustion waves in counterflow systems

Generally the medium in front of the reaction zone represents a mixture of a condensed fuel with an inert material. Behind the combustion front, there is a porous residue containing condensed combustion products. A heterogeneous reaction between the solid fuel and gaseous oxidant in the filtration combustion wave may result in both condensed and gaseous products. The reaction scheme can be written as follows:

† Agglomeration is a thermal process of lumping components of metallurgic charge (ore fines, metal-containing ore concentrate fines, *etc*.) by their sintering to impart a desired shape and properties (composition, structure) necessary for casting work. The agglomeration of iron ore invented in the late 19th century was already widely used in the early 20th century.

‡ It should be noted that the term 'superadiabatic heating' is used to designate the concentration of heat in a relatively narrow zone.

fuel (solid) + oxidant (gas) + inert component (solid, gas) ⟶

⟶ products (solid, gas) + inert component (solid, gas)

The inert components are gases and condensed substances not involved in the oxidation and gasification reactions. These are atmospheric nitrogen, solid fuel ash, *etc*.

As mentioned above, the main distinctive feature of gasification in the superadiabatic heating regime consists in efficient recuperation of the heat released in the combustion zone due to heat exchange between the hot products and initial reactants. High content of the solid inert material in the fuel enables intense pre-heating of the gaseous oxidant during filtration to the reaction zone. Thus, not only the solid fuel, but also the oxidant appear to be heated to relatively high temperatures when entering the reaction.

A schematic of filtration combustion of a solid fuel in the counterflow regime is shown in Fig. 2. The initial reactants are heated as they move towards the reaction zone. Heat released in the reaction is transferred to the counter flow of matter; as a result, one deals with self-sustaining reaction wave propagation.

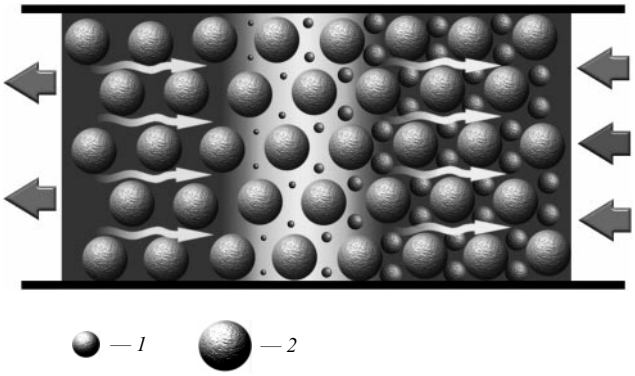


Figure 2. Schematic view of the combustion zone with superadiabatic heating of solid fuel (*1*) and inert material (*2*).
The solid material flow moves from the right to the left, and the gas flow moves from the left to the right. The high-temperature combustion zone is shown by the lighter colour of the background.

Intense heat transfer and mass transfer between the solid and gas phases during filtration and continuous counterflow of two phases significantly complicate the theoretical description of the filtration combustion wave and interpretation of experimental results.[10] Studies of such systems require taking into account not only the temperature and concentration fields, but also the dynamics of the gas flow and the specific features of chemical reactions. In addition, since the densities of the components of the system differ fundamentally, a joint consideration of processes with significantly different characteristic velocities is required. In the one-dimensional approximation, the simplest case of filtration combustion in the counterflow regime represents a chemical reaction between the counterflows of the solid fuel and the gaseous oxidant during filtration of the latter, resulting in a sole reaction product.[5] Generally, the fuel contains not only a combustible, but also an inert component which is not involved in chemical reactions. Depending on state of the reaction product (gaseous state as in, *e.g*., the oxidation carbon, or solid state as in the oxidation of aluminium), it is added to the corresponding flow of matter through the reaction zone.[10] One deals with interphase mass transfer of either the solid fuel to the gaseous product of the gaseous oxidant to the solid product.

The oxidation with heat release is localized in a narrow reaction zone. The width of the reaction zone in the heterogeneous process is determined by the particle size, temperature and reactant concentrations. Usually, the width of the reaction zone is small compared to that of the heated combustion wave zone.[11] The higher the temperature of the combustion wave (usually, it exceeds a value of 1000 °C for filtration combustion of carbon systems during filtration of air) the narrower the reaction zone. The temperature profiles (thermal structure) of combustion waves depending on reaction conditions (the fuel and oxidant concentrations) are shown in Fig. 3. The type of the thermal structure is determined by the ratio of the heat capacities of the counterflows of the gas and solid phases through the reaction front, or the parameter δ.[4, 12] The heat capacity of a phase flow equals the product of the density, heat capacity and linear velocity of the phase. Heat released in the combustion front is carried away from the high-temperature zone by the gas flow at $\delta > 1$ and by the solid phase flow at $\delta < 1$; this determines the shape of the temperature profile of the combustion wave. The heat capacities of the phase flows can be equal to each other ($\delta = 1$). In this case, thermal energy is continuously concentrated in the combustion wave. However, heating to infinite temperatures is impossible because even for adiabatic reactors there exist thermodynamic limitations reducing the heat of chemical reactions at higher temperature.[5, 12] For carbon systems, these limitations manifest themselves at temperatures above 1000 °C because CO_2 is unstable under these conditions and CO becomes the major oxidation product. Changes in the product compositions reduce

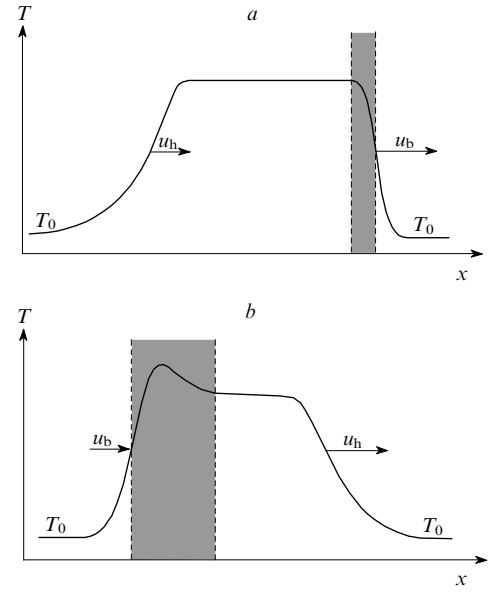


Figure 3. Temperature profiles of a combustion wave obtained assuming no lateral heat loss: $\delta < 1$ (*a*) and $\delta > 1$ (*b*).
The areas with the grey background are the reaction zones; u_b and u_h are the propagation velocities of the burning zone and thermal wave, respectively.

the heat of reaction; also, this parameter is equal to zero at ionization (atomization) temperatures. In addition, the heat capacity depends on the temperature and composition, which vary over a wide range during filtration combustion; taking into account variation of the heat capacity, the condition $\delta = 1$ cannot be simultaneously met for the entire domain under consideration.[13]

Not only the reaction zone, but also the heat exchange zones are of great importance. If the reactor is sufficiently long, heat exchange is completed and all substances are carried away at the initial temperature. Continuous accumulation of thermal energy causes expansion of the heated zone towards the gas flow or solid phase flow depending on the thermal structure of the combustion wave. The high-temperature zone expands until the heat loss (both lateral heat loss and the heat carried away from the reactor by gaseous and solid products) becomes equal to the heat release in the combustion wave front. This is the mechanism of formation of a steady filtration combustion wave. With no lateral heat loss, a steady process is only possible for incomplete heat exchange. In this case, either the gas or the solid matter is carried away from the reactor at a temperature somewhat exceeding the temperature of the environment.

The existence region of autowave regimes of carbon gasification during filtration of air (air gasification) extends largely towards low contents of fuel in the initial mixture due to the concentration of thermal energy in the combustion zone.[14] Stable propagation of a combustion wave is possible if the carbon system contains at least a few per cent of carbon. Experimentally, air gasification was observed when the carbon content was as low as 2%.[15,16]

III. Mathematical modelling of combustion waves in counterflow systems

Theoretical foundations of mathematical models for filtration combustion were mainly developed by Merzhanov and Aldushin *et al.*[1,5,12] They were the first who theoretically studied the propagation of slow combustion waves in a porous medium during the filtration of a gas. This consideration is based on the physical ideas and mathematical formalism of the classical theory of combustion. Mathematical description of filtration combustion waves is reduced to a system of differential equations of the mass and energy balances, the kinetics of combustion of the initial reactants and the formation of a condensed product, supplemented with the equations of state and filtration of components in the one-dimensional, one-temperature approximation.

It should be noted that one-dimensional treatment is inappropriate for the description of hydrodynamic phenomena; however, it can correctly describe such important steps as heat and mass transfer, heat and mass exchange and the reaction kinetics. The problem was solved by approximate methods of the classical theory of combustion, which are based on selection of various characteristic scales and on the successive zone-by-zone description of the reaction wave. In particular, the Zeldovich – Frank-Kamenetskii method[17] was used. The conclusions of approximate analysis were compared with the results of numerical solution of the systems of equations.

It was shown the under the conditions of counterflow of the gaseous oxidant and solid fuel, conversion behind the reaction front is usually complete because the oxidant concentration in the region of products equals its initial concentration. Incomplete conversion is only possible in the case of strong kinetic retardation of the reaction.[18] A criterion for distinguishing between the regimes with complete and incomplete consumption of the oxidant in the reaction was proposed.[5] Expressions for the key parameters of the process (temperature, front velocity, depth of conversion, *etc.*) for all regimes were derived.

As the gas filtration velocity increases (heat exchange coefficient decreases, particle size decreases, *etc.*), the zone of interphase heat exchange expands and the one-temperature approximation is no longer valid. In this case, one should take into account the difference between the temperatures of the phases. A two-temperature model for steady filtration combustion of solid fuel in an infinite reactor was proposed.[19]

Despite the scatter of the published values of the kinetic parameters of carbon oxidation, attempts were made to develop a correct mathematical model for the filtration combustion of carbon systems taking into account the reaction kinetics.[4,13] Such models were constructed assuming an adiabatic reactor, and they ignored detailed kinetics of actual heterogeneous processes, namely, they included only the main reactions and used generalized kinetic data for them. Nevertheless, the results of numerical calculations and experimental data were in qualitative (sometimes, quantitative) agreement.

Researchers developing mathematical models for filtration combustion usually consider one generalized exothermic reaction.[5,20,21] This makes it possible to use known kinetic parameters to calculate the key parameters of combustion. Models including two consecutive reactions are also available.[22] However, filtration combustion of carbon in oxygen-containing gas is characterized by at least an uncertainty related to the yields of the oxidation products (CO or CO_2), which cannot be described by the simplest chemical scheme. Also, many empirical (fitting) coefficients are required owing to the lack of exact kinetic data.

If the temperature in the reaction zone is high enough, filtration combustion of a carbon system depends only slightly on the kinetic parameters. Uncertainty with the yield of the carbon oxidation products can be resolved provided that the gaseous products of combustion are in thermodynamic equilibrium.[19] In this case, we get a closed system and can calculate the product concentrations and the combustion temperature provided that the composition of the solid fuel (carbon : inert component ratio) and the pressure and composition of the gaseous oxidant are specified.[23] The applicability of the models for the filtration combustion of carbon systems, based on the assumption of thermodynamic equilibrium in products, is limited by the region of stoichiometric regimes.[21] Nevertheless, the results obtained using such models can be treated as estimates in comparing the calculated combustion regimes.

Generally, the maximal temperature in the combustion wave nonmonotonically depends on the carbon content in the mixture and on the water vapour : oxygen molar ratio in the oxidant (Fig. 4).[1,5,23,24] When air is used as the gaseous oxidant, the dependence passes through a maximum in the region 17% – 25% carbon.[24] This maximum corresponds to the optimal concordance between the heat capacities of the counterflows of the solid fuel and the gas in the heat

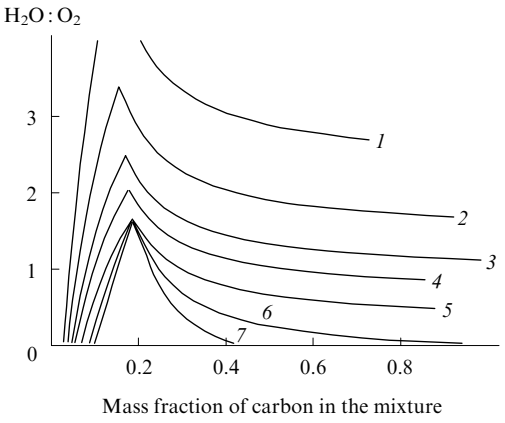


Figure 4. Temperature in the combustion front plotted *vs.* mass fraction of carbon in the mixture.[23]
T/°C: 650 (*1*), 700 (*2*), 750 (*3*), 800 (*4*), 1000 (*5*), 1500 (*6*) and 2000 (*7*).

exchange zones, which ensures maximal recuperation of heat from products to the initial reactants. The thermal structure of the combustion wave is determined by the condition $\delta < 1$ at low carbon contents (on the left of the maximum; see Fig. 3 *a*) and by the condition $\delta > 1$ at high carbon contents (see Fig. 3 *b*). Numerous experiments and the results of numerical calculations confirm the character of this dependence and the presence of a maximum temperature in the region specified above.[4, 7, 12] The dependence of the combustion temperature on the oxygen content in the gaseous oxidant exhibits a similar maximum.[25]

The addition of water vapour to the oxidant does not change the pattern of the dependence of the temperature in the combustion front on the fuel content in the mixture, but the maximum in the curve becomes less pronounced due to the occurrence of endothermic reactions. Nonmonotonic behaviour of the dependences of the combustion parameters on the fuel content predetermines uncertainties in the response of the combustion wave to the action of various factors, because changes in the combustion wave parameters depend strongly on the type of its thermal structure, *viz.*, the behaviour of a wave characterized by $\delta < 1$ is significantly different from that of a wave characterized by $\delta > 1$. For instance, the addition of an inert material to the solid fuel causes the temperature to decrease at $\delta < 1$ and to increase at $\delta > 1$. Abrupt changes in the fuel or oxidant composition on propagation of the combustion wave will be accompanied by the change in the type of its thermal structure; this may lead to a considerable local increase in the combustion temperature.[26]

Efficient conversion of the energy of the solid fuel to the energy of combustion gas§ requires that heat release in the gasification zone be minimal because the heat undergoes conversion to the potential energy of combustion gas, which can be utilized further. As mentioned above, high temperatures necessary for combustion in the counterflow regimes to occur can be attained through efficient internal heat exchange between the products and initial reactants. In the case of autowave combustion, even if the thermal effect of the reaction is low, accumulation of thermal energy may be high enough for intense gasification.[12, 15] The chemical energy efficiency (ratio of the heat of combustion of the gaseous product to the heat of combustion of the initial fuel) of air gasification of a simple carbon solid fuel cannot exceed a value of 72% (complete conversion of the whole carbon to CO). However, if the gaseous oxidant contains water vapour, the latter can react with the surface of carbon at temperatures above 800 °C. Under these conditions, the product gas is enriched with hydrogen and carbon monoxide, and the restriction imposed on the chemical energy efficiency (see above) is removed.[24] The addition of carbon dioxide to the gaseous oxidant has a similar effect. Moreover, these endothermic reactions more efficiently proceed in the regions with the highest temperatures, thus reducing the thermal stress in the reactor. When heat exchange is completed and there is no heat loss, the chemical energy efficiency of gasification can approach 100% provided that the overall thermal effect in the reaction zone tends to zero.

Figure 5 presents the plots of the energy efficiency of vapour/air gasification of carbon – inert material mixtures *vs.* (i) mass fraction of carbon in the mixture and (ii) water vapour : oxygen molar ratio in the gaseous oxidant. Calculations were carried out by the model with allowance for thermodynamic equilibrium in products.[23] In this case, the energy efficiency equals the ratio of the heat content of the gaseous products formed in the reaction of carbon with oxygen and water vapour under the filtration combustion wave conditions to the heat of combustion of the initial mixture (taking into account the energy of vaporization). For gasification of pure carbon, an increase in the water vapour : oxygen ratio in the gaseous oxidant initially leads to some increase in the energy efficiency, but then the energy efficiency decreases. The content of water vapour has much more pronounced effect on the gasification of mixtures with high content of the inert material. In particular, for mixtures containing about 80% of inert material an increase in the water vapour : oxygen ratio to nearly 1.7

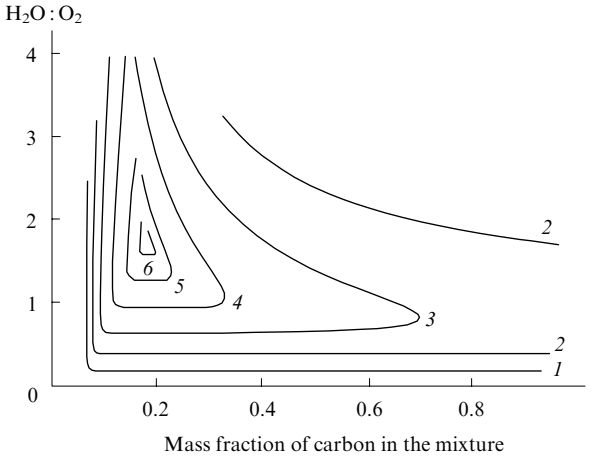


Figure 5. Calculated values of the energy efficiency for the vapour/air gasification of mixtures of carbon with an inert component.[23]
Energy efficiency: 0.76 (*1*), 0.8 (*2*), 0.84 (*3*), 0.88 (*4*), 0.92 (*5*) and 0.94 (*6*).

§ Gas leaving the reactor, which contains gasification products including pyrolysis resins in the form of fog.

causes the energy efficiency of gasification to increase to almost 0.94 (see Fig. 5). Thus, low-grade fuel with high ash content can be gasified in the superadiabatic regime more efficiently than high-grade fuel.

The one-temperature models ignore specific features of interphase heat exchange which play a significant role in filtration combustion. In this connection, models with allowance for the different temperatures of the gas phase and condensed phase were proposed. A one-dimensional non-stationary, two-temperature mathematical model for filtration combustion of a solid carbon fuel in a flow of a vapour/air mixture was reported.[24] It includes the reaction kinetics, the dependences of thermophysical parameters of the phases on the temperature and chemical composition, as well as the finite dimensions of the reactor. The process design used by the authors was proposed by Kantorovich[27] and includes the following chemical reactions:

$$2C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

$$2CO + O_2 \longrightarrow 2CO_2$$

$$C + CO_2 \longrightarrow 2CO$$

$$C + H_2O \longrightarrow CO + H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

This model was used to obtain the temperature profiles of the combustion wave and the dependences of the composition of gaseous products on the mass fraction of carbon in the fuel and on the amount of water vapour in the gaseous oxidant. The most important gasification products are carbon monoxide and hydrogen. These gases determine the heat content of the products and can also be used as raw materials for the synthesis of hydrocarbons. As the vapour content in the gaseous oxidant increases, the fraction of CO decreases and the concentration of hydrogen in the products increases. A comparison of the results of calculations and experimental data[4] for vapour/air gasification of carbon (graphite) showed that the model based on the thermodynamic equilibrium in products overestimates the combustion temperature at low content of vapour in the initial oxidant and underestimates the combustion temperature at high vapour contents. Gasification of solid fuel is characterized by high combustion temperatures (>1000 °C). In this case, water vapour can react with reaction products and with the fuel until establishment of thermodynamic equilibrium, but this equilibrium is not attained owing to insufficient residence time of the reactants in the high-temperature zone. A more correct description of the process can be obtained using the model with allowance for the reaction kinetics (Fig. 6).

The two-temperature model gives qualitatively new information, namely, it shows that, in addition to the classical mechanism of thermal conductivity in porous media, a convective mechanism of combustion wave propagation can be realized.[28] The heat loss in the system is an important factor affecting the macrokinetic parameters of filtration combustion. It was shown[29] that doubling the heat transfer coefficient at $\delta < 1$ causes the width of the thermal wave to reduce by 1.5–2.5 times. Owing to changes in the stoichiometry of the carbon oxidation reaction the temperature and the energy efficiency of the process can

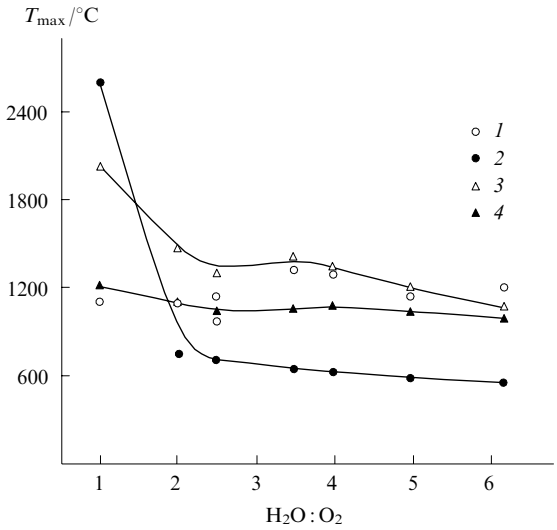


Figure 6. Combustion temperatures: experimental data[4] and the results of calculations for vapour/air gasification of carbon using the model based on the thermodynamic equilibrium in products[23] and the model with inclusion of the reaction kinetics:[4] experimental data (*1*), thermodynamic model (*2*), kinetic model (gas, *3*) and kinetic model (solid, *4*).

vary to some extent. A comparison of the existence regions of steady autowave regimes of air gasification of fuels with different reactivity (birch charcoal, graphite, carbon composite) showed[14] that the minimum feed flowrates and fuel concentration at which a steady filtration combustion wave exists were observed for mixtures containing the most reactive birch coal while the maximum velocity (narrowing of the parametric domain of existence of a steady wave) was observed for the least reactive carbon composite.

IV. Stability of the filtration combustion front

Since filtration combustion represents a number of physicochemical processes, the combustion front stability is a complex function of many factors. The nature of the wave front instability can be different. A classical case for diffusion-thermal instability of the flame front was considered in a monograph.[11] It was shown that the flame front stability to deformation is determined by the ratio of the molecular coefficients of thermal conductivity and diffusion; the flame stability regions were established. When the concentration and temperature fields are similar, *i.e.*, the Lewis number (Le) equals unity, the flame is always stable. At Le > 1, the flame front can be unstable to deformation, while at Le < 1, the flame is unstable to one-dimensional perturbations. Experimentally, the decomposition of the front surface of a laminar gas flame into individual burning 'islands' and the formation of 'cellular' flame structure was for the first time observed by Kokochashvili[30] and Karpov.[31] Usually, these effects are due to internal instability of laminar flame; therefore, its lifetime is not too long. Heat dissipation influences minor perturbations, which affect the structure of the flame front but cause insignificant gasdynamic perturbations.

The front instability of a filtration combustion wave was mathematically studied by Aldushin and Kasparyan.[32,33] The influence of parameters of the system and the process

design on the stability of the process was studied using the response of the steady combustion front to a small perturbation. The emphasis was placed on the kinetic regimes because they can be unstable due to positive feedback between the temperature and combustion rate. It was shown that gas evolution in the combustion front decreases the front stability.

Bending of a flat front due to the fact that some regions of the combustion front propagate faster than neighbouring regions is a kind of instability. As a result, a tilted combustion front is formed; this causes no breakdown of the overall structure. Such a combustion front instability was found in the filtration combustion of gases. Here, the tilted front can be rather stable. It can propagate through the mixture over rather long periods of time with retention of the tilt angle.[34,35] The front plane is not perpendiculr to the gas filtration direction. Probably, the combustion front stabilizes at some tilt angle value. Similar results were obtained by researchers from Belarus,[36] who showed that small disturbances of the front appeared for one or another reason should be amplified. The increase in the perturbations until some value is proportional to the width of the high-temperature zone.

In filtration regimes the front velocity is limited by the supply of the oxidant to the combustion zone and a gas-dynamic instability of the reaction front surface can develop.[37] It was shown that this instability in the counterflow system is analogous to the known Saffman–Taylor[38] effect, namely, instability of the interface between two immiscible liquids with different viscosities. The reason is that the increased local gas permeability causes accelerated formation of burning-emptied region in the solid fuel in this zone; consequently, the gas permeability increases even more. This predetermines the formation of specific channel combustion regimes characteristic of low-gas-permeability systems. It is believed that an instability in filtration combustion should appear if the gas-dynamic resistance of the initial solid bed is higher than that of the solid ash residue.[37] The development of instability should lead to an alternative combustion regime, so-called fingering.

The results of numerical modelling of filtration combustion reported by other researchers[39–41] also revealed the possibility of formation of various spatial structures of channels in such systems owing to combustion front instability. The existence of alternative combustion regime was experimentally reported by Aldushin and Braverman,[42] who used sawdust and birch charcoal of different dispersity as the fuel. Ignition was followed by the formation of a combustion front in the form of a single channel. In this case, the effect of the free (frontal) surface of the bed on the combustion front stability was ignored. In the presence of the free surface of the bed, one can expect manifestation of certain features at some distance from the combustion front, because the nearness of the free surface may favour the development of a gas-dynamic instability. Even if the gas-dynamic resistance of the initial solid bed is higher than that of the solid ash residue, one can expect that an increase in the particle size and, therefore, the overall gas permeability, will stabilize the combustion front. The problem thus posed has not been solved so far. Also, the model treats the motion of the solid phase as the motion of a homogeneous medium but ignores the motion of particles relative to one another, which may have a complex character[43] and strongly influence the stability of the system.

To preclude the development of the gas-dynamic instability in the filtration combustion and the formation of a channel (burning-emptied region), it is sufficient to introduce a transversal mixing factor. Practically, this can be either forced mixing of fuel ahead of the combustion front or natural subsidence upon fuel burnout. Transversal mechanical motion of the solid material in the vicinity of the combustion zone leads to equalization of the gas permeability and filling of the burning-emptied region.[44] However, the design of a mixer faces severe technical difficulties, because motion of solid materials in different directions requires considerable efforts. In addition, the device should not create obstacles to the flow of the solid material and should be stable to high temperatures. Also, it can 'provoke' nonuniform gas permeability, as well as crush and grind the material, which will reduce the gas-dynamic stability.

A possible solution to this problem is to use tilted rotating cylindrical reactors in which the solid material is mixed under the action of the gravity force. The combustion front stabilization in a rotating reactor was studied taking mixtures of charcoal (or sawdust) with a solid inert material (crushed fire clay bricks) as examples.[45–47] Experiments were carried out using materials of different fractional composition (particle size 2–17 mm) and tilted rotating cylindrical reactors 66 and 160 mm in diameter with different rotation rates (6–28 rpm) and tilt angles (20–90°).

It was shown that stopping the rotation always led to the development of the burning-emptied region along the top generatrix of the reactor. Figure 7 *a* demonstrates a bright

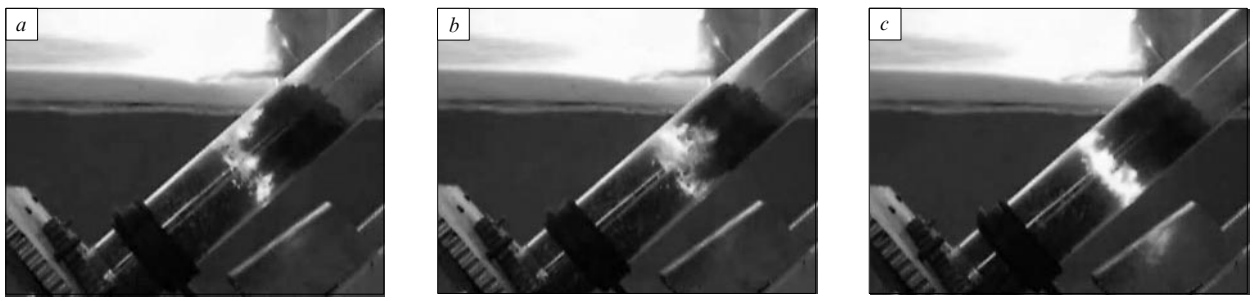


Figure 7. Filling of a burning-emptied region in a tilted (45°) rotating reactor.[47]
The initial state of the burning-emptied region (curved combustion front); no rotation (*a*); stabilization of combustion front 1 s (*b*) and 6 s (1 revolution, *c*) after resuming the rotation.

bent combustion front which is not perpendicular to the reactor axis. As rotation is resumed, the burning-emptied region rapidly disappears (Fig. 7 *b*,*c*) and the combustion front again becomes a narrow zone perpendicular to the reactor axis. Interestingly, the width of the glowing zone depends on the tilt angle of the reactor. The minimum width of the glowing zone was observed for the tilt angle $45 \pm 10^{\circ}$. In this case, narrowing of the glowing zone indicates filling of the burning-emptied regions and stabilization of the combustion front. A fundamental advantage of the tilted rotating reactor is due to the fact that the material is first of all mixed in the pyrolysis and combustion zones where the volume of the fuel significantly decreases and voids are formed.[48] In the tilted rotating reactor, the burning-emptied regions formed upon burnout of low-density materials are filled with portions of unburnt material caved under the action of the gravity force, thus stabilizing the combustion in the reactor. This suggests a new technology of combustion front stabilization.[49]

V. Accompanying processes: evaporation and condensation

From the standpoint of macrokinetics, the oxidation of matter in a filtration combustion wave can be considered as single exothermic step responsible for the existence of the overall structure of the combustion wave. In addition to oxidation, various independent processes interrelated through temperature and concentrations of components can occur in the wave. These are, *e.g.*, evaporation and condensation due to the presence of an evaporating component ¶ in the solid fuel (in addition to the fuel *per se* and the solid inert component). Evaporation is due to convective heat flow from the combustion front. The evaporated component is carried away by the counterflows of the gas phase and the condensed phase from the combustion front to colder fuel layers (Fig. 8 *a*) where its condensation occurs. Depending on the concentration of this component and the gas flow rate, the mass fraction of the evaporated component can vary. Condensation is possible both on the surface of cold fuel and in the bulk. In the latter case, a finely disperse aerosol is formed. The condensed component will partially deposit during filtration through the fuel layer and partially be carried away by the gas flow. The larger the size of the liquid droplets the more readily they deposit on the solid material during filtration. If the temperature gradients in the filtration combustion wave are very high, high cooling gas rates will favour the formation of very small droplets (< 10 μm), which are poorly deposited during filtration and can be carried away from the reactor by the gas flow in the form of fog. All these series-parallel processes can hardly be described due to a large number of undefined parameters.

The propagation of an exothermic reaction in a porous medium with a typical evaporating inert component, namely, fuel moisture was considered.[5] In this case, an expanding zone of saturated vapour is formed in front of the combustion zone. If the thermal structure of the

¶ Here, the evaporating components include not only fuel moisture, but also any other compounds capable of going to the gas phase upon heating of the fuel in the absence of oxygen. Since the initial fuel can be heated to rather high temperatures, some metal compounds may also fall into this category (for details, see the text below).

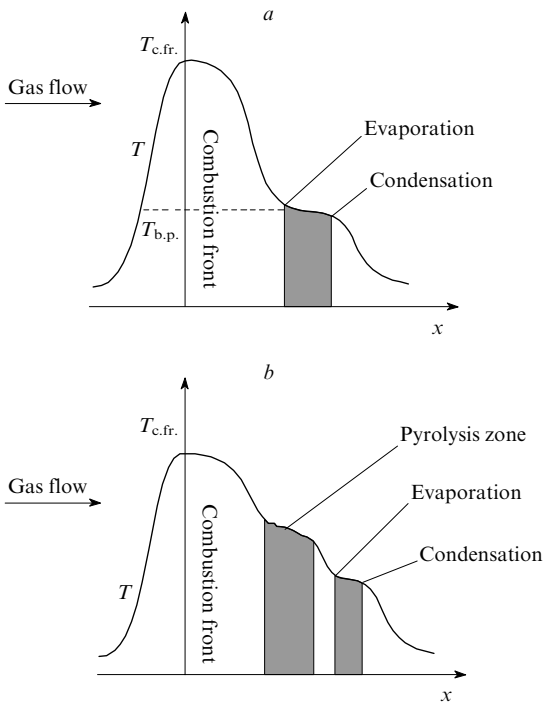


Figure 8. Thermal structure of a combustion wave propagating through a solid porous fuel:[10] the case of an evaporating component (*a*) and the case of pyrolyzable organic fuel with an evaporating component (*b*).

combustion wave is characterized by $\delta < 1$, the evaporation zone will be localized near the combustion front. Owing to considerable heat loss to evaporation, the temperature of the combustion front may decrease, which will unavoidably affect all parameters of the combustion wave. For the thermal structure with $\delta > 1$, heat loss to evaporation will cause the temperature in the heating zone rather than in the combustion front to decrease. Such heat loss does not influence the heat release to the combustion front. This is a remarkable feature of this filtration combustion regime. The condensation zone of the evaporated component is localized somewhat downstream the gas flow. Condensation is accompanied by some heat release; therefore, in this case, the process involves not only mass transfer, but also thermal energy transfer from one zone to another.

Filtration combustion of moist coal was studied experimentally.[50] It was shown that propagation of the combustion wave is only slightly influenced by the fuel moisture in the counterflow reactor. Gasification of carbon fuel with the superadiabatic heating can proceed in such regimes where propagation of a stable combustion wave is unaffected by the high content of fuel moisture. For instance, a combustion study [51] of a mixture of moist charcoal with an inert material showed that gasification in the counterflow regime proceeds steadily in the whole range of moisture values even in a laboratory setup 46 mm in diameter (despite high heat losses). Evaporation of fuel moisture requires supply of energy; therefore, a decrease in temperature is possible. However, as the stoichiometry of carbon oxidation changes towards the formation of CO_2, the thermal effect of the reaction in the combustion zone increases and to a great extent compensates the heat loss

to evaporation. Owing to this effect, the temperature and mass velocity of gasification appear to be low sensitive to changes in the fuel moisture. The stability of filtration combustion of carbon systems is due to self-regulation of combustion temperature wave through an increase in the thermal effect of the reaction.

VI. Filtration combustion of pyrolyzing fuel

In addition to evaporation and condensation, heating of a fuel in a filtration combustion wave can be accompanied by thermal decomposition of some components in the absence of oxygen, in particular, pyrolysis of organic components of the fuel.[52–54] Filtration combustion of organic fuel (wood, peat, naturally occurring coals, *etc*.) represents a typical example of propagation of a combustion wave accompanied by thermal decomposition. Usually, such fuels heated in a combustion wave undergo pyrolysis with the formation of liquid and gaseous products and coke residue. When strongly heated, a solid fuel can be pyrolyzed in the oxygen-free region; this proceeds outside the combustion zone, being related to it through the temperature and reactant concentrations (see Fig. 8 *b*). An experimental temperature profile for filtration combustion of cellulose is shown in Fig. 9.

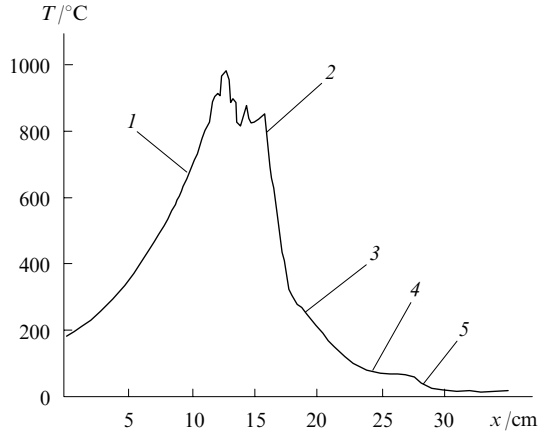


Figure 9. Temperature profile for filtration combustion of cellulose.[55]
Processes: cooling (*1*), heating and oxidation (*2*), pyrolysis (*3*), drying (*4*) and condensation (*5*).

Pyrolysis of organic fuels obeys complex kinetic regularities.[56,57] Specific features of the kinetics and mechanisms of chemical processes in solid and viscous media including natural and synthetic polymeric materials are described using non-traditional methods of the so-called polychronous kinetics, which take into account dispersion of the kinetic parameters of the system.[58] However, simpler regularities of generalized pyrolysis are more often used.[59,60] Usually, the thermal effect of pyrolysis is small compared to the heat release in the filtration combustion wave front. Pyrolysis results in a solid coke residue (it arrives at the combustion zone and is burnt there), pyrolysis resins and gaseous decomposition products. The chemical compositions and amount of the decomposition products mainly depend on the heating temperature and rate, on the environmental conditions and on the nature of the fuel. In particular, the time needed for complete decomposition of a fuel at a specified temperature depends strongly on this temperature, namely, the lower this temperature the longer the time required for completion of pyrolysis. Depending on the heating rate, there are a slow and a fast pyrolysis regimes.[59] Slow pyrolysis of organic fuels affords larger amounts of gaseous products and solid coke residue and smaller amounts of liquid decomposition products compared to fast pyrolysis. It is believed that a feature of fast pyrolysis is very intense molecular decomposition and that molecular fragments leave the reaction zone without experiencing consecutive conversions with the carbon component of the residue as is the case for slow pyrolysis. These features influence the dependence of the product yields on the initial content of the organic fuel.[52]

Experiments showed[52] that at relatively high temperatures, pyrolysis resins, *i.e*., various hydrocarbons, are in the gaseous state and transferred by the gas flow from the pyrolysis zone to lower-temperature regions where they undergo condensation to aerosol which is carried away from the reactor in the form of fog droplets by the gas flow. Unlike moisture and other incombustible components, pyrolysis resins can be burnt in the presence of the gaseous oxidant. The yields of liquid products of pyrolysis of solid organic fuels heat-treated in different manner, by oxygen-free pyrolysis, counterflow gasification[59–63] and filtration combustion with the superadiabatic heating, are presented in Table 1. It was established that the maximal yield of pyrolysis resins during filtration combustion can be as high as 65% of the fuel mass. This is close to the corresponding value for oxygen-free pyrolysis, but in the case of filtration combustion there is no need for additional energy supply.

Table 1. Yields of liquid products (% of the initial mass) in thermal processing of organic fuels.[52]

Fuel	Gasification	Pyrolysis	Filtration combustion
Wood	20	75	65
Cellulose	—	to 100	30
Peat	10	10–12	12–14
Brown coal	7–9	5–15	8–10
Rubber	—	20–45	40–50

Plastics represent a large class of pyrolyzable materials. Experimental studies on the behaviour of plastics in the filtration combustion wave in counterflow systems showed[50,64] that they are partially oxidized in the reaction zones, being partially pyrolyzed on heating of the fuel and carried away by the gas flow. The mass fraction of the pyrolyzed polymer depends on the thermal structure of the combustion wave. At $\delta > 1$, almost the whole polymer undergoes degradation before its arrival at the combustion zone. Also, intense deposition of liquid products of pyrolysis in cold bed layers was observed; this can decrease the gas permeability of the porous medium.

The mathematical model for steady combustion of a mixture of particles of the pyrolyzable solid fuel with an inert material in a counterflow with the gaseous oxidant[53] is based on the phenomena observed in experiments with pyrolyzable fuel. The model was developed to study the

influence of pyrolysis on the parameters of filtration combustion of fuel. The model includes the following chemical reactions:

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

— oxidation of gaseous products,

— oxidation of the coke residue.

The process was calculated for an infinite reactor taking into account lateral heat loss. The one-dimensional one-temperature model included equations for the energy conservation law for the whole system and the mass conservation law for each component. The initial system of equations was solved for each type of the thermal structure of the combustion wave by the asymptotic method using the narrow combustion zone. Analytical expressions relating the key macrokinetic parameters of the process were derived. The dependences of the combustion temperature (T), oxygen content in the combustion gas (ρ^*), mass velocity of fuel combustion (u) and the mass fraction of the fuel oxidized in the combustion zone (η) on the fuel content in the initial mixture are presented in Fig. 10. The limiting yield of coke was assumed to be 15%.

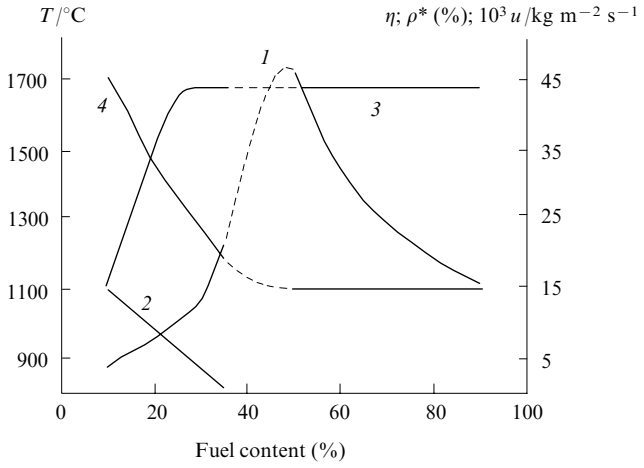


Figure 10. Combustion temperature (*1*), oxygen content in the combustion gas (*2*), mass velocity of combustion (*3*) and mass fraction of fuel oxidized in the combustion zone (*4*) plotted *vs.* fuel content in the initial mixture.
Dashed lines correspond to the fuel content range for which no calculations were performed.

The dependence of the combustion temperature on the fuel content in the initial mixture is nonmonotonic and has a maximum at a fuel content of 50 mass %. An increase in the fuel content from 10 mass % to 35 mass % causes a linear decrease in the oxygen concentration in the gaseous products from 15 mass % to 0 mass %. As the fuel content increases from 10 mass % to 30 mass %, the mass velocity of combustion increases from 0.016 to 0.044 kg m^{-2} s^{-1} and remains constant upon further increase in the fuel content. An increase in the mass velocity of combustion at low fuel contents in the mixture can be explained by a greater extent of oxygen consumption and by a decrease in the amount of oxidized coke residue. Constant combustion velocity at high fuel contents is due to complete consumption of reactants and to constant stoichiometry of the process.

The results of numerical calculations using this model showed autolocalization of the conversion zones at low content of the solid inert component (region with $\delta > 1$). In other words, the pyrolysis and combustion steps are separated in the space, *viz.*, the pyrolysis zone is distant from the combustion (front) zone. At $\delta < 1$, no spatial separation of these steps occurs. In this case, partial oxidation of gaseous products in the combustion front is observed.

Summing up, the main advantages of gasification in the superadiabatic regime (high energy efficiency, the possibility of using off-grade fuel, low content of pollutants in smoke fumes) are retained when using pyrolyzing fuels. The method allows the following processes to be carried out in the same reactor:

— oxidation of coke residue by oxygen and water vapour to produce carbon monoxide and hydrogen;

— pyrolysis of organic raw materials without energy supply from the outside to afford liquid hydrocarbons; and

— drying of the initial fuel.

Since the pyrolysis and oxidation zones are spatially separated, the former reaction proceeds much like the same as in pyrolysis reactors. The yield of liquid products can be as high as 65% of the mass of the organic components. The spatial separation can occur provided that heat capacity of the gas flowing through the combustion zone is higher than that of the solid fuel flow.

VII. Regularities of filtration combustion in the presence of metal compounds

So-called transport reactions involving mass transfer of metals through the formation of volatile compounds have been studied since the mid-20th century.[65] These processes are based on reversible interaction of the condensed phase and the gas phase with the formation of a gaseous product transferred to some other region of the system where it decomposes with isolation of the initial condensed substance due to a change in the conditions. The volatility of some types of metal compounds (halides, hydrides, organoelement compounds) can be used for mass transfer to obtain high-purity substances.[66]

Non-isothermal, autowave filtration combustion provides the possibility of efficient mass transfer of chemical compounds.[10] A feature of the filtration combustion in the counterflow regime in complex systems where various physicochemical processes can occur, is the spatial separation of the conversion zones of the solid fuel (see above). This makes it possible to extract metals of value and their compounds in the combustion wave.

Combustion of systems containing molybdenum sulfide, catalysts based on mixed Ni- or Co-doped molybdenum oxides and autoclave bottoms after soda treatment of tungstenite was studied experimentally.[67] It was shown that molybdenite MoS_2 can be efficiently burnt in the filtration combustion regime without additional heat supply (temperature in the combustion wave reaches 900 – 1300 °C) and quantitatively converted to high-purity molybdenum trioxide. Experiments showed that reactions analogous to transport reactions, namely, continuous oxidation of molybdenum in the oxidation zone and transport of gaseous molybdenum trioxide to the region where it is reduced to lower nonvolatile forms and goes to the solid phase, occur

throughout the process studied. When the combustion wave arrives at that region, molybdenum thus again appears in the oxidation zone, undergoes oxidation to the trioxide, *etc*. This cycle is repeated numerously with accumulation of molybdenum compounds near the combustion front; therefore, the ash residue contains high-purity molybdenum trioxide crystals.

Autowave filtration combustion of systems containing dead molybdenum-containing aluminosilicate catalysts [67–69] requires the addition of fuel to the burden. The highest degree of extraction of molybdenum trioxide ($\sim$80%) is attained at 5%–6% coal in the burden; in this case, the temperature in the combustion front reaches 800–1000 °C.

The conclusion [67] that tungsten can be transported with ease in the form of hydroxide is incorrect. It was based on the results of thermodynamic equilibria calculations using the 'Terra' programme [70] whose database included erroneous values of the thermodynamic parameters of gaseous WOH (incorrect sign of the standard enthalpy of formation). Experiments showed a 30% decrease in the amount of tungsten in the processed charge. This can be due to a low accuracy of quantitative determination of tungsten.

A number of studies are devoted to investigation of the behaviour of zinc compounds in the filtration combustion wave. Studies of autowave filtration combustion of Zn-containing systems in laboratory-scale setups showed that the degree of zinc extraction to Zn sublimate depends on the initial concentration of zinc in the charge.[71–73] When using systems with high zinc oxide content (10 mass %–30 mass %), changes in the ZnO content at different stock bed heights during combustion were observed. The ZnO content in the charge decreased along the direction of the oxidant flow at low mass velocities of the gas flow (<0.1 m s^{-1}) and increased at high mass velocities of the gas flow (0.4–1.7 m s^{-1}), which confirms that mass transfer of zinc-containing combustion products does occur. The degree of extraction of these products to Zn sublimate increased with an increase in the maximal temperature in the combustion wave and varied from 3.0% to 34%. At low zinc content in the charge (2 mass %–4 mass %), the degree of extraction of zinc-containing combustion products to Zn sublimate depended on the oxidant flow velocity and on the fuel content; in some case, it reached 100% at low oxidant flow velocities. It should be noted that no free (elemental) zinc was found [72, 73] in the extracted product. Only zinc oxide was obtained, although thermodynamic estimates predicted mass transfer of elemental zinc. At the same time, in the course of iron smelting under conditions similar to the filtration combustion conditions, zinc impurity leaves the reaction mass, being in the gaseous state.[74] The absence of elemental zinc among the combustion products [72, 73] can be explained by the fact that the experiment was carried out in the periodic reactor, *i.e*., free zinc thus formed was probably oxidized by atmospheric oxygen.

Theoretical investigations of filtration combustion in the counterflow regime, when the initial product contains a number of metals with different volatilities,[75] predicted the possibility of lead mass transfer in the form of both elemental Pb and PbO. Studies of systems containing to 50 mass % iron and 5 mass %–18 mass % zinc in the burden (large-tonnage waste of ferrous metal industry) showed that zinc is transferred along with gaseous products as the combustion wave propagates and, as a consequence, the unburnt fraction of the charge is enriched with Zn. Thus, it was propose to enrich one portion of the product at the expense of the other portion. Zinc-rich concentrate thus obtained can be efficiently processed by traditional techniques (this requires at least 15 mass % zinc content in the concentrate). If the autowave process is carried out to provide mass transfer of a certain metal, the combustion regime should correspond to the conditions in which the degree of mass transfer of the most volatile form of the metal is maximal.[67] In the case of metals with highly volatile reduced forms (*e.g*., zinc), the process should be performed in the regime of combustion wave with $\delta > 1$ (see Fig. 3*b*). Here, zinc compounds will be reduced in the pre-heated zone ahead of the combustion front and then zinc vapour will be carried away by the gas flow. Condensation of zinc vapour will occur in the region with a particular temperature.

Mass transfer of other metals, *e.g*., lead, can be practically implemented in the regime of combustion wave with both $\delta > 1$ and $\delta < 1$. Mass transfer involves lead vapour in the former case and gaseous oxides in the latter case. Using the two-temperature model for transfer of volatile products from a finite-size reactor,[76] it was shown that the process can be organized in such a fashion that the metal be present in the ash residue or metal vapour be partially or completely carried away from the reactor by the gas flow. The concentration of metal in the exhaust gas (assuming saturated vapour pressure of the metal-containing product) and, consequently, the degree of extraction depend on the temperature of the exhaust gaseous products and on the velocity of the gas flow. In turn, the temperature of gaseous products depends on the temperature in the combustion zone, stock bed height, carbon content in the system and on the heating rate of particles of the solid phase.

There are a few metals that form relatively volatile products (elemental metals, oxides, hydroxides, nitrides) in the temperature range 1200–1300 °C and are thus suitable for carrying out economically viable industrial processes. These include Zn, Cd, Hg, Te, Tl, Se, Mo, Pb, As and Re. However, the list of metals that can be extracted from complex mixtures during autowave non-isothermal filtration combustion can be extended considerably by introducing chlorine or fluorine into the system,[77] *i.e*., if we admit the formation of chlorides or fluorides; most of these compounds are highly volatile at temperatures below 1200 °C.

From the aforesaid it follows that filtration combustion can be used in extraction processes of elements of value from traditional and, which is of particular importance, non-traditional sources including poor ores, various kinds of waste, *etc*.[78] Studies on the behaviour of metals during filtration combustion are necessary not only for extraction of valuable products, but also for better environmental safety of production facilities utilizing thermal processes. A topical problem is to search for combustion conditions of systems containing environmentally hazardous compounds (a main requirement is such that the pollutant concentrations in exhaust gas should be lower than the maximum permissible concentrations). Undoubtedly, in this connection the use of filtration combustion in the counterflow regime seems to be more promising than traditionally used combustion in furnaces or fireboxes, as low temperatures of gaseous products leaving the reactor preclude the removal of pollutants. Therefore, taking into account low concen-

trations of metal compounds in the exhaust gas (they are ten times and more lower compared to other methods),[8] it is possible to abruptly reduce the clean-up costs that are a large part of maintenance costs.

VIII. Autowave processes in counterflow systems

1. Industrial applications

A large number of studies on non-isothermal autowave processes in the counterflow regime are aimed at optimizing various stages of industrial production, such as *in situ* coal gasification,[79] *in situ* combustion of oil-saturated rocks,[80] agglomeration of metallurgic charge,[7,81,82] roasting of sulfide ores, oxidative regeneration of catalysts,[83,84] self-propagating high-temperature synthesis (HTS),[85–89] *etc*.

The idea of *in situ* coal gasification, *i.e*., coal conversion to combustible gases in the interior of the earth, was for the first time put forward by D I Mendeleev in his work 'Future force resting on the banks of the Donets'.[90] Chemical reactions proceeding during *in situ* gasification are similar to processes occurring in a gas generator. The first project of *in situ* coal gasification was developed in the USSR in the 1930s. Experiments were carried out on deposits in the Podmoskovny and Kuznetsk coal basins.[79] In the mid-20th century, experiments on *in situ* gasification were carried out in the USA and Italy. However, the method is of limited use due to lower economic efficiency compared to the development of natural gas fields. Currently, there has been a new tide of interest in the *in situ* coal gasification. Now this technology, intensively improved in Australia and China,[91] is used on a large scale in those countries; also, there has been considerable interest in the subject in South Korea, India, Ukraine and other countries.

In situ combustion of oil-saturated rocks is much like *in situ* coal gasification. This is a method of oil field development based on exothermic oxidation of hydrocarbons (mainly in-place oil) with the oxidant (usually, atmospheric oxygen) injected into the oil pool.[92,93] In some cases, a hydrocarbon gas and water is also supplied to the heat generation zone. This method was for the first time proposed by domestic researchers[80] and used on a pilot plant scale in Romania, USA and other countries. The salient features of this process are as follows:

— moderate temperatures in the combustion zone;

— relatively low gas and liquid filtration velocities due to low gas permeability of the oil pool; and

— the need for considerable increase in the pressure in the injection well.

Pioneering studies on the concentration of thermal energy in the autowave non-isothermal process with the counterflow regime were related to the development of technology of agglomeration of metallurgic charge.

Voice and Wild[7] reported the results of experiments on propagation of heat waves and combustion waves in a bed analogous to agglomeration of metallurgic charge. The most important result obtained was that blowing gas through the reacting porous media may lead to thermal resonance at which the amplitude of the thermal wave is maximal owing to the highest efficiency of heat recuperation provided that the heat transfer (thermal wave) and combustion wave (reaction front) velocities are equal to each other. At different velocities, the temperature decreases and the width of the heated zone increases.

To obtain the general picture of combustion fuel in a bed and design an algorithm of engineering analysis for the determination of parameters of agglomeration in different conditions, combustion of agglomeration charge was studied and an attempt to theoretically describe gas production was made.[81] Experiments showed[82] that the ignition velocity of the fuel particles and the propagation velocity of the combustion wave depend on the velocity of air filtration and on the thermophysical properties of the charge. It was established that gaseous products of agglomeration usually contain a large amount of oxygen.

Fateev[94] proposed a two-temperature mathematical model for heat and mass exchange during agglomeration. Using this model, it was shown that, depending on the thermal wave : reaction front velocity ratio, the heated bed can be either in front of or behind the reaction zone. A subsequent criterial analysis of the process[95] revealed that the efficiency of the process is to a great extent determined by not only that velocity ratio, but also by heat dissipation to the environment.

Oxidative regeneration of catalysts is used in various industries. Catalysts used in petrochemical industry for processing hydrocarbon raw materials are known to become less efficient with time; usually, this is due to coking of surface grains. Regeneration of catalysts involves burning-off carbon when blowing the gaseous oxidant. A feature of oxidative regeneration is that the process should be carried out in at such temperatures that do not lead to catalyst structure degradation and the properties of the active surface should be retained. In addition, the presence of catalyst may strongly influence the key parameters of the propagating wave.

A mathematical analysis of the possible regimes of oxidative regeneration of catalysts was performed.[84] Since the catalyst being regenerated is usually unstable to high-temperature treatment, the emphasis was placed on the investigations of the kinetic regimes of oxidation reactions. Mathematical models for carbon oxidation in coked catalyst, as well as numerical solutions to the equations of this model are available.[96] The model allows one to evaluate the parameters of the system and the influence of the control parameters. A criterial analysis of the model allowed the key parameters of the system affecting the width of the reaction zone to be established. It was found that the process is governed by the following parameters:

— temperature of the inlet gas;

— flow rate of the inlet gas;

— oxygen concentration in the inlet gas;

— reaction-to-internal diffusion rate ratio; and

— external-to internal diffusion rate ratio.

The regularities established allow one to monitor how a particular value affects the parameters of oxidative regeneration of catalysts.

More recently, a number of simple and complex models for propagation of thermal front through a bed of a catalyst were proposed, their specific features and applicability were established and the thermal front structures were analyzed.[83] These models allow for heat and mass transfer in a bed and in an individual grain. It was found that for the complex reactions, the thermal structure of the front is divided into zones with respect to the 'hierarchy' of temperatures. The estimates obtained were used to construct the dependences of the thermal front parameters on the system values. Noteworthy is a particular conclusion, namely,

stabilization of the maximal temperature requires at least one mechanism of heat transfer from the hot zone of the thermal front.

A large number of studies of non-isothermal autowave processes were carried out in connection with the development of technologies involving self-propagating high-temperature synthesis of inorganic compounds.[1,85–89] This method is promising for production of solid refractive compounds (borides, nitrides, carbides, hydrides, *etc.*). Metal nitrides or hydrides are synthesized in the filtration combustion regime due to intrinsic energy of metal + nitrogen or metal + hydrogen interaction with no heat supply from the outside. Within the framework of the one-temperature mathematical model, the superadiabatic effect of heat accumulation was described by Aldushin and Seplyarskii,[97] who used the Frank-Kamenetskii approximation[17] for evaluating the key combustion wave parameters for one generalized chemical reaction.

Aldushin and Seplyarskii[97] rejected the existence of steady regimes of filtration at $\delta > 1$ and proposed to use inert components to attain steady combustion in systems with high heat capacity of the gas flow. They also reported[98] a detailed study on the propagation regimes of a combustion wave with $\delta > 1$ in the Frank-Kamenetskii approximation and revealed an additional limitation on the range of parameters suitable for realization of this structure of the combustion wave. An expression was derived for the critical gas flow rate (or critical concentration of the oxidant); at lower flow rates, no steady combustion wave can occur. It was shown[28] that, taking into account the temperature differences between the gas phase and the condensed phases (two-temperature model) a filtration combustion wave can propagate through convection rather than thermal conductivity as in the one-temperature model. The applicability conditions for the one-temperature model and realization of the mechanisms of combustion wave propagation were established. This approach was developed in more recent studies and the theory of combustion of HTS systems was elaborated in detail for different conditions.[5,12,88,99] Mathematical models for numerical calculations of the key parameters of combustion waves were developed and fields of their application were established.

The chemical scheme of HTS is usually rather simple, which makes it possible to perform a thorough theoretical analysis of the system and to design efficient algorithms of numerical calculations. In the case of HTS systems, the emphasis is placed on obtaining valuable condensed products. If there are no gaseous reaction products, the problem is complicated,[100] namely, the possibility of naturally occurring filtration of the oxidant through both the products and the initial powder and even through the lateral surface of the sample is assumed. Yet another feature of HTS systems is the high pressure (hundreds and thousands of atmospheres) that can be used to provide a necessary amount of the gaseous oxidant in pores of the sample (filtration of the oxidant in the reaction zone is not always sufficiently intense). In addition, the particle and pore sizes in typical HTS systems are of the order of 0.01–0.1 mm; this influences the conditions and regularities of filtration of the gas.

Studies on HTS systems contributed largely to the science of filtration combustion due to the fact that they were based on the methodology of the classical theory of combustion. The authors who developed the theory of filtration combustion of metallic samples did not restrict themselves to the HTS technologies and elaborated a more general scientific approach which can often be applied to almost all known cases of filtration combustion.

Filtration combustion of gases is yet another kind of autowave combustion in porous media. Interest in this phenomenon is first of all due to the high rate of interphase heat exchange, which makes it possible to attain intense internal recuperation of thermal energy released during filtration of a gas through a porous medium without using additional heat exchangers. As a consequence, the temperature and the completeness of combustion increases and the combustion process is stabilized by the inertness of the inert porous cage.[101–106] Now it is possible to significantly decrease the lower concentration limit of stable propagation of a combustion wave and, in particular, to use low-calorie mixtures. Application of filtration combustion for thermochemical conversion of hydrocarbons seems to be particularly attractive;[107–110] the process is performed at high temperatures and requires intense heat supply.

Superadiabatic heating in a combustion wave is characterized by high accumulation of thermal energy; as a consequence, the temperature can increase without large energy expenditure. Combining energy-producing filtration combustion and energy-consuming conversion of hydrocarbons may appear to be a highly efficient method. Its practical implementation on a large scale will make it possible to save a large amount of energy.

A large series of experimental and theoretical research on filtration combustion of gases was carried out at the A V Lykov Institute of Heat and Mass Transfer, National Academy of Sciences of Belarus. Main results obtained in these studies have been documented.[103,106] A feature of the approach used by researchers from Belarus is that they use rather complex kinetic schemes and the enthalpy form of the laws of conservation,[111–113] which implies taking account of the dependence of the heat capacity on the temperature and composition. Considerable attention to filtration combustion of gases is paid by domestic researchers at the ICKC SB RAS, Novosibirsk. Babkin and coworkers[114] proposed a classification of regimes of the process in question, developed a number of mathematical models, carried out extensive experimental studies of the process,[105,115] investigated various nonstationary phenomena[116,117] and proposed innovative technological solutions related to practical applications of filtration combustion of gases.[118] Despite the presence of superadiabatic heating, these processes are significantly different from heterogeneous filtration combustion. The gas being filtered is a premixed mixture of the fuel and oxidant, while the solid porous cage only plays the role of heat transfer agent, which affects the regularities of the processes under study.

2. Prospects for application

Two clearly seen fields of industrial use of autowave filtration combustion in the counterflow regime include production of thermal and electrical energy from nontraditional sources, as well as processing of different kinds of problem waste. Often, these fields overlap, thus giving additional advantages.[8] Prospects for industrial applications of filtration combustion in the counterflow regime are rather wide. By optimizing gasification of solid fuels through equalization of the heat flows of the reacting phases, one can significantly increase the utilization factor of solid fuels, which will increase the energy efficiency of the

whole industrial field. High energy efficiency becomes possible due to the above-mentioned specific features of the process in the counterflow regime, namely:

— intense internal heat exchange between products and reactants, which occurs during the counterflow of the solid fuel and the gaseous oxidant without using additional equipment;

— concentration of heat released in the chemical reactions in a narrow combustion zone (products leaving the reactor have relatively low temperatures);

— autolocalization of zones in the reactor (physicochemical processes occurring in each zone are specified by the conditions in that zone), which allows one to readily isolate the desired components and efficiently carry out several processes in the same reactor.

Usually, gasification of solid fuel is carried out in vertical gasifiers in the counterflow regime (Fig. 11) with the superadiabatic heating in the 'dense' bed. Raw materials to be processed are loaded into the reactor through a transfer cell. Air and water vapour are fed from the bottom. Combustion gas is removed in the upper part of the reactor and ash residue is unloaded in the lower part of the reactor. The working mass in the reactor moves under the action of the gravity force. There is a number of specific zones along the height of the gasifier. In the upper part, the temperature is in the range 70 – 150 °C. Here, raw materials supplied to the reactor are dried by blowing the combustion gas; as a result, the latter is to some extent mixed with water vapour. The next is the zone in which the pyrolysis and sublimation of organics dominate. Thermal decomposition and coking of organic mass occurs in the oxygen-free medium. The combustion gas is enriched with volatile pyrolysis products. In the middle part of the reactor there is the gasification zone where reactions between coke residue and oxygen, water vapour and carbon dioxide resulting in CO and H proceed at 1000 – 1200 °C. The necessary temperature in the gasification zone is maintained through burning of a fraction of carbon with the formation of carbon dioxide. In the lower zone, the solid residue mainly composed of mineral compounds is gradually cooled in the flow of oxygen-rich gasifying agent. Here, the combustion of carbon and organic compounds goes to completion and the combustible materials are completely converted to ash. Final cooling of the solid residue occurs at the bottom of the reactor.

Summing up, the fuel is processed using the two-step technique, *viz*., the first step involves gasification of the fuel in the filtration combustion regime with superadiabatic heating while the second step consists in combustion of combustible gaseous products in a conventional device to produce energy. The two-step processing design ensures a decrease in pollutant emission due to the following factors:

— low linear velocities of the gas flow in the reactor and the gas filtration through the bed of the initial material being processed ensure a very low degree of removal of dust particles with the combustion gas; conditions in the upper part of the reactor favour retention of dust particles from the gas flow through adhesion of pieces of the initial material to the surface; favourable conditions for neutralization of acid impurities (HF, HC1) with mineral components of the charge are created; this makes it possible to significantly reduce the expenditures for gas-cleaning systems and power engineering equipment;

— if gas emissions should be cleansed of sulfur, chlorine or fluorine compounds, dust, and mercury vapours, it is

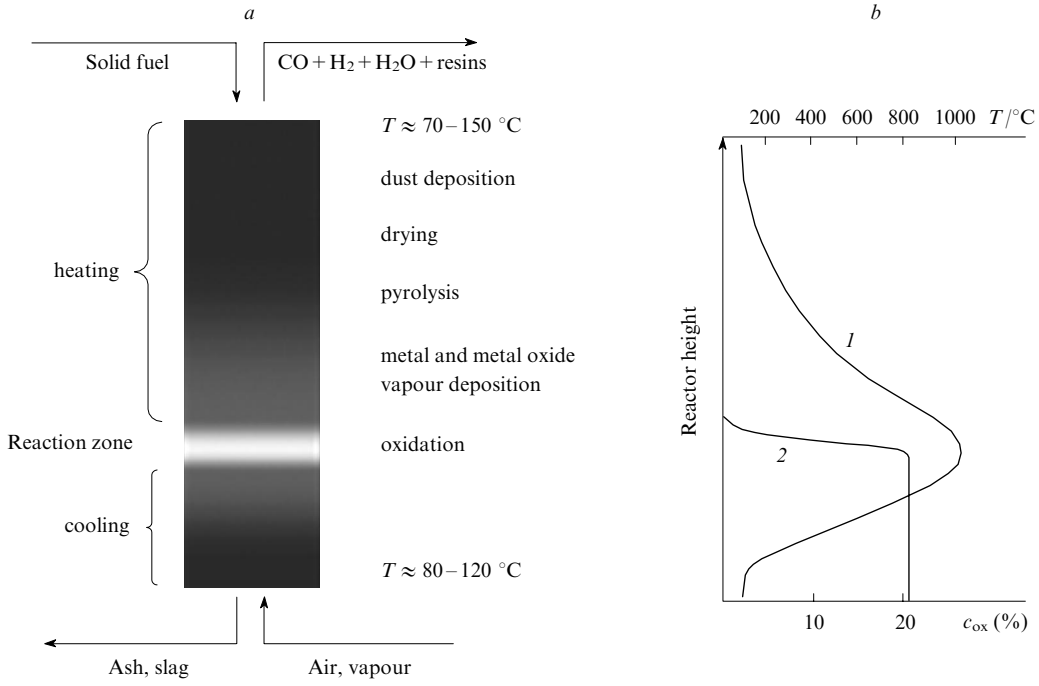


Figure 11. Localization of conversion zones in filtration combustion in a vertical counterflow reactor (*a*) and the temperature (*1*) and oxidant concentration (*2*) profiles (*b*).
(*a*) The gas flow moves upwards, and the condensed phase moves downwards; light-coloured areas: the lighter the colour the higher the temperature.

more appropriate to cleanse the combustion gas rather than smoke fumes due to a low temperature, much smaller volume, and higher concentration of pollutants; in addition, sulfur is present in the combustion gas in the form of H_2S and COS that can be absorbed much easier than SO_2; organochlorine compounds under the pyrolysis conditions in the reductive hydrogen-containing atmosphere are at least partially dehydrochlorinated with the formation of HC1 rather than Cl_2;

— nitrogen-containing organic compounds partially decompose in the oxygen-free medium during gasification; as a consequence, the content of nitrogen oxides in smoke fumes decreases;

— gas combustion in modern gas burners is the most environmentally safe combustion technique, *viz*., due to the high completenes of combustion, smoke fumes contain very small amounts of CO and residual hydrocarbons including carcinogenic polyaromatics;

— the formation of dioxins (polychlorinated dibenzodioxins and dibenzofurans) abruptly reduces because the appearance of soot particles and aromatic compounds (precursors of dioxins) in smoke fumes is suppressed even in the presence of chlorine in the pre-mixed flame; as a consequence, the content of dust particles (catalysts of the formation of dioxins in smoke fumes) remains low;

— ash unloaded from the reactor has a low temperature and contains almost no unburnt carbon and organics.

By optimizing heat exchange through equalization of the heat capacities of the counterflows of the gas phase and the solid phase, one can carry out efficient gasification of low-grade fuels, high-ash coals, waste coal, peat, slate coal, biomass of different origin (mill ends, wood processing waste, agricultural waste, *etc*.), as well as any combustible † domestic and industrial waste.[119] Thus, using autowave filtration combustion in the counterflow regimes, one can abruptly reduce the requirements for fuel quality.

A promising alternative energy source is biomass. There are tremendous resources of biomass; it is readily available, renevable and contains a minimum amount of environmentally hazardous pollutants. Wide use of biomass as energy source is precluded by its high humidity and relatively low heat of combustion. There is a need for developing modern green technologies for production of thermal and electrical energy from low-grade fuels. The method of gasification of solid fuels by filtration combustion in the counterflow regimes elaborated at the IPCP RAS makes it possible to significantly reduce the requirements for the fuel to be processed, in particular, to extend the admittable humidity range.

It was found that filtration combustion in the superadiabatic regime is suitable for efficient thermal processing of some kinds of biomass including such that cannot be processed by other methods.[54] During the filtration combustion process, the heat of combustion of the initial fuel is converted to the energy of gas and gaseous products. In some cases, gaseous products can represent valuable chemical raw materials. However, these processes are currently in the early stage of development and their practical implementation is not materially profitable.[120] Therefore, the most obvious way to use gaseous products involves their combustion with utilization of thermal energy. Direct burning of resins that leave the gasifier with the combustion gas in the form of an aerosol makes it possible to avoid a preliminary step, namely, nozzle delivery of the liquid fuel. The caloric value of the gaseous products is high enough. For instance, in the case of vapour/air gasification of wood in the filtration combustion regime, nearly 2/3 of the heat of combustion of the initial wood is converted to the heat of combustion of gaseous products.[52, 54]

The admittable moisture content in the material to be gasified by filtration combustion in the superadiabatic regimes is much higher than when using other known methods.[51] Also, materials with high content of the solid inert component can be processed without significant changes in the parameters of the process.

Methods of thermal processing of solid waste still remain very attractive despite considerable expenses due to multistep purification of waste until regulatory values. They allow one to considerably decrease the volume of the waste, to decompose hydrocarbons including toxic ones and to produce large amounts of energy. To date, many technologies of thermal processing of waste are available.[120–122] The technology based on filtration combustion in the counterflow systems is one of the most promising methods because it combines efficient solution of both energy and environmental problems.[8] This technology can even be used for processing some types of radioactive waste materials,[123] because an abrupt decrease in the volume is more appropriate for safe disposal of radioactive materials *per se*.

The content of pollutants in non-purified smoke fumes typical of direct combustion of solid domestic waste in a grate furnace, the corresponding parameters of gasification in the superadiabatic heating regime (method developed at the IPCP RAS) and the existing emission standards in the EU countries are listed in Table 2.[124]

The pollutant concentrations in rows 2, 5, 7 and 11 (nitrogen oxides, carbon, organic carbon) of Table 2 mainly characterize the environmental safety of the combustion gas. When a solid fuel is burnt in a grate furnace, the formation of these pollutants is due to unavoidable formation of the zones of incomplete mixing with air. Burning of gaseous fuel (including combustion gas) under conditions precluding the formation of soot and carbon oxide is much easier compared to burning of condensed fuels. Hydrogen chloride and hydrogen fluoride are formed during the pyrolysis and combustion of chlorine(fluorine)-containing polymers present among solid domestic waste. In the case of filtration combustion, these acids are partially neutralized with mineral components of the waste and undergo condensation in the upper part of the gasifier. As a result, most chlorides and fluorides are unloaded from the reactor with ash residue. Emission of dust particles with the combustion gas is considerably reduced owing to relatively low linear velocities of the gas flow and filtration combustion of gas through the bed of the initial fuel (waste). Owing to low content of dust and chlorine compounds in the combustion gas being burnt and to a good mixing of the combustion gas with air, subsequent formation of dioxins (see Table 2) is much reduced compared to direct combustion in a furnace. Summing up, using filtration combustion with the superadiabatic heating during processing of solid domestic waste, it is possible to significantly reduce the formation of pollutants and to abruptly simplify the system for purification of smoke fumes.

† In this case, the term 'combustible waste' denotes the presence of at least a few per cent of combustible components.

Table 2. Pollutant concentrations (mg m^{-3}) in smoke fumes prior to purification; calculated with respect to anhydrous smoke fume containing 11 vol.% of oxygen under normal conditions.

No.	Pollutant	Grate furnace [122]	IPCP RAS technique [8] (see [a])	EC Target values
1	dust	2000	200	10
2	organic carbon [b]	–	8	10
3	HCl	600	6	10
4	HF	5	0.5	1
5	NO_x	350	150	200
6	SO_2	230	171	50
7	CO	–	4	50
8	Hg	0.3	0.01	0.05
9	Cd + Tl	1.6	0.1	0.05
10	Sb + As + Pb + Cr + Bi Co + Cu + Mn + Ni + V	60	7.5	0.5
11	dioxins [c]	3	0.2	0.1

[a] Data were obtained in combustion of unsorted solid domestic waste in Lappeenranta (Finland). [b] Overall concentration of soot and all hydrocarbons including polyaromatic ones. [c] Concentration in ng m^{-3}.

When utilizing some kinds of waste, one can extract commercial raw materials from combustion gas for further processing. The choice of the equipment for utilizing heat during burning of combustion gas is not limited to steam generators or water-tube boilers; it seems likely that gas turbines and diesel plants will be used in the future. The process design can be incorporated with ease into the available infrastructure, for instance, combustion gas can be supplied to the furnace to partially replace high-grade fuel.

The results of experiments with model compositions of solid domestic fuel confirmed that the process can be successfully used for their processing.[8, 9, 26, 125] In all cases, one deals with high-quality burning of organics containing in the ash residue. The ash content in the waste has little effect on the course of the process. Taking particular kinds of problem waste of some industrial facilities in the Moscow Region (Russian Federation) as examples, a technology of joint processing of waste was elaborated and proved. The method provides a high purity of emissions of gaseous combustion products to atmosphere.

Filtration combustion in the counterflow regime can be used for processing not only solid, but also liquid fuels.[126] These can be non-recyclable industrial oils, mixtures formed in the course of thermal or mechanical treatment of metals including waste oil and partially degraded oils containing asphalt pitch, furnace clinker, other mechanical inclusions and water. The solid products remaining after combustion of a liquid contain no organics including carcinogens.[127] Currently, plastics form a considerable part of the overall amount of waste. Decomposition of polymers under atmospheric conditions is a very slow process; they are almost not biodegradable, which means that bacteria cannot break them down. Many plastics can release extremely toxic compounds. Gasification in the filtration regime with the superadiabatic heating can be successfully used for processing of non-recyclable polymeric materials including processing of such abundant kind of waste as tires.[64]

Yet another severe problem is to process such an abundant kind of waste as sewage sludge from sewage filtration fields.[128, 129] The main difficulty in thermal processing of slusges consists in high energy expenditure for dewatering this highly moist material. Gasification in the superadiabatic combustion regime makes it possible to avoid the main drawbacks of modern methods of thermal processing of such materials and to retain their advantages.

IX. Conclusion

Filtration combustion in counterflow systems has been intensively studied by domestic researchers in the last two decades. Investigations on the mechanisms and regularities of filtration combustion of systems in which several processes can occur revealed self-localization of heat release in a relatively narrow zone and the spatial separation of the zones of physicochemical conversion of the solid fuel in the case of counterflow of two phases. Self-localization on the atomic level is well known, being observed in, *e.g.*, nanotechnologies. In chromatography or distillation processes, one deals with macroscopic localization of components of a mixture in the space. It is the concentration of heat released in a narrow zone and the strong dependence of the rate of filtration combustion on the temperature and reactant concentrations that are responsible for self-localization of the zones of physicochemical conversion. In the heat localization zone, superadiabatic heating much exceeding the adiabatic heating occurs owing to partial recuperation of thermal energy with the flows of the system components. Because of this, the main advantages of gasification in the superadiabatic heating regime include:

— high energy efficiency approaching 90%;

— the possibility of stable occurrence of the process at any ash content (to 95%) and humidity (to 70%) of the components;

— high completeness of combustion; and

— thermal stability of the process.

Spatial separation of the oxidation, pyrolysis, evaporation and condensation, and isolation of target products was established for solid organic fuels and metal-containing mixtures. It was shown that these processes are kinetically independent and their mutual influence is determined by the concordance of mass flows. The possibility to carry out each process selectively thus appears, where each zone corresponds to a particular step. This allows the following processes to be conducted efficiently in the same reactor:

— drying of the initial fuel;

— selective concentration and extraction of metals and their derivatives;

— pyrolysis of organic raw materials (without energy supply from the outside) with the formation of liquid hydrocarbons and coke residue;

— oxidation of coke residue to produce synthesis gas.

Steady-state processes have been studied experimentally and theoretically in quite detail. Various non-steady-state regimes (ignition, flame-out, wave regimes, *etc.*) in complex systems are also of considerable interest. Self-localization was studied taking the filtration combustion of solid fuels as an example, but the phenomenon *per se* is rather common. For instance, in geology the mechanisms analogous to those observed in filtration combustion can be responsible for self-localization of deposits upon filtration of reactants through rocks under non-isothermal conditions. In biolog-

ical systems, counterflows can also cause localization of some processes. In spite of relatively short history of research activity in the field of filtration combustion, a number of technological processes were proposed and developed to date. Gasification of various (including nontraditional) types of solid fuel and waste followed by combustion of gaseous products and resins obtained leads to an abrupt increase in the efficiency of energy production. Sometimes, it is more appropriate to extract liquid pyrolysis products (pyrolysis resins) and use them as chemical raw materials for, *e.g.*, production of motor fuels and other products instead of their combustion. Taking into account this fact and an abrupt decrease in the formation of toxic combustion products and, therefore, environmentally hazardous materials release, the use of nontraditional solid fuels as energy sources becomes economically justified.

Filtration combustion in the counterflow regime can be successfully used for processing and unitizing various raw materials. In addition to efficient use of known low-grade solid fuels, this makes it possible to produce energy from waste that are economically unsuitable for processing by traditional technologies. Also, prospects for utilization of unusual sources to obtain valuable chemical products are opened. Application of new technologies for extraction of metals of value and their compounds may lead to transformation of some industries from energy-consuming to energy-producing ones.

Recently, a number of technologies for processing combustible high- and low-calorie waste based on filtration combustion in the counterflow regime and extraction processes of compounds of metals of value from unusual sources were developed. This not only ensures environmental safety of production, but also enables efficient utilization of thermal energy of combustion of waste. Taken altogether, this gives grounds to predict intensive development in the field of research on non-isothermal autowave processes with the counterflow regimes in the nearest future.

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