APPLICATION OF A TUBULAR FLOW REACTOR FOR OIL SHALE PYRO-GASIFICATION

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Abstract. *This article presents the results of testing a horizontal tubular reactor for pyro-gasification of pulverized oil shales to obtain shale gas. The parameters characterizing the thermokinetics of pyro-gasification and heat exchange between the chemically reacting flow of shale gas suspension and the wall of the reactor have been obtained. The algorithm for the reactor design, and the inherent calculation data are provided: residence time for particles in the reactor 0.3–0.4 s and thermal stress volume of reaction 18–27.2 GJ/(m³·h). It is shown that a unit having a tubular reactor exhibits higher performance characteristics compared to existing systems for thermal processing of solid fuels.*

Keywords: *oil shale, pyrolysis, gasification, tubular reactor, thermokinetics, heat exchange, specific indicators.*

1. Introduction

Energy and chemical application of oil shales using a technology based on pyrolysis and gasification is cost effective and environmentally friendly. Additionally, the chemical and energy potential of the fuel can be utilized to the maximum degree. The current research provides the key concepts of the main pyro-gasification processes:

1) high-speed heating of the processed fuel (103–104 K/s) to control chemical transformations, which involves processing pulverized fuel with a particle size of 0.25–0.35 mm;
2) limiting the maximum temperature to avoid softening of the fuel ash;
3) limiting the residence time for fuel particles in the reaction zone to fractions of a second to avoid unwanted secondary reactions;

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4) controlling the process by introducing additives into the fuel dissociation zone, where these are primarily gaseous, oxidizing and reductive;

5) quenching gases recovered through pyro-gasification to maximize the amount of target components.

The above requirements for the pyro-gasification process can be achieved using tubular flow reactors operating on a "gas-suspension" basis. One of the key advantages of tubular reactors is the possibility of supplying large amounts of heat from the external source into the reaction zone through the wall. Figure 1 shows the designed experimental unit [1] for the thermal treatment of pulverized oil shale with a horizontal tubular reactor placed in a fluidized bed of inert materials.

The dried oil shale within the gas flow is transported via reactors where it is heated to the temperature t_p needed for the processing. Thus the heat is received through the reactor wall from the fluidized bed. If necessary, the additional heat required for the process can be obtained using the carrier gas to oxidize a certain amount of organic matter from the transported shale. Upon exiting the reactor the gas suspension separates into phases inside the separator. The gas which is the target product from the oil shale processing is transported from the separator and is directed to quenching and further processing. The separated coke is partially burned in the furnace. The greatest

Fig. 1. Experimental equipment setup: 1 – vessel; 2 – gas distribution grid; 3 – fluidized bed; 4 – tubular reactor; 5, 8 – feeders; 6, 9 – separators; 7 – quench coil; 10 – ash heat exchanger; 11 – technological furnace; 12 – "gas-air" heat exchanger; 13 – riser.

amount of coke is utilized for external purposes. The combustion gases coming from the furnace are used as a coolant and fluidizing agent in the high-temperature fluid bed.

A more detailed description of the principles of operation of the unit is given in [1].

Air (for thermo-oxidative pyrolysis), steam, recycled gas or other gases can be used as the carrier gas in the tubular reactor. The choice of carrier gas depends on the source of oil shale and the desired product. High-speed heating of shale gas suspension in the tubular reactor and rapid cooling of the steam end-products in the quenching heat exchanger, as well as the possibility of regulating the temperature level and residence time of the two streams in the area of heat treatment, can effectively manage the process and thereby influence the composition of the resulting products.

In a complex set of processes that take place in the tubular reactor, heat transfer processes are the primary, and to a great extent influence the operational performance of the entire system. When calculating the heat transfer it is important to take into account the occurrence of chemical reactions in the flow of the fuel gas suspension, and the variability of the flow properties, including the other distinguishing features of thermo-destructive transformations of the original fuel in the flow reactor. Moreover, you need to have relationships which characterize the kinetic and technological parameters of the pyrolysis process.

2. Thermokinetic and technological parameters of pyrolysis

According to experimental data [2], thermo-oxidative pyrolysis of the shale dust occurs in the kinetic response region; therefore, the decomposition rate of the oil shale kerogen under a given level of air consumption is completely determined by the temperature of the process t_p. Kashirskij [2] describes oil shales of the Volga basin (dry weight – 58.47% ash, 13.29% carbonate, 28.47% kerogen), which underwent oxidative pyrolysis using an externally heated tube with the diameter $D = 16$ mm and the length $L = 3.8$ m. The shale particle size d_p was 0–0.250 mm with the initial, as-fired moisture content $W^r \leq 6\%$, and air was the carrier gas. It was found that for the shale particle sizes $d_p < 0.300$ mm, active kerogen decomposition at a heating rate $dt_p/d\tau$ of about 10^3 °C/s starts at a temperature of 200–250 °C. The increase in the amount of the gas phase flowing along the reactor during the pyrolysis of oil shale is close to linear. The curve describing the increase in gas consumption is similar to that depicting the temperature increase of the gas suspension flowing along the reactor.

Due to using carbon steel as material of reactor, which can significantly reduce its manufacturing costs, the selection process temperature $t_p = 600$–750 °C.

Analysis of the gathered data [2] showed the following dependences for the thermo-kinetic and technological pyrolysis characteristics of Kashpirsky oil shale (one of the oil shale fields of the Volga basin) within the temperature range of 600–750 °C:

1) specific yield of pyrolysis gas:

$$g_g = g_v \cdot (9.4 \cdot 10^{-5} \cdot t_p - 0.04) \cdot t_p^{0.613} \cdot (1.66 + 0.046 / g_v^{1.77}), \qquad (1)$$

where g_g is the specific yield of pyrolysis gas, kg/kg of dry oil shale; g_v is the specific consumption of feed air, kg/kg of dry oil shale; t_p is the process temperature, °C;

2) specific yield of coke from the reactor:

$$g_c = 0.95 + 0.6 \cdot g_v \cdot (1 - g_g), \qquad (2)$$

where g_c is the specific yield of coke from the reactor, kg/kg of dry oil shale.

The thermal effect of pyrolysis reactions was calculated in accordance with the Hess law as the difference in the amount of heat between the final and initial reaction products, using data from [2] on the component composition of the gas suspension flowing at the inlet and outlet of the reactor. The results of calculating the heat effect in the temperature range 670–680 °C are approximated by:

$$q_r = 1634 \cdot g_v, \qquad (3)$$

where q_r is the thermal effect of pyrolysis reactions, kJ/kg of dry oil shale.

This defines the specific value of the exothermic heat effect at $g_v \geq 0.04$ kg/per kg of dry oil shale. The dependence of q_r on g_v in Equation (3) is shown in Figure 2. It can be seen that the value of q_r is positive, i.e. the reaction is exothermic, and only in case when $V_v < 30$ l/kg of dry oil shale does q_r change negative and the reaction becomes endothermic.
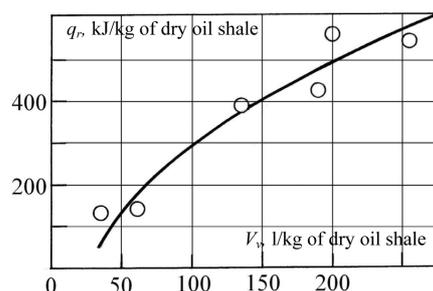

Fig. 2. Dependence of the thermal effect (q_r) of the thermooxidative Kashpirsky oil shale pyrolysis on the air (V_v) introduced into the reactor; $t_p = 640$–680 °C; (circles – calculated experimental data [2]).

According to [3], the amount of heat released in the combustion reactions of fuel required for its complete combustion air g_v is:

$$q_{com} = 4913 \cdot g_v, \tag{4}$$

where q_{com} is the amount of heat released during combustion reactions, kJ/kg of fuel.

It is found that $q_r < q_{com}$.

Based on the heat balance of the pyrolysis process the formula for heat to be delivered through the wall of the reactor is as follows:

$$\tilde{q} = 1.65 \cdot g_v \cdot t_p + 1.3 \cdot g_c \cdot t_p - 1.1 \cdot t_{T,0} - g_v \cdot t_{v,0} - q_r, \tag{5}$$

where $\tilde{q}$ is the amount of heat which must go through the wall of the reactor, kJ/kg of dry oil shale; $t_{T,0}$ and $t_{v,0}$ are the initial temperatures of shale and air, respectively, °C.

3. External and internal heat transfer

The heat transfer coefficient of the fluidized bed reactor with horizontal pipes, for fluidization velocity values $w_{wor} \geq w_{opt}$, where w_{opt} is the optimum speed (corresponding to the maximum rate of heat transfer), can be calculated according to the Zabrodsky formula [4], as shown by Equation (6):

$$\alpha_{k.sl.} = 35.8 \cdot \lambda_{p.c.}^{0.6} \cdot \rho_p^{0.2} \cdot d_{p,k.sl.}^{-0.36}, \tag{6}$$

where $\alpha_{k.sl.}$ is the heat transfer coefficient of the fluidized bed reactor with horizontal pipes, W/(m²·K); $\lambda_{p.c.}$ is the thermal conductivity of coke combustion products, W/(m·K); ρ_p is the density of solids, kg/m³; $d_{p,k.sl.}$ is the size of particles in a fluidized bed, m.

If substituting the numerical values of the fluidizing gas properties and particles, the result is as follows:

$$\alpha_{k.sl.} = 43 \cdot d_{p,k.sl.}^{-0.36}. \tag{7}$$

When placing the tube bundle with a relative pitch of $S/D \geq 2.5$ within 0.2 m above the gas distribution grid to H (height of the original dense layer), heat transfer patterns are the same as for single tubes [4]. A relatively dense arrangement of pipes is possible without reducing the heat transfer.

The specific area of the fluidized bed section per kg/s of dry processed shale is:

$$f_{k.sl.} = \frac{F_{k.sl.}}{G_s} = \frac{g_{p.c.}}{\rho_{p.c.} \cdot w_{wor}}$$
$$= 5.18 \cdot 10^{-9} \cdot \tilde{q} \cdot (1050 - t_{k.sl.})^{-1} \cdot (18 + 5.5 \cdot 10^6 \cdot d_{p,k.sl.}^{1.5}) \cdot d_{p,k.sl.}^{-2}, \tag{8}$$

where $f_{k.sl.}$ is the specific cross-sectional area of the fluidized bed, m²·s/kg of dry oil shale; $F_{k.sl.}$ is the surface area of the fluidized bed, m²; G_s is the mass flow of the solid phase, kg/s; $g_{p.c.}$ is the specific consumption of coke combustion, kg/kg of dry oil shale; $\rho_{p.c.}$ is the density of the products of combustion of coke, kg/m³; w_{wor} is the working fluidization velocity, m/s; $t_{k.sl.}$ is the temperature of the fluidized bed, °C.

The specific surface area of heat transfer reactor tubes in a fluidized bed, per 1 kg/s of dry processed shale:

$$f = \frac{F}{G_s} = \frac{10^3 \cdot \tilde{q}}{q_w} = 10^3 \cdot \tilde{q} / \left[\alpha_{k.sl.} \cdot (t_{k.sl.} - t_w) \right], \tag{9}$$

where f is the heat transfer surface area of the reactor tubes in a fluidized bed, m²·s/kg of dry oil shale; F is the integral (total) heat exchange surface of the reactor tubes, m²; t_w is the pipe wall temperature, °C; q_w is the heat flux at the wall, W/m².

Using (7), Equation (9) will acquire the form:

$$f = 23.26 \cdot \tilde{q} \cdot d_{p,k.sl.}^{0.36} \cdot (t_{k.sl.} - t_w)^{-1}. \tag{10}$$

Dividing (10) by (8) term by term, we have:

$$F / F_{k.sl.} = f / f_{k.sl.} = 4.485 \cdot 10^9 \cdot d_{p,k.sl.}^{2.36} \cdot (1050 - t_{k.sl.})$$
$$\times \left[(t_{k.sl.} - t_w) \cdot (18 + 5.5 \cdot 10^6 \cdot d_{p,k.sl.}^{1.5}) \right]^{-1}. \tag{11}$$

The ratio $F / F_{k.sl.}$ can be determined by the structural characteristics. The height of the particle bed prior to its fluidization should be no less than 0.6 m to ensure the necessary degree of fluidized bed uniformity. The heating surface is at the height corresponding to the dense layer. In this case maximum heat transfer coefficients are provided which are the same for all rows of posted reactor tubes.

Calculation of the internal heat transfer in the reactor tube is performed using similarity equations for the average heat flow of gas suspension to the decomposition of solid particles [5], and a numerical method to estimate the heat transfer of the chemically reacting gas suspension flow [6].

4. Calculation results

An algorithm has been developed for various pyrolysis calculations. Some of the results of calculations related to reactor diameters of 0.02 and 0.04 m are shown in Table 1.

The data in Table 1 show that feeding the reactor with wet slate requires an increase in the length of the reactor. The amount of coke, g_c, produced from oil shale pyrolysis under the conditions given in Table 1 equals 0.75–0.85 kg/per kg of dry oil shale. The need for coke combustion in the furnace process is significantly lower at 0.184 kg/per kg of dry oil shale at $t_p = 600$ °C and 0.208 kg/per kg of dry oil shale at 700 °C. Thus the process of oxidative pyrolysis of oil shale described in [1] is enclosed in terms of heat energy.

Table 1. Reactor parameters and process conditions of the oxidative pyrolysis of Volga basin oil shales

D, m	L, m	g_t, kg/kg of dry oil shale	W^r, %	t_p, °C	t_0, °C	$t_{k.sl}$, °C	$G_{s,0}$, kg/s	K_0, kg/kg	g_g, kg/kg of dry oil shale	w_0, m/s	Q, kW	Q_r, kW
0.02	12.00	0.065	0	600	214	722	0.047	15.4	0.40	13.4	23.72	5.62
0.02	5.30	0.130	0	600	232	692	0.020	7.7	0.36	11.8	7.92	4.66
0.02	4.70	0.130	0	600	274	683	0.018	7.7	0.36	11.7	6.33	4.3
0.02	3.00	0.195	0	600	192	704	0.013	5.1	0.40	11.0	5.1	4.65
0.02	3.20	0.195	0	700	367	773	0.009	5.1	0.50	10.8	3.75	3.34
0.04	9.40	0.162	0	600	242	682	0.070	6.4	0.38	12.9	26.1	19.91
0.04	7.70	0.195	0	600	192	693	0.061	5.1	0.40	12.4	23.7	21.1
0.04	6.10	0.195	0	600	253	679	0.053	5.1	0.40	12.4	18.6	16.2
0.04	8.24	0.195	6	600	171	698	0.064	5.1	0.40	12.5	26.0	22.1
0.04	9.30	0.195	12	600	128	709	0.071	5.1	0.40	12.5	32.9	24.6

Indicated: D and L – diameter and length of the reactor; W^r – moisture of the source shale; t_0 – temperature of the flow at the intake; $t_{k.sl.}$ – temperature of the fluidized bed; $G_{s,0}$ – consumption of oil shale; Q – total heat of the process; Q_r – reaction heat.

Heat exchange between the shale gas suspension flow and the wall is of high intensity. For example, at the initial concentration of particles $K_0 = 5.1$ (kg/h)/(kg/h), the air velocity $w_0 = 11$ m/s, the reactor diameter $D = 0.02$ m, and the average particle diameter $d_p = 0.150$ mm, the average heat transfer coefficient, α, of the reacting flow of gas suspension equals 180 W/(m^2·K). Under the same conditions, the average heat transfer coefficient, α, of the flow of clean air without particles equals 83 W/(m^2·K).

The curves depicting the change in the values of parameters along the reactor under the above process conditions are shown in Figure 3.

The data in Figure 3 are typical and show that the temperature of the reactor wall increases with the length of the stream reactor, x. The difference between temperatures of the wall at the output and input of the reactor under the considered conditions may amount to 100 °C or more.

Almost over the entire length of the reactor during the heating the flow temperature $t_{p,aw.}$ is below the temperature $t_{g,aw}$. As seen from Figure 3, at the end of the reactor the temperature $t_{p,aw.}$ becomes higher than $t_{g,aw}$. The temperature rises with an increase in V_v. This is the result of exothermic oxidation reactions of shale particles during the heating process.

A significant decrease in the concentration of particles K along the length of the stream reactor x (Fig. 3) is due to gasification. The sliding speed factor of the particles, φ_v, increases at the initial part of the reactor where rapid warming of the flow occurs, and slowly decreases along the length of the reactor, x.

In Figure 3 parameters (dashed lines) for the chemically inert flow at $Q_r = 0$ and those of the reacting flow are provided, so they can be compared.

Data on external heat exchange are shown in Figure 4, which depicts the change of the working fluidization velocity and temperature of the fluidized bed (Fig. 4a), as well as parameters $F/F_{k.sl.}$ and $f_{k.sl.}$ (Fig. 4b) with the particle diameter $d_{p,k.sl.}$. On the computational model adopted the change of the particle diameter $d_{p,k.sl}$ does not affect the length of the reactor and its heat
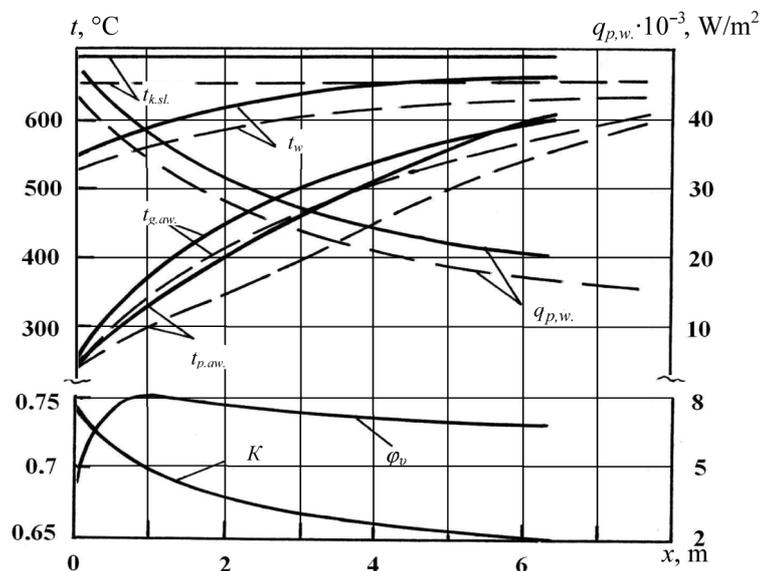

Fig. 3. The change of values of $q_{p,w.}$ along the flow reactor: $D = 0.02$ m; $d_p = 0.150$ mm; $V_v = 100$ l/kg of oil shale; $t_0 = 232$ °C; $Q = 7916$ W; $Q_r = 4661$ W; (solid lines – reacting flows, dashed lines – chemically inert flow).
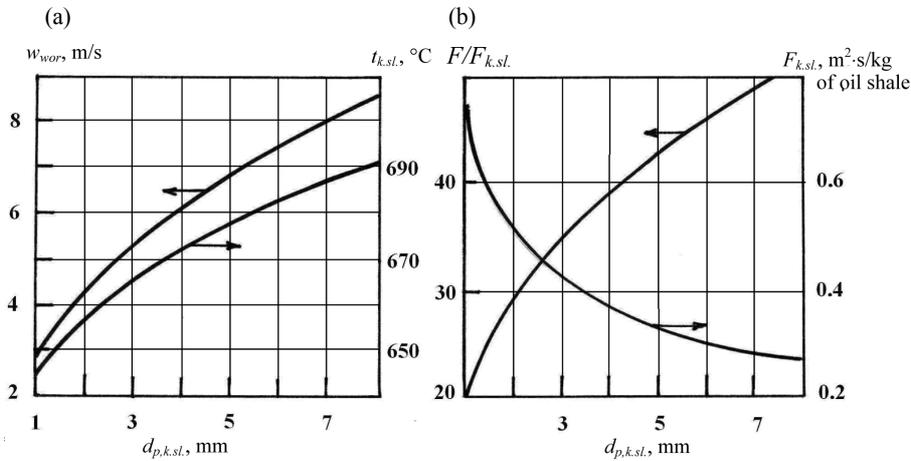
Fig. 4. Effect of the particle diameter $d_{p,\ k.sl}$ on the regime for fluidized bed (a) and design (b) with $D = 0.04$ m; $d_m = 150$ mkm; $t_0 = 253$ °C; $W^r = 0\%$; $V_v = 150$ l/kg of oil shale.

output. This effect is mediated via the temperature of the fluidized bed, $t_{k.sl.}$, which increases with $d_{p,k.sl.}$ (Fig. 4a). The correlation of $F/F_{k.sl.}$ and $f_{k.sl.}$ with the particle diameter $d_{p,k.sl.}$ (Fig. 4b) allows management of the design dimensions and layout of the fluidized bed reactor in the layer by varying $d_{p,k.sl.}$.

For the particle size $d_{p,k.sl.} = 6$ mm, as an example, the following space arrangement can be considered. With a fluidized bed height of 1.8 m and an area of the gas distribution grid of 5.3 × 1 m calculations yielded $S_1 = 3D$ and $S_2 = 0.866S_1$ for the reactor diameter $D = 0.02$ m and number of reactors $N = 630$, and the surface area of heat transfer $F_\Sigma = 212$ m^2.

At the oil shale flow rate $G_{s,0} = 0.02$ kg/s in one reactor, the capacity of the unit based on processed fuel is 46 t/h or 1104 t/day. At $t_p = 600$ °C the amount of pyrolysis gas produced G_g is 400 t/day ($V_v = 100$ l/kg of dry oil shale) and coke (net supply to the furnace) G_c is 618 t/day. The thermal output from the fluidized bed will be close to 5 MW and the total heat output, including the heat of pyrolysis reactions, is 8 MW.

Table 2 compares the characteristics of contemporary processes of gasification of solid fuels [7–9] and thermooxidative Volga shale pyrolysis in tubular reactors. It can be seen that the consumption of processed oil shale per unit reactor volume and pyrolysis gas yield per unit cross-sectional area of the reactor for tubular reactors is one–two orders of magnitude higher than that for the other known reactor devices with dense or fluid layers.

Table 2. Key parameters for the current gasification of solid fuels and thermooxidative pyrolysis of the Volga basin oil shale in tubular reactors

Process	Data									
	Single productivity for installation on fuel, t/h	d_p, mm	t_p, °C	Residence time for particles in the reactor, s	Gas output, thousand m³/h	Heat at gas combustion, kJ/m³	Thermal stress reaction volume, GJ/(m³·h)	Specific fuel consumption, kg/(m³·h)	Intensity of the gas, kg/(m²·h)	Volume of the reactor apparatus, m³
Lurgi (dense layer of steam-oxygen blowing, P = 20–25 am)	coal 40–75	5–30	1100	5000	75	12000–16300	2.9–5.4	250	2000	160
Winkler (fluidized bed, steam-oxygen or air blast, P = 1 am)	coal 20–35	≤ 10	1000	100–500	60	7500–9400	0.9–8.4	71	3000	550
Koppers-Tottsek (dust-coal flame, steam-oxygen blast, P = 1 am)	coal to 40	≤ 0.1	1500	ca 1	50	10300–11700	3.6–25	360	3000	60 (with 4 nozzles)
UTT-3000 (P = 1 am)	oil shale 139	≤ 20	500	ca 2000	5–8	48400	–	463	400	300
Tubular reactors (air blast, P = 1 am): D = 0.02 m; N = 630 pcs;	oil shale 46	0.15	600	0.3	16.7	12000	27.2	4822	230000	9.5
D = 0.04 m; N = 315 pcs	69.2	0.15	600	0.4	27.7	11000	18	2563	180121	27

5. Conclusions

The residence time for the oil shale particles in the reaction zone of tubular reactors is within the range 0.3–0.4 s, which distinguishes the gas-suspended pyrolysis mode from long-residence time processes with a dense layer of particles or fluid. In contrast to those devices, high-speed pyrolysis in tubular reactors is manageable. The tubular reactors provide the needed heat input via the tube walls from an external source, and they produce a quality gas product which is not diluted with other components.

The specific parameters, such as consumption of processed oil shale per reactor volume and yield of pyrolysis gas per cross section of reactor, are much higher for tubular reactors than for existing reactor devices with dense and fluid layers.

SYMBOLS: D – tube diameter, m; dp – size of solid particles, equal to the diameter of the ball, which is equivalent to the particle surface, m; F – surface area, m^2; G – mass flow, kg/s; g – specific consumption, kg/kg of dry oil shale; V_v – air flow, l/kg of dry oil shale; K – expenditure mass concentration of shale particles in the gas stream, (kg/h)/(kg/h); Q – capacity of the heat flow, W; q – heat flux, W/m^2; t – temperature, °C; w – average speed of the continuous phase in the section of the channel, m/s; x – length of the reactor, m; α – heat transfer coefficient, W/(m^2·K); λ – thermal conductivity, W/(m·K); ρ – density, kg/m^3; τ – time, s; $\varphi_v = u/w$ – particle velocity slip factor; u – average speed solids section of the channel, m/s.

INDICES: v – air; g – gaseous phase; s – solid phase; w – parameter on the wall or at a wall temperature; $av.$ – option when the average temperature of; r – chemical reaction; p – flow, process; $p.c.$ – gaseous products of combustion of coke; $k.sl.$ – fluidized bed.

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