area; d_v, inner diameter of outer tube. Subscripts: ev, evaporator; con, condenser; f, friction; ac, acceleration; l.r., local resistance; k, heat transfer coefficient; ex, external diameter of inner tube; i, inner tube; ℓ, liquid; v, vapor.

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A MATHEMATICAL MODEL OF SOOT FORMATION IN NATURAL GAS COMBUSTION.

1. KINETIC EQUATION AND CRITICAL TEMPERATURE OF THE DEHYDROGENIZATION PROCESS

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Elements of a mathematical model are presented for the process of soot formation in natural gas combustion, based on thermal decomposition of the CH_4 methane molecule. The expressions obtained can be used for calculation of the size and concentration of soot particles and their thermal radiation in a natural gas flame.

The thermal radiation produced by a natural gas flame depends significantly upon the size and concentration of soot particles within the flame, which substance, together with the gaseous products of complete combustion (CO_2, H_2O) determine its optical thickness and emissivity [1].

In turn, the soot-formation process depends on the conditions of internal heat-mass exchange between the various zones of the flame, related mainly to the turbulent microstructure. Analysis of well-known expressions for the turbulent mixing time indicates that increase in the scale of turbulent pulsations increases mass exchange within the flame and leads to a reduction in soot-formation time. On the other hand, retardation of the soot-formation process can be achieved by reducing the scale of turbulent pulsations.

It follows from the above that the possibility of controlling the soot-formation process and, thus, the emissivity of a flame rests upon the ability to control the aerodynamic microstructure of the turbulent flame in the segment where that structure is formed, by controlling the processes of fuel and air mixing. It then becomes possible to organize combustion temperature regimes and the dynamics of the soot-formation process.

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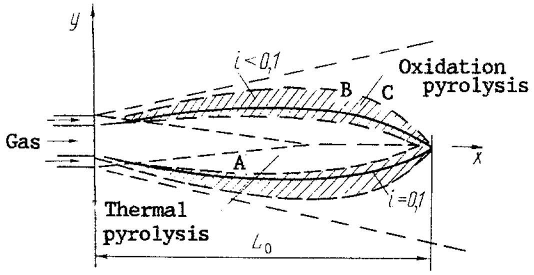

Fig. 1. Diagram of turbulent diffusion flame.

Under the conditions which we will consider in a natural gas flame (Fig. 1) the processes of oxidation (combustion) and thermal decomposition (pyrolysis) of methane occur simultaneously. These are accompanied by condensation of carbon and formation of corresponding carbon complexes. Three distinctive zones can be distinguished within the flame as regards the character of the processes occurring and the distribution of combustion products.

The first zone (zone A) is the zone of soot particle generation. In this zone thermal pyrolysis (decomposition) of the CH_4 molecule and its radicals dominates, with subsequent formation of free carbon atoms and complexes thereof in the last stage of the process. Formation of free carbon atoms also occurs simultaneously within the volume due to bimolecular chemical reactions between the radicals $\dot{C}H_3$, $\ddot{C}H_2$, and $\dddot{C}H$. Reverse chemical reactions also occur, leading to reformation of CH_4 molecules. This zone is characterized by an excess of fuel and lack of oxidizer, with temperature of the order of magnitude of 900-1000 K.

In contrast to zone A, the second zone (zone B) is characterized by an excess of oxidizer. The highest temperature, close to adiabatic, is attained in this zone. Under the conditions indicated, CH_4 oxidation (combustion) reactions predominate, determining the thermal regime of the flame. Simultaneously, interaction of carbon atoms and their complexes leads to disruption of the latter with formation of carbon dioxide.

The third zone (zone C) is the burnup zone, in which all chemical reactions are completed and the equilibrium concentrations of complete combustion products established.

Naturally these zones interact with each other, insuring stability of the methane combustion process. Thus, the temperature regime of zone A is determined mainly by turbulent heat-mass transport between the zone and zone B. Because of turbulent pulsations products of incompleted reactions and oxygen are brought into zone A from zone B. Turbulent heat transport into this zone encourages the process of methane dehydrogenization with formation of radicals and atomic carbon.

Considering that marked thermal decay of methane occurs at temperatures above 900 K [2, 3] we will assume the basic zone of soot particle (carbon complex) formation to be zone B.

Thus, the process of atomic hydrogen formation can be considered as a process of CH_4 molecule dehydrogenization and its radical due to removal of hydrogen atoms therefrom. Depending on temperature conditions hydrogenization reactions may also occur, i.e., reactions wherein hydrogen combines with hydrocarbon radicals with final formation of a CH_4 molecule. We will note that as consequence of the high chemical activity of the radicals bimolecular reactions between radicals can also occur at lower values of activation energy. The carbon atoms formed in the flame act as seed nuclei of soot particles, the dimensions of which are determined by the processes of combination of free carbon atoms and destruction of the corresponding hydrocarbon complexes.

In the final outcome the equilibrium concentration of stable carbon complexes and sizes thereof are determined by two oppositely directed processes: formation and enlargement of complexes, on the one hand, and destruction and decrease in size of complexes on the other. In the final reckoning these two processes determine both the size of soot particles (carbon complexes) and their concentration in the gas volume.

Under equilibrium conditions carbon complexes C_n, containing various numbers of carbon atoms n, must always exist in the gas volume. The size r_n of the complex C_n is determined by the number n of carbon atoms forming this complex. If we denote the volume of a single carbon atom by V_0, then for a complex C_n of n carbon atoms the volume of the complex can be written in the form

$$V_n = V_0 n. \tag{1}$$

Denoting by i_n the number of complexes C_n having a volume of V_n each, it is simple to determine the relative content of carbon complexes of various size in the gas volume:

$$N(V_n) = \frac{i_n n}{\sum_{n=1}^{\infty} i_n n}. \tag{2}$$

Equation (2) defines the distribution of carbon complexes over volume under equilibrium conditions. The total mass of complexes formed is

$$M = \sum_{n=1}^{\infty} m_0 n i_n, \tag{3}$$

where m_0 is the mass of a carbon atom.

In accordance with the pattern of the process which we will consider, formation of free carbon radicals C occurs in stages of sequential splitting from the original CH_4 hydrocarbon of a single hydrogen atom $\dot{H}$.

Splitting of a hydrogen atom from the CH_4 molecule and the hydrocarbon radicals ($\dot{C}H_3$, $\ddot{C}H_2$, $\dddot{C}H$) is accompanied by appearance in the gaseous phase of a free hydrogen radical $\dot{H}$. Oppositely directed processes of hydrogen combination with the above-mentioned radicals can also occur due to collisions.

The equilibrium concentration of the hydrocarbon atoms $\dot{C}H_3$, $\ddot{C}H_2$, $\dddot{C}H$ and hydrogen in the gaseous phase is determined by conditions of dynamic equilibrium between the processes of splitting and combining of hydrogen atoms with the hydrocarbon radicals.

Under the conditions considered, the change per unit time in number of hydrogen atoms n_H in hydrocarbon radicals can be described by a known kinetic equation of the form

$$\frac{dn_H}{d\tau} = \frac{n_H^-}{t^-} - \frac{n_H^+}{t^+}. \tag{4}$$

Here n_H^+ is the mean number of hydrogen atoms leaving a hydrocarbon radical over time t^+; n_H^- is the mean number of hydrogen atoms combining with hydrocarbon radicals over the time t^-.

Considering that the ratio

$$\frac{t^+}{n_H^+} = \tau^+ \tag{5}$$

characterizes the mean time over which one hydrogen atom splits from a hydrocarbon radical, while the ratio

$$\frac{t^-}{n_H^-} = \tau^- \tag{6}$$

characterizes the mean time over which a hydrogen atom combines with a hydrocarbon radical, we write Eq. (4) in the form

$$\frac{dn_H}{d\tau} = \frac{1}{\tau^-} - \frac{1}{\tau^+}. \tag{7}$$

In essence, the quantities τ^- and τ^+ represent the mean-free-path time of a hydrocarbon radical and the mean time of existence of a hydrogen atom in combination with a hydrocarbon radical. The ratio of these quantities determines the conditions under which the hydrocarbon dehydrogenization process occurs, related to disappearance and reappearance of hydrocarbon radicals.

The higher the value of the mean-free-path time of hydrocarbon radicals τ^- the smaller the probability of collision with hydrogen radicals and, thus, the lower the probability of reestablishment. Conversely, the smaller the mean time for splitting of a hydrogen atom from a hydrocarbon radical τ_+, the higher the probability of its loss, i.e., the probability of free carbon formation. Thus, the quantity $1/\tau^-$ characterizes the probability of survival, and $1/\tau^+$, the probability of loss, of hydrocarbon radicals per unit time.

The condition

$$\tau^- = \tau^+ \tag{8}$$

corresponds to detailed dynamic equilibrium, where the total number of hydrogen atoms departing from a hydrocarbon radical per unit time becomes equal to the number of hydrogen atoms combining with such radicals.

In accordance with the kinetic theory of gases the mean-free-path time of a hydrocarbon radical in a hydrogen atmosphere is determined by the expression

$$\tau^- = \frac{1}{pN_H \cdot 10^3 \left(\frac{kT}{2\pi M_H} \frac{M_p + M_H}{M_p}\right)^{1/2} \pi (r_p + r_H)^2}, \tag{9}$$

in which the coefficient $p = 1.6 \cdot 10^{-2}$ [3, 4]; N_H is the volume concentration of hydrogen; T, temperature; M_p, mass of the hydrocarbon radical; M_H, mass of the hydrogen atom; r_p, radius of the hydrocarbon radical; r_H, radius of the hydrogen atom; k, Boltzmann's constant.

The mean stay of a hydrogen atom in a hydrocarbon radical can be defined by

$$\tau^+ = \tau_0 \exp\left[\frac{E(n_H)}{kT}\right], \tag{10}$$

where τ_0 is the period of natural oscillation of the hydrogen atom, and $E(n_H)$ is its binding energy in the hydrocarbon radical.

The period of natural oscillation of the hydrogen atom in the hydrocarbon radical is given by

$$\tau_0 = \frac{\Delta}{\left(\frac{kT}{2\pi M_H}\right)^{1/2}}, \tag{11}$$

where Δ is the amplitude of hydrogen atom oscillation.

Since the hydrogen atom enters into the radical in a bound state, the amplitude of its oscillations is determined by the mean distance between adjacent molecules and the number of such molecules in the volume considered. In a first approximation we may assume that the value of Δ is inversely proportional to the molecular packing density $\Delta = 1/n$.

Considering Eq. (11), we rewrite Eq. (10) in the form

$$\tau^+ = \frac{\Delta}{\left(\frac{kT}{2\pi M_H}\right)^{1/2}} \exp\left[\frac{E(n_H)}{kT}\right].$$

Making use of Eqs. (8) and (10), it is simple to determine the probability of entrance into the volume of free hydrogen atoms per unit time ($1/\tau^+$) and the probability of departure of such atoms from the volume ($1/\tau^-$) due to combination with hydrocarbon radicals in collision processes. The quantity $1/\tau^+$ then characterizes the rate of entrance into the volume of free hydrogen atoms W_H^+, while the value $1/\tau^-$ characterizes their loss rate W_H^-.

On the basis of molecular-kinetic theory we can write

$$W_H^- = N_H p \left(\frac{kT}{2\pi M_H} \frac{M_p + M_H}{M_p}\right)^{1/2} \pi (r_p + r_H)^2, \tag{12}$$

$$W_H^+ = \frac{1}{\Delta} \left(\frac{kT}{2\pi M_H}\right)^{1/2} \exp\left[-\frac{E(n_H)}{kT}\right]. \tag{13}$$

As is evident from these expressions, the quantities W_H^- and W_H+ depend on the temperature T. It is simple to define a temperature T equal to T* at which the rate of free hydrogen atom arrival in the volume becomes equal to the rate of their loss from the volume ($W_H^- = W_H^+$). This temperature T* at which this equation is satisfied will be called the critical temperature for the hydrocarbon dehydrogenization process.

On this basis we can write

$$pN_H\left(\frac{kT}{2\pi M_H}\frac{M_p+M_H}{M_p}\right)^{1/2}\pi(r_p+r_H)^2=\\=\frac{1}{\Delta}\left(\frac{kT}{2\pi M_H}\right)^{1/2}\exp\left[-\frac{E(n_H)}{kT}\right]. \tag{14}$$

In Eq. (14) we have the value of the net volume concentration of hydrogen atoms N_H formed by breakoff of one, two, three, and four hydrogen atoms from the original CH_4 hydrocarbon.

If we denote the activation energy for the process of breakoff of the first atom by E(1), and the corresponding volume concentration of free hydrogen atoms by N_{1H}, on the basis of Eq. (14) we can write the condition for equilibrium between $\dot{C}H_3$ radicals and free hydrogen atoms $\dot{H}$ in the form

$$p,\ N_{1H}\left(\frac{kT_1^*}{2\pi M_H}\frac{M_p+M_H}{M_p}\right)^{1/2}\pi(r_p+r_H)^2=\\=\frac{1}{\Delta}\left(\frac{kT}{2\pi M_H}\right)^{1/2}\exp\left[-\frac{E(1)}{kT_1^*}\right]. \tag{15}$$

Using Eq. (15) it is simple to determine the critical temperature of the dehydrogenization process T_1^* for breakoff of the first hydrogen atom from the CH_4 molecule. At this temperature there is an equilibrium between the number of hydrogen atoms arriving in the volume due to breaking of a C—H bond in the CH_4 molecule and the number of hydrogen atoms disappearing from the volume due to combination with CH_3 radicals during collisions with the latter. For the breakaway of n hydrogen atoms the critical temperature for the dehydrogenization process is given by the equation

$$T^*=-\frac{1}{k}\frac{E(n_H)}{\ln\left[p\left(\frac{M_H+M_p}{M_p}\right)^{1/2}\pi(r_p+r_H)^2\right]}. \tag{16}$$

Due to indefinite knowledge of the gas-kinetic dimensions of the radicals in the calculations we take them equal to the molecule diameter. Then the value of the quantity $(M_H + M_p)/M_p$ can be determined from the first stage of thermal decomposition of methane. Calculations show that this assumption is acceptable, since the numerical value of the argument of the logarithm increases with increased depth of methane decomposition by no more than 0.02%.

The rate of thermal decay of the CH_4 molecule and its radicals [4] is controlled by the energy required to break a C—H bond. Under the conditions considered,

$$CH_4\rightarrow C\dot{H}_3+\dot{H}-427\ \text{kJ/mole},\quad C\dot{H}_3\rightarrow \dot{C}\dot{H}_2+\dot{H}-355.8\ \text{kJ/mole},\\ \dot{C}\dot{H}_2\rightarrow C\ddot{H}+\dot{H}-535.8\ \text{kJ/mole},\quad \dot{C}\ddot{H}\rightarrow C+\dot{H}-334.9\ \text{kJ/mole}. \tag{17}$$

The critical temperatures for the subsequent stages of dehydrogenization of methane and its radicals comprise: $T^*_{CH_4}=1162$ K; $T^*_{C\dot{H}_3}=968$ *K*; $T^*_{C\dot{H}_2}=1458$ K; $T^*_{C\dot{H}}=911$ K.

The quite high temperature $T^*_{C\dot{H}_2}$ required for the reaction $\ddot{C}H_2 \rightarrow \ddot{C}H + \dot{H}$ in essence limits the ability to form atomic hydrogen in the gaseous volume. If the real gas temperature $T<T^*_{C\dot{H}_2}$, the chain is broken and $\ddot{C}H_2$ radicals accumulate in the volume. Further development of the process is then determined by the need to attain a temperature $T>T^*_{C\dot{H}_2}$ in the gas volume.

We will now determine how the ratio between the quantities W_H^+ and W_H^- varies with deviation of the gas temperature T from the critical temperature T^*. Considering Eqs. (12) and (13) we write

$$\frac{W_{\mathrm{H}}^{+}(T)}{W_{\mathrm{H}}^{+}(T^{*})}=\sqrt{\frac{T}{T^{*}}}\,\frac{\exp\left[-\frac{E(n)}{kT}\right]}{\exp\left[-\frac{E(n)}{kT^{*}}\right]} \tag{18}$$

and

$$\frac{W_{\mathrm{H}}^{-}(T)}{W_{\mathrm{H}}^{-}(T^{*})}=\sqrt{\frac{T}{T^{*}}}. \tag{19}$$

Denoting

$$\Delta T=T-T^{*}, \tag{20}$$

we obtain

$$\frac{W_{\mathrm{H}}^{+}(T)}{W_{\mathrm{H}}^{-}(T)}=\exp\left[\frac{E(n)}{kT}\,\frac{\Delta T}{T^{*}}\right]. \tag{21}$$

As is evident from Eq. (21), the quantity $W_H^+(T)/W_H^-(T)$ depends on two parameters: the relationship between E(n) and kT and the magnitude of the ratio $\Delta T/T^*$.

In Eq. (21) the quantity kT characterizes the mean kinetic energy of translational motion of free hydrogen atoms $\varepsilon = 3/2kT$.

Under the conditions considered herein for thermal decomposition of hydrocarbobs by energetic breaking of C—H bonds the binding energy of hydrogen atoms in hydrocarbon radicals and the CH_4 molecule E(n) exceeds the mean kinetic energy of hydrogen atom translational kinetic energy $\bar{\varepsilon}$. Therefore,

$$\frac{E(n)}{kT}>\frac{E(n)}{\bar{\varepsilon}}>1.0.$$

Consequently, the direction of the process (dehydrogenization-hydrogenization) is completely determined by the sign of the ratio $\Delta T/T^*$. For $\Delta T/T^* > 0$, i.e., at $T > T^*$, $W_H^+(T)/W_H^-(T) > 1.0$. This means that under conditions in which the gas temperature slightly exceeds the critical temperature T^*, the dehydrogenization process dominates over hydrogenization, as a result of which the concentration of free hydrogen atoms increases.

On the other hand, for $\Delta T/T^* < 0$, i.e., $T < T^*$, $W_H^+(T)/W_H^-(T) < 1.0$, and hydrogenization dominates over dehydrogenization, as a result of which the free hydrogen atom concentration decreases.

The most favorable conditions for free carbon formation are reached in that stage of the process where the original CH_4 hydrocarbon loses all four hydrogen atoms over a time τ_{ind} which we will call the induction time, due to breaking of C—H bonds. The free carbon atoms thus formed act as seed nuclei upon which soot particles of varying size are then formed.

An important role in the process of thermal decomposition of the original hydrocarbon molecule is played by turbulent pulsations: their frequency, scale, and speed, which determine the mixing time τ_m for the flame components [5] and the soot formation time τ_{soot} (Fig. 2).

In the case of isotropic turbulence it is simple to determine the mixing time for the combustion components which ensures sufficient preheating of the gas layer and its saturation by oxidizer.

The maximum soot output is reached under conditions where the mixing time τ_m exceeds the induction time τ_{ind}.

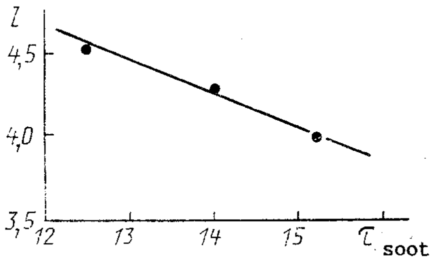

Fig. 2. Soot formation time vs pulsation scale. ℓ, mm; τ_{soot}, msec.

Depending upon the relationship between the quantities τ_{ind} and τ_m, one or the other equilibrium concentration of soot particles in the flame is reached. The induction time τ_{ind} is then basically determined by the thermokinetic characteristics of the process, while the mixing time τ_m is determined by the turbulence characteristics of the gas flow.

The second portion of this study will be dedicated to questions related to calculation of the induction time and the dynamics of carbon complex formation. A third part will consider the effect on the soot formation process of the turbulent flame microstructure.

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ROTATIONAL INSTABILITY OF THE LAMINAR FLOW OF PSEUDOPLASTIC FLUIDS IN A COAXIAL-CYLINDRICAL CHANNEL*

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UDC 532.582.82

Measurements of the stability limit of a spiral flow of a non-Newtonian fluid ($n \le 1$) in a coaxial-cylindrical channel are presented and substantiated.

INTRODUCTION

Many problems in mechanical and chemical engineering involve the motion of a fluid in an annular slit with a rotating cylindrical inside surface and a stagnant outside surface: the cooling of the rotors of electrical machinery [1]; dynamic filtration on a cylindrical interface [2]; the lubrication of bearings [3]; the operation of electrochemical reactors with a rotating cylindrical electrode [4]. Such flows are termed spiral flows and offer a particular advantage for high-viscosity pseudoplastic fluids. In this case, it is possible to reach high shear rates regardless of how long the fluid has been in the unit, i.e., regardless of the flow rate [5].

In the hydrodynamic analysis of spiral laminar flows, special attention is paid to the problem of their stability. Numerous theoretical and experimental studies have been conducted for Newtonian fluids. A survey of these investigations can be found in [6-8]. It is well known that a rotational flow becomes unstable when the angular velocity of the moving cylinder is sufficiently high. In this case, there is an abrupt disturbance of the axial (longitudinal) head flow. The boundaries of stability of the spiral flow are determined by two dimensionless parameters: the axial Reynolds number and the critical value of the rotational Taylor number. Within the region of small Re, the critical value of Ta increases monotonically with an increase in Re. The monotonic stabilization of circular Couette flow by the axial flow is disturbed at sufficiently high Re and the value of Ta_c decreases slightly with a further increase in Re [6]. The rotational instability of spiral flow is known to be

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