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EXPERIMENTAL STUDY OF THE CHARACTERISTICS OF A MIXING D_2–CO_2-GDL

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UDC 621.373.826.038.823

Higher values of laser characteristics were obtained in a mixing D_2–CO_2-GDL than in N_2–CO_2-, N_2–N_2O-, and D_2–N_2O-mixing GDL with stagnation temperatures $T_0 \leq 1600$ K.

The D_2–CO_2 system is of interest for the development of low-temperature GDL with a high specific output energy. The distinguishing feature of this molecular couple is the existence of a large energy defect between the vibrational quantum of deuterium ($\Theta_4 = 4310$ K) and the 00^01 level of the CO_2 molecule ($\Theta_3 = 3380$ K). The possibility of pumping the antisymmetric mode of CO_2 with deuterium through the combination level of CO_2 (01^11) was demonstrated in [1, 2]. The antisymmetric mode of CO_2 is heated up to temperatures exceeding the stagnation temperature of the gas flow as a result of such nonresonant exchange between the vibrational levels of the energy-carrying and radiating components. Gains of ~1 m^{-1} at $T_0 \simeq 840$ K have been obtained in a GDL with a premixed mixture $D_2 + CO_2$ [2]. For $T_0 > 1000$ K, however, the chemical reaction between D_2 and CO_2, reducing the amount of CO_2 in the mixture and forming D_2O [4], can have a negative effect. For this reason it is of interest to study the scheme of a mixing GDL (MGDL) with selective heating of deuterium.

In [3, 4] the specific laser energy in D_2–CO_2 was found to be ~100 J/g for $T_0 = 2000$ K under the assumption of instantaneous mixing. The approximate character of the mixing model employed does not permit objective evaluation of the possibilities of this layer. Since the molecular masses of the mixing flows differ by a factor of 11 and deuterium is a strong deactivator of vibrational excitation in CO_2 [5], the mixing of D_2 and CO_2 can be accompanied by large losses of vibrational energy.

In this paper we present the results of an experimental study of an active medium consisting of D_2–CO_2 compared with N_2–CO_2-, N_2–N_2O-, and D_2–N_2O-media, obtained by gas-dynamic mixing, with stagnation pressures exceeding the atmospheric pressure.

The operation of a mixing GDL was modeled on a gas-dynamic stand with impulsive electric heating of the gas-energy carrier in a chamber with a finite volume (see Fig. 1). This type of heater was chosen because of the longer efflux time of the heated gas, for example, compared with shock tubes, which is significant in impulsive modeling of a mixing D_2–CO_2-GDL, since the large difference in the molecular weights can substantially increase the time for reaching the computed efflux regime in the nozzle.

The gas was heated by a pulsed electric discharge and, after a diaphragm was ruptured, flowed through the nozzle block of the mixing unit into the channel of the GDL (see Fig. 1). The stagnation temperature was calculated from the experimentally measured dependence of the pressure of the energy carrier in the heater taking into account the equations describing the consumption and state of the gas. The pressure P_0, the temperature T_0, and the consumption of the gas-energy carrier G decreased monotonically during the experiment. The corresponding parameters of the radiating gas with the diluent were maintained constant. The duration of the working pulse of the setup equaled 15-20 msec.

The effect of dissociation and recombination processes in the heater chamber accompanying the cooling of the gas on the magnitude of the vibrational energy stored in deuterium E_V was studied by a computational method. The vibrational excitation of the molecules was described

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with the help of the harmonic oscillator model. The dissociation and VT relaxation processes were described by the following system of equations:

$$\frac{1}{2}\frac{d[X]}{dt}=K_{d1}[X_2]^2-K_{a1}[X]^2[X_2]+K_{d2}[X][X_2]-K_{a2}[X]^3, \tag{1}$$

$$\frac{dE_V}{dt}=-\frac{1}{2}\varepsilon_a\frac{d[X]}{dt}-\frac{E_V-E_r}{\tau_{V-T}}, \tag{2}$$

$$[X]+[X_2]=n_0,\ P_0=n_0kT_0. \tag{3}$$

The pressure $P_0(t)$ and the temperature $T_0(t)$ were determined experimentally.

The solution of the system of equations (1)-(3) on a computer showed that as a result of the cooling of the gas in the chamber the concentration of atoms is "frozen" 5-6 msec after completion of the discharge at a level not exceeding 0.08-0.1% of the total number of molecules of the energy carrier. In addition, this fraction is virtually independent of the temperature at which the cooling started. The presence of nonequilibrium atoms does not significantly affect the relaxation of the vibrational energy of the molecules. For example, for T_0 = 2.3 kK and P_0 = 1.0 MPa the contribution of atoms to VT relaxation does not exceed 4% for deuterium and 1% for nitrogen.

As the temperature and pressure of the gas in the heater drop the VT-relaxation time increases and at some point exceeds the characteristic cooling time. This leads to the appearance of vibrational nonuniformity in the gas, when $E_V > E_r$. This effect is more significant in nitrogen, and at T_0 = 1 kK the difference between E_V and E_r can reach 40-100% [6]. The magnitude of the vibrational nonuniformity is determined by the ratio of the rate of cooling of the gas in the heater and the VT relaxation rate. The rate of cooling depends on the geometric parameters of the chamber, i.e., on the ratio of the volume to the area of the critical cross section of the nozzle S^*, and on the stagnation parameters (P_0 and T_0).

The range of stagnation parameters in which the thermal method of heating is being modeled was determined for the experimental stand under study: for nitrogen T_0 > 1.5 kK and P_0 > 0.7 MPa and for deuterium T_0 > 0.8 kK and P_0 > 0.4 MPa.

The active media of mixing D_2–CO_2-GDL and N_2–CO_2-GDL were studied by probing with the help of LG-74 frequency-tunable electric-discharge lasers. The use of such frequency-stabilized lasers makes it possible to study pulsed processes with any operating time and guarantees measurement of the gains K_0 at the center of the line, which is especially important for probing active media with a lower pressure than in the probing lasers.

The scheme of two-frequency sounding with a small spatial separation of the beams was employed (see Fig. 1). The characteristics of the active medium were calculated from the results of simultaneous recording of $K_0(t)$ on two different vibrational-rotational transitions J_1 and J_2 of the band $00^01 \to 10^00$ (P branch) and the measurements of the stagnation parameters of the mixing flows. The following system of equations was solved:

equation of mass balance

$$G_3=G_1+G_2 \tag{4}$$

and the equation of energy of the mixing flows

$$E_3=\frac{E_1G_1+E_2G_2}{G_3}, \tag{5}$$

where

$$E_i=\frac{\gamma_i}{\gamma_i-1}\frac{P_i}{\rho_i}+\frac{U_i^2}{2},\quad \gamma_i=\frac{C_{Pi}}{C_{Vi}},\ i=1,\ 2,\ 3,$$

and the equations relating the two gains with the parameters of the medium T, P, ξ_{CO_2}, T_3:

$$T=\frac{0{,}56\,[J_2(J_2+1)-J_1(J_1+1)]}{\ln(K_{01}/K_{02})+\ln(J_2/J_1)+c'}, \tag{6}$$

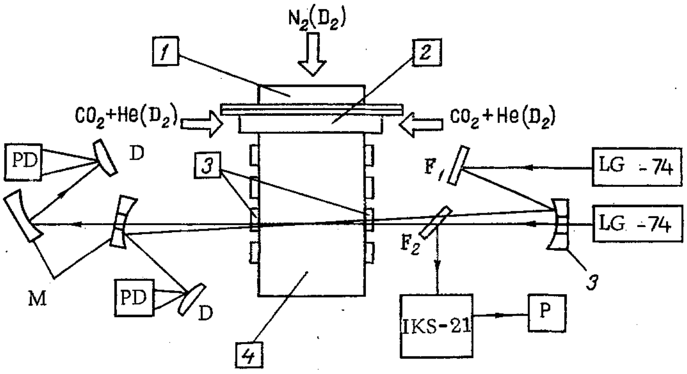

Fig. 1. Diagram of apparatus: 1) heater; 2) nozzle block; 3) window of GDL channel; 4) GDL channel; PD —infrared photodetectors; M — spherical mirrors; F_1 — flat mirror; F_2 — KCl half-transmitting beam-splitting plate; D — diffuse mirror.

$$T_3 = -\Theta_3 \Big/ \ln\left[0{,}5\left(1 + B_i y \pm \sqrt{(1-B_i y)^2 - 4K_{0i}/A_i\,(1-y)\left[1-\exp\left(-\frac{\Theta_2}{T_{1,2}}\right)\right]^2}\right)\right], \tag{7}$$

where

$$c' = \ln\frac{|R_{VV'}|^2_{(2)}}{|R_{VV'}|^2_{(1)}} + \ln\frac{H^2_{(2)}(a,\ 0)}{H^2_{(1)}(a,\ 0)} + \ln\left[1 + \frac{(B_1 - B_2)\,y}{x - B_1 y}\right],$$
$$x = \exp\left(-\frac{\Theta_3}{T_3}\right),\quad y = \exp\left(-\frac{\Theta_1}{T_{1,2}}\right), \tag{8}$$
$$A_i = f(T,\ P,\ \xi_{CO_2},\ J_i),\ B_i = \exp\left[-\frac{1{,}12\,(J_i+1)}{T}\right].$$

The expressions (6)-(8) are presented for the P branch of the transition 00^01—10^00. It was assumed that $T_{1,2} \cong T$ in the mixture D_2—CO_2, while in N_2—CO_2 the dependence $T_{1,2} \cong T + F$ was taken from the solution of the gas-dynamic and kinetic equations in the boundary-layer approximation for conditions close to our experiments. According to the calculations, starting with the second millisecond after the explosion of the wire the magnitude of the difference between $T_{1,2}$ and T remained virtually unchanged in the course of the experiment. For example, for CO_2:He = 1:1 F = 200-250 K.

The system of equations (4)-(7), supplemented by the relation $T_{1,2} = T + F$, was solved numerically on an ES-1033 computer by an iterative method. The first step in the iterations was performed with c' = 0, and at subsequent steps c' was taken into account. The ratios of the squares of the matrix elements of the dipole moments $|R_{VV'}|^2_{(i)}$ for different J_1 and the value of the Voight functions $H_{(i)}(a,\ 0)$ recommended in [7] were employed. The calculation gave the pressure in the gas flow P, the velocity U, and the temperatures T and T_3. The measured static pressure at the wall of the GDL channel within the limits of experimental error (±(15-20%)) equalled the computed value. The effect of the value of F on T_3 was analyzed. Two variants with $T_{1,2} = T + F$ and $T_{1,2} = T$ were calculated. It was found that for low translational temperatures ($T \le 250$ K) and the ratio CO_2:He = 1:1 taking into account F changes T_3 by not more than 10%. As T is increased up to 350 K this contribution increases up to 20-30%. Increasing the helium concentration ξ_{He} decreases F. In (6) F affects T through c'.

The errors were estimated by the method of indirect measurements. The dependence of the error in determining T on the choice of vibrational—rotational transitions was evaluated. According to (6), we have

$$\frac{\Delta T}{T} = \frac{[(\Delta K_{01}/K_{01})^2 + (\Delta K_{02}/K_{02})^2]^{\frac{1}{2}}}{\ln(K_{01}/K_{02}) + \ln(J_2/J_1) + c'}. \tag{9}$$

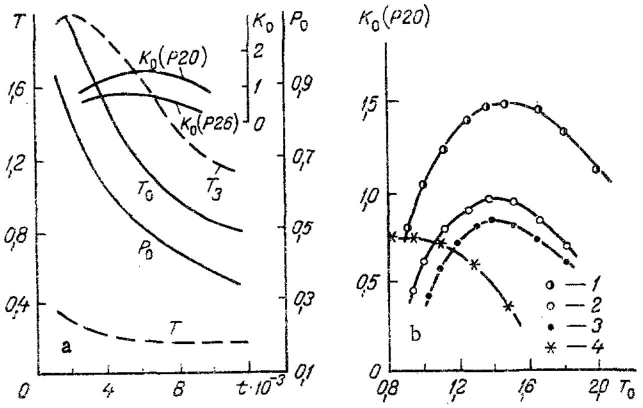

Fig. 2. Typical results of the study of the active medium of a mixing D_2—CO_2-GDL: a) time dependence of the two gains $K_0(P20)$ and $K_0(P26)$, stagnation parameters of deuterium P_0 and T_0, and the translational T and vibrational temperature T_3 of the antisymmetric mode of CO_2; b) the gain K_0 versus T_0 for different composition of the ejected gas: CO_2:He: 1) 1:2; 2) 1:6; 3) 1:10; 4) 1:0; T, T_0 are given in kK; K_0 in m^{-1}; P_0 in MPa; and, t in sec.

The error $\Delta T/T$ decreases, if the terms in the denominator (9) all have the same sign, i.e., if $J_2 > J_1$, then $K_1 > K_2$, and vice versa. Measurement of K_1 in the region of maximum gain and K_2 for $J_2 > J_1$ gives the lowest error $\Delta T/T$. A large difference between J_2 and J_1 can result in the fact that the magnitude of one of the gains will decrease and the error with which it is determined will increase. The calculations show that it is undesirable to increase $\Delta J = J_2 - J_1$ above 10-12 when recording oscillographically. For errors $\Delta K_{0i}/K_{0i} = 0.03$-$0.04$, $\Delta P_0/P_0 = 0.04$-0.07 and $\Delta J = 6$-8 the total error equaled $\Delta T/T = 0.14$-0.16; $\Delta T_3/T_3 = 0.09$-0.12.

Figure 2a shows typical results of the study of a mixing D_2—CO_2-GDL. Throughout virtually the entire experiment $T_3 > T_0$; this is attributable to the nonresonant vibrational exchange between the modes of D_2 and CO_2. When the CO_2 concentration is reduced, with other conditions remaining unchanged, T_3 increased. The maximum value $T_3 \approx 3$ kK was obtained for CO_2 = 5-6% and T_0 = 1.5-1.6 kK. Figure 2b illustrates the dependence of $K_0(P20)$ on the stagnation temperature of deuterium with different degrees of dilution of CO_2 with helium. The maximum values of K_0 are realized for T_0 = 1400-1500 K, CO_2:He = 1:2. Dilution of CO_2 with helium reduces the losses accompanying mixing owing to the decrease in the difference of the molecular masses of the flows. Reducing the number of radiating molecules, however, reduces K_0 for higher helium concentrations. It is important to note that replacing helium with deuterium (cold) does not appreciably reduce K_0. Thus it is in principle possible to operate with the two-component mixture D_2—CO_2. The laser energy stored in the active media D_2—CO_2 and N_2—CO_2 per unit mass was calculated as done in [8]:

$$E_{store} = \frac{(\Theta_3 - \Theta_1) R}{\mu} [(\varepsilon_3 - \varepsilon_3^0)\xi_{CO_2} + (\varepsilon_4 - \varepsilon_4^0)\xi_{D_2,N_2}]. \tag{10}$$

The vibrational temperature of nitrogen T_{N_2} is given by

$$\frac{\Theta_{N_2}}{T_{N_2}} = \frac{\Theta_3}{T_3} + \frac{\Theta_{N_2} - \Theta_3}{T}, \tag{11}$$

and that of deuterium T_{D_2} is given by

$$\frac{\Theta_{D_2}}{T_{D_2}} = \frac{\Theta_3}{T_3} + \frac{\Theta_2}{T_{1,2}} + \frac{\Theta_{D_2} - \Theta_2 - \Theta_3}{T}. \tag{12}$$

The rate of transfer of vibrational excitation from D_2 ($V = 1$) to CO_2 ($00^{\circ}1$) and VT deactivation of the vibrational levels of CO_2 by deuterium with translational temperatures of the active medium $T = 200$-300 K are comparable. Therefore the vibrational temperature of deuterium, calculated from the formula (12), is too low and the value of E_{store} for D_2—CO_2 determined by (10) is a lower limit.

The laser energy stored per unit mass E_{store} increases monotonically as the relative fraction of CO_2 in the mixture is reduced. The maximum value $E_{store} \geq 55 \pm 16$ J/g was obtained for $T_0 = 1500$-1600 K, $P_0 = 0.6 \pm 0.05$ MPa, $\xi_{CO_2} = 5$-6 and K_0 (P20) $= 0.95$ m^{-1}. Reducing $\xi_{CO_2} <$ 5% increased the error in determining E_{store} ($\delta E_{store} > 30\%$) owing to the decrease in the value of K_0. Figure 3 shows E_{store}, $E(T_0)$, $E(T_*)$, E_{CO_2} as a function of T_0. The specific laser energy of the mixture stored in deuterium (nitrogen) with a stagnation temperature of T_0 and a temperature T_* in the critical section of the nozzle are denoted by $E(T_0)$ and $E(T_*)$:

$$E(T_*) = \frac{(\Theta_3 - \Theta_1) R}{\mu} \left[\frac{1}{\exp[\Theta_{D_2,N_2}/T_*] - 1} - \varepsilon_4^0 \right] \xi_{D_2,N_2}. \tag{13}$$

One can see from the figure that for $T_0 \leq 1500$ K E_{store} is close to the limiting value, equal to $E(T_0)$. The sharp drop in the value of E_{store} for $T_0 \geq 1800$ K could be linked with the increase in the relaxational losses, arising at the starting stage of outflow. For $T_0 \leq 1600$ K E_{store} for K_2—CO_2 exceeded the laser energy per unit mass stored in mixing N_2—CO_2-GDL. For the mixing N_2—CO_2-GDL the maximum stored laser energy ~90 J/g for $T_0 = 2600$-2700 K.

The dependence of the extracted laser power W and the specific energy extracted $E = W/G$ on the composition, the stagnation parameters, and the dimensions of the critical section of the nozzle setup was studied. The measurements were performed in single- and triple-pass resonators. Mirrors with a transmission t = 6, 7, 8, 11, and 14% were employed in both resonators, while mirrors with a transmission t = 26% were employed only in the triple-pass resonator.

The optimal degrees of dilution with which the maximum gains K_0 and laser power W were obtained: CO_2:He = 1:2-1:3 and the concentration $\xi_{CO_2} = 11$-14%. Thus in a D_2—CO_2 medium, unlike N_2—CO_2, the quantities K_0 and W have virtually the same dependence on ξ_{CO_2}. It was found that for $T_0 \leq 1400$ K the laser power W in a mixing D_2—CO_2-GDL exceeds the corresponding value in a mixing N_2—CO_2-GDL for the same values of ξ_{CO_2} and ξ_{He}. This is attributable to the high velocity of the mixture along the channel of the resonator part, nonresonant heating of the upper laser level in CO_2, and the high rates of VT relaxation of the lower laser level. As P_0 was increased W increased under the conditions of the experiment, while E decreased slightly. The maximum value E = 15 J/g was obtained with $T_0 = 1.5$ kK and $\xi_{CO_2} = 12\%$, which exceeds the energy extracted in a mixing N_2—CO_2-GDL with the same stagnation parameters.

In the regimes studied, in a mixing D_2—CO_2-GDL, unlike N_2—CO_2, after the single-pass resonator K_0 practically does not rise above the threshold value. For this reason, the transfer from a single-pass resonator to a triple-pass resonator did not give a significant increase in the power. In N_2—CO_2 a large part of the stored laser energy is concentrated in nitrogen, and the value of K_0 is maintained virtually constant along the nozzle owing to the constant "pumping" of the $00^{\circ}1$ level on the nitrogen side and the low rate of collisional deactivation of this level. In D_2—CO_2 a large drop in K_0 along the resonator is observed. This is attributable to nonresonant VV' exchange, as a result of which as the temperature of the active medium decreases a significant part of the vibrational energy is redistributed in CO_2, as well as to the fact that the deuterium is a stronger deactivator of vibrational excitation than is N_2. The "threshold" energy, remaining in the energy carrier (D_2) and transferred to CO_2 during passage through the resonator is less than for N_2—CO_2. The resonator length in the direction of motion of the gas mixture can be less for the mixing D_2—CO_2-GDL than for N_2—CO_2.

The extracted specific laser energy in a single-pass resonator equals 40-50% of E_{store} with the approximate efficiency of the resonator $\eta = 30$-45%. This indicates that the true value of E_{store} is not significantly higher than the estimate obtained from the formula (10) taking into account (12).

Figure 4 shows the comparative characteristics for the extracted laser power W for two energy carriers: deuterium and nitrogen and the radiating components of CO_2 and N_2O under close gas-dynamic conditions. In the low-temperature region ($T_0 < 1.4$-1.6 kK) the value of W is higher for the mixing D_2—CO_2-GDL than for the laser systems under study. In transferring from D_2—CO_2 to D_2—N_2O the laser power decreases (by approximately a factor of five), which agrees with [9].

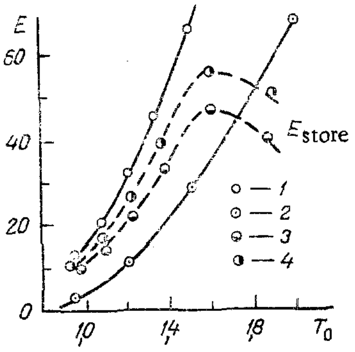

Fig. 3

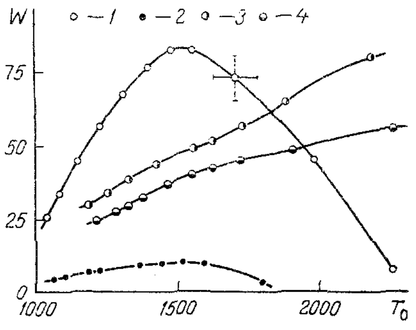

Fig. 4

Fig. 3. The vibrational energy stored in deuterium versus T_0 for the stagnation parameters (1) and in the critical section (2); E_{store} is the laser energy stored in CO_2 molecules (3) and in the mixture $D_2 + CO_2$ (4), E is given in J/g.

Fig. 4. Comparative dependence of the extracted laser power W on T_0: 1) $D_2 - (CO_2 + He)$; 2) $D_2 - (N_2O + He)$; 3) $N_2 - (CO_2 + He)$; 4) $N_2 - (N_2O + He)$; The degree of dilution of the radiating gas component by helium is 1:2. W is given in W and T_0 is given in K.

Thus nonresonant exchange between the vibrational levels of the energy-carrying and radiating components leads to significant heating of the upper laser level. The low molecular weight of deuterium and the high rates of passage through the resonator give high values of the laser power and the laser power per unit mass compared with N_2–CO_2-, N_2–N_2O-, and D_2–N_2O-mixtures in the range of stagnation temperatures $T_0 < 1.4$–1.6 kK. For a nonoptimized resonator the specific laser energy extracted equaled ~15 J/g with $T_0 \cong 1.5$ kK. The laser energy stored in the active medium of the order of 55 J/g with a quite high gain of ~1 m^{-1} indicates that it is possible to build a gas-dynamic laser with high energy parameters for stagnation temperatures $T_0 \sim 1.5$–1.6 kK.

NOTATION

$[X_2]$, $[X]$, concentration of molecules and atoms; $K^{V-T}_{X_2-X_3}$, $K^{V-T}_{X_2-X}$, rate constants for quenching of the vibrational energy for collisions of molecules with one another and with atoms; $\tau_{V-T} = \{K^{V-T}_{X_2-X_2}[X_2] + K^{V-T}_{X_2-X}[X]\}^{-1}$, characteristic V–T relaxation time; K_{d_1}, K_{a_1}, rate constants for dissociation and recombination for the process $X + X_2 \rightleftarrows 2X_2$; K_{d_2}, K_{a_2}, rate constants for dissociation and recombination for the process $X + X + X \rightleftarrows X_2 + X$; ε_a, recombination energy of atoms; μ, molecular weight of the gas mixture; R, gas constant; ε_3 and ε_4, number of vibrational quanta per mole of CO_2, N_2 (D_2) with no resonator; ε_3^0, ε_4^0, same numbers under the condition that the threshold gain K_0 equals zero and are given by the formulas $\varepsilon_3^0 = [\exp(\Theta_3/T_3^{th}) - 1]^{-1}$; $\varepsilon_4^0 = [\exp(\Theta_{D_2,N_2}/T^{th}_{D_2,N_2}) - 1]^{-1}$; $T_3^{th} = (\Theta_3/\Theta_1)T_{1,2}$; $T^{th}_{N_2,D_2}$ were found from (11) and (12) by substituting T_3^{th}.

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GAS FORMATION FROM A SOLID FUEL BURNING IN A FLUIDIZED BED

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UDC 662.62:66.096.5

A method is given for calculating combustion performance, which incorporates various factors in boiler processes.

There are numerous model concepts [1-3] on fluidized-bed combustion and gasification, but most of them are too complicated for engineering calculations such as [1] or do not incorporate major features [2, 3].

The following reactions are usually considered [4] in describing gasification in carbon combustion:

$$2C + O_2 = 2CO, \tag{1}$$

$$C + O_2 = CO_2, \tag{2}$$

$$CO_2 + C = 2CO, \tag{3}$$

$$2CO + O_2 = 2CO_2. \tag{4}$$

Unfortunately, the true rate constants in (1)-(3) are unknown for most coals, with most of the data [5] relating to (2), with simultaneous allowance for (1) and (4). Carbon monoxide reacts with oxygen in the boundary layers around the coal particles, which is fairly complicated because the process is nonisothermal, and also because the combustion function is nonlinear. Mathematical analysis applied to a single particle shows [6] that the composition of the primary oxides formed by carbon reacting with oxygen is unimportant at temperatures exceeding the CO ignition point (about 700-750°C), since the carbon monoxide combines with oxygen at the surface and becomes the dioxide. We therefore neglect (1) and (4) individually on the basis that only (2) and (3) occur at the surface. The distributions for the concentrations of oxygen C, the monoxide C_1, and the dioxide C_2 over the combustion chamber height in the steady state are therefore defined [4] by

$$v\frac{\partial C}{\partial x} = -\alpha SC, \tag{5}$$

$$v\frac{\partial C_2}{\partial x} = -\alpha_2 SC_2 + \alpha SC, \tag{6}$$

$$C_0 = C + (1 + \beta^*)C_2 + (0{,}605 + \beta^*)C_1. \tag{7}$$

Here β^* is a fuel characteristic dependent on the composition [7].

The specific oxygen flux j to a single carbon particle is

$$j = \alpha^* C_p. \tag{8}$$

The overall rate constant for the reaction of a carbon particle is determined by the constant for the reaction rate (in general, allowance must be made for reaction in the pores) and the oxygen diffusion from the outer phase via the boundary layer to the burning particle:

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