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Thermal ignition of coal–gas suspensions containing natural gas and oxygen

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Gases evolving during the heat treatment of coal powder have a strong inhibiting effect on the combustion of natural gas but a weak one on H_2 combustion.

Dust explosions are dangerous for many processing and mining industries, when the performance of technological processes is accompanied by the formation of suspensions of combustible particles in a gas containing an oxidant. Experimental investigations showed that the danger of dust explosion became much higher if even minor amounts of a combustible reactant were contained in the gas.[1] Thus, the minimum energy of ignition of a gaseous suspension of coal could be decreased by a factor of 20–30 with addition of small amounts of methane (2–3%).[2] Such conditions are typical of the coalmines, where both combustible components, a coal dust and methane, are present simultaneously. This may bring even greater hazard in closed volumes, *e.g.*, mines, within which the explosion aftereffects are particularly destructive and may result in fatalities. Therefore, the regularities of combustion of coal–gas suspensions containing natural gas and oxygen at room and higher temperatures are of considerable current interest.

The investigation is aimed to finding out the influence of the coal powder of different types of coals on the induction period of self-ignition (τ), *i.e.*, on the flammability of the stoichiometric mixture of 33% natural gas + O_2. In the experiments, reactor walls were coated with coal powder (particle size of ~90 μm).

Experiments were carried out at a total pressure of 73 Torr in the temperature range 685–855 °C in a heated quartz cylinder 3.6 cm in diameter and 25 cm in length. The reactor was pumped to 10^{-2} Torr. The process of self-ignition was recorded by means of a CCD camera. The signal of the camera was stored in computer memory. Natural gas (98% CH_4, 2% propane and butane) had a low concentration limit of 4.66% in air at 1 atm. In separate experiments, the self-ignition of a stoichiometric mixture of $2H_2 + O_2$ over coal coating was investigated. In the experiments, the following types of coals were used: high volatile steam coal (~38% volatiles, GOST 10101-79), coking coal (~17% volatiles, GOST 25543-88), and anthracite (~8% volatiles, GOST 25543-88). A suspension of coal powder (0.3 g) in ethanol (2 ml) was placed in the reactor and rotated under pumping to remove the liquid. Emission spectra of initiated ignition were recorded with a spectrograph with crossed dispersion equipped with a CCD camera sensitive over the range 420–900 nm. The emission of the flame was focused on the enter slit of the spectrograph. The spectra were analyzed using the AmLab Hesperus 3.0 beta program package.

The induction period τ of the stoichiometric mixture (33% natural gas + O_2) over a quartz surface treated with HF was 48±2 s at 685 °C in accordance with published data.[3] However, over high volatile steam coal coating the mixture did not self-ignite at 740 °C. After thermal annealing of the reactor at 855 °C for 12 h and lowering the temperature to 695 °C, the self-ignition of a stoichiometric mixture was observed; the induction period τ was 280±20 s.

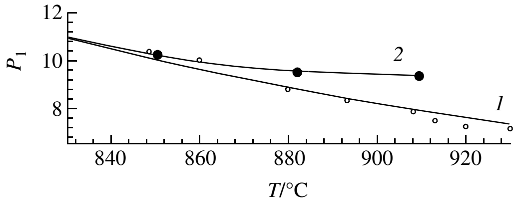

Figure 1 The temperature dependence of the lower self-ignition limit of $2H_2 + O_2$ over (*1*) MgO coating (diffusive area of chain termination[3]) and (*2*) coking coal coating.

The self-ignition of stoichiometric $2H_2 + O_2$ mixtures over coking coal coating was also investigated. The dependence of the lower self-ignition limit P_1 of the stoichiometric hydrogen–oxygen mixture ($2H_2 + O_2$) over MgO coating (diffusive area of chain termination[4]) and coking coal coating are shown in Figure 1. The coal coating provides diffusive area of chain termination. With increasing temperature, the value of P_1 exceeds the diffusive one. It means that volatiles evolving from heated coal powder have an inhibiting effect on $H_2 + O_2$ combustion. However, the effect of coated surface is weak, as compared to the self-ignition of natural gas–oxygen mixtures over coal coatings. In accordance with published data,[5] hydrogen atoms do not play a noticeable role in chain branching in the oxidation of hydrocarbons, *i.e.*, H atoms take part in longer chains than in hydrogen oxidation.

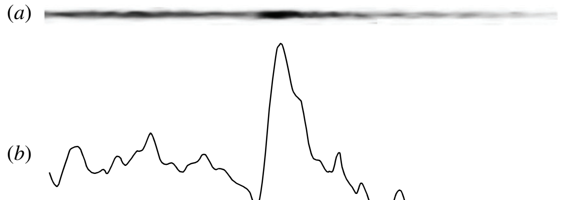

Figure 2 Emission spectra of CH radicals ($A^1\Delta–X^2\Pi$) at 431 nm in reaction of oxygen (73 Torr) with coal coating at 700 °C: (*a*) initial spectrum and (*b*) the spectrum after computer analysis.

The stoichiometric mixture of 33% natural gas + O_2 did not self-ignite at 740 °C over coking coal coating and anthracite coating. The self-ignition of a mixture of natural gas + O_2 was observed only after thermal treatment at 855 °C for 3.5 h (coking coal coating) or 2 h (anthracite coating). For these surfaces the values of τ were 0.5 and 0.2 s, respectively. The self-ignition was accompanied by initiation of many bright sparks in the reactor. Therefore, the described procedure including thermal treatment allows recognizing the type of coal using the values of τ. It implies that under thermal treatment coal powder evolves chemical substances, which inhibit the combustion of natural gas. Moreover, the thermal treatment of coal powders of coking coal and anthracite causes the self-ignition of the powder ($\tau << 48$ s) in oxygen in the presence of flammable mixture and the following initiation of the ignition of the mixture.

In the following experiments, gas was allowed to bleed into the reactor coated with anthracite coal powder. The reactor was heated up to 695 °C; the procedure of thermal treatment (degassing) was not performed. It was shown that 73 Torr of pure oxygen gave many sparks in the reactor in 0.2 s; in this case, the stoichiometric mixture of natural gas with oxygen did not self-ignite in accordance with the above results corresponding to the absence of thermal treatment.

It was found that 73 Torr of oxygen over thermally treated (855 °C, 5 h) high volatile coal coating gave a blue flash immediately after bleeding-in at 695 °C. The intense emission of CH radicals ($A^1\Delta$–$X^2\Pi$) at 431 nm[6] was observed in the spectrum of the blue flash (Figure 2). The emission spectrum shows that the volatile substances evolving from coal powder burn in oxygen yielding exited CH radicals. The only volatiles evolving from heated coal powder can provide the inhibiting effect on the combustion of natural gas; the volatiles are evidently hydrocarbons, probably, polycyclic aromatic hydrocarbons. Both the lower and upper concentration limits of the higher hydrocarbons are considerably low.[8] This explains the experimental fact of the occurrence of a blue flash in reaction of pure O_2 with a coal coating. According to low concentration limits, the vapor of the higher hydrocarbons self-ignites in pure O_2 but does not ignite in the mixture of natural gas and oxygen where fuel content exceeds an upper concentration limit at a given temperature.

By this means in accordance with aforesaid at higher temperatures self-ignition of the coal coating in oxygen can precede the combustion of natural gas and initiate the ignition of natural gas. Coal powder can ignite methane–oxygen mixtures, though it is commonly accepted that the two processes go in the reverse order, namely, the explosion of methane–air mixtures in mines causes the combustion and detonation of coal dust.[1]

It follows from the results obtained that if a stream of a gas picks up coal particles from a surface, the particles can self-ignite in O_2. The particles can initiate the ignition of the mixture of natural gas with O_2 only if the reactor surface coated with coal is degassed (in our case, at 855 °C). The time of degassing is determined by the type of coal. The experiments performed showed that the gases evolving during thermal annealing have a marked inhibiting effect on the combustion of natural gas; the inhibiting action of these gases on H_2 oxidation is considerably small. Thus, hydrogen atoms do not play a noticeable role in chain branching in the oxidation of hydrocarbons.

The experiments showed that the mixtures of natural gas with oxygen self-ignite over coal coating much worse than oxygen over coal coating due to volatiles having an inhibiting effect to methane combustion. It means that coal dust may be the major source of danger because, under certain conditions, it self-ignites before the combustion of methane–oxygen mixtures.

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