

Suppression of the ignition of coal powders in the presence of oxygen and natural gas with small additives of octadecafluorodecahydronaphthalene vapour

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The inhibition of the ignition of coal powders and natural gas in oxygen by octadecafluorodecahydronaphthalene ($C_{10}F_{18}$) vapour (6%) at 85 Torr and 600–750 °C was demonstrated.

Dust explosions are dangerous in coal processing and mining due to the formation of combustible powder–air mixtures.¹ Therefore, the suppression of such explosions, including chemical means, is an urgent problem. In most cases, not only coal dust, but also methane occurs in coal mines. Such powder–gas mixtures (PGMs) are called hybrid PGMs. The presence of methane makes PGMs even more explosive.^{1,2} It means that the suppression of coal PGM containing gaseous fuel and an oxidizer by means of chemical additives is of both practical and scientific interest.

It has been recently shown³ on the basis of the experiments on the inflammability of coal powders with various contents of volatiles in oxygen at a total pressure of 85 Torr and temperatures 650–750 °C that the ignition of separate coal particles occurs right after oxygen admission. Then, after the delay period, the ignition of volatiles from coal powder proceeds; the ignition expands over the entire reactor volume. It was shown that a hybrid PGM consisting of soot or graphite powder, which do not contain volatiles, and a stoichiometric mixture of natural gas (NG) and oxygen, intensively ignite at lower temperatures than a hybrid PGM consisting of coal powder and oxygen. It was also shown³ that soot powder promotes (completely reduces the ignition delay time) the ignition of a stoichiometric mixture of NG and oxygen at the expense of fractions of soot particles with the mean size of <1 μm. It follows from published data^{3–5} that the gases released upon the heating of coal powder have a considerable suppressing influence on the spontaneous ignition and combustion of hybrid coal PGM with a nearly stoichiometric methane content in air. Note that volatiles in coal consist of more than 200 chemical compounds.^{1,2} Therefore, it is difficult to identify compounds that inhibit methane combustion.

Small dichlorosilane (SiH_2Cl_2) additives promote the combustion of hybrid coal PGM.⁵ As the promotor is found out there should be a chemical compound inhibiting the combustion of hybrid PGM. Octadecafluorodecahydronaphthalene ($C_{10}F_{18}$) was tested as an inhibitor. $C_{10}F_{18}$ is nontoxic; it is widely known in medicine as artificial blood. Its saturated vapour pressure is 6 Torr⁶ at 20 °C. The fact that $C_{10}F_{18}$ is formally one of the halons that possess appreciable inhibiting action on combustion⁷ of hydrocarbons contained in coal⁵ and also its nontoxicity caused the choice of $C_{10}F_{18}$ as an inhibiting additive.

The work was aimed at the investigation of the inflammability of coal powders with different contents of volatiles in oxygen at a total pressure of 85 Torr and temperatures of 650–750 °C in the presence of saturated vapour of $C_{10}F_{18}$ as an active additive.

The influence of $C_{10}F_{18}$ on the ignition of hybrid PGM containing soot powder and a stoichiometric mixture of NG and oxygen was also studied.

Experiments were performed in a heated cylindrical quartz reactor 3.6 cm in diameter and 25 cm in length. Hybrid PGM in the reactor was produced in a way described previously.³ Note that one atmosphere of air contains ~150 Torr of oxygen. Therefore, if the inhibitor is effective in oxygen, it will be especially effective in air. Coal, soot or graphite powder (0.2 g, particle size of ~60 μm) was poured into a quartz trough placed in the reactor at its inlet (Figure 1), the reactor was pumped to 10⁻² Torr and heated to a necessary temperature. Before each experiment, the reactor was washed out by 30% HF. Then, the coal powder was thrown into the evacuated reactor with a sharp stream of a gaseous test mixture from a buffer volume so that the total pressure in the reactor reached 85 Torr. The pumped out buffer volume was filled preliminary with 6 Torr of $C_{10}F_{18}$; then, oxygen (or a stoichiometric mixture of NG with O_2)[†] was admitted up to 100 Torr and maintained for 3 min to be well mixed. At the achievement of the pressure, the reactor was shut off the buffer volume. Ignition was recorded by means of a Casio Exilim F1 Pro colour high-speed digital camera (1200 frames s⁻¹); each set of frames was stored in computer memory; the resulting frame sequence was analyzed. It was shown that the hybrid PGM

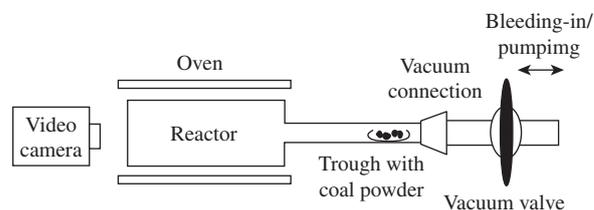


Figure 1 Experimental setup for creating hybrid PGM in the reactor.

[†] NG contained 98% methane and 2% propane and butane. Chemically pure $C_{10}F_{18}$ and O_2 were used.

The following different types of coals with a particle size of ~60 μm were used: high volatile steam coal [HV, ~38% volatiles, GOST (state standard) 10101-79], coking coal (C, ~17% volatiles, GOST 25543-88), anthracite (A, ~8% volatiles, GOST 25543-88, average particle size of 55 μm), and also powders of P840T soot (GOST 38154-88, particle sizes of 0.2, 0.5, 1.1, 5 and 10 μm), and graphite (GOST 7478-75, average particle size of 55 μm). The analysis of the sizes of particles was performed using an Analyzette 22 laser diffraction analyzer (Germany).

obtained as described above occurred in the reactor volume at 680 K for no less than 10 s. To be certain that coal particles remain in PGM the particle cloud was imaged using a horizontal sheet of laser light ($\lambda = 524$ nm) formed by means of a cylindrical lens along with camera recording (not shown in Figure 1) as described previously.⁵ Therefore, in our experiments, coal particles remained in the mixture at ignition delays $\tau < 10$ s.

For any type of coal powders,[†] it was revealed that immediately at the moment of injection of coal particles into the reactor by oxygen stream, bright sparks occur in the reactor, representing the ignition of separate particles of coal powder. The ignition is not accompanied by gaseous combustion. This process lasts for ~ 0.01 s, and then light emission of the sparks dies away. For lack of $C_{10}F_{18}$ after time interval τ_L reaching several seconds during which radiation in the reactor was not observed, intense luminescence occurred both in the reactor volume and at its walls and then extended over all the reactor volume.³ This luminescence is caused³ by the combustion of volatiles released from heated coal powder in oxygen. The time interval τ_L between the injection of PGM into the reactor and ignition is comprised of the time of heating of powder particles t_1 , the time of evolving volatiles from heated powder to gas phase t_2 , and the ignition delay of volatiles in oxygen t_3 , *i.e.*, $\tau_L = t_1 + t_2 + t_3$.

It was observed that, in the presence of 6% $C_{10}F_{18}$, τ_L considerably increases. Sequences of video images of the ignition of coal A powder arising at injection of coal powder into the reactor by oxygen stream containing 6% $C_{10}F_{18}$ and the subsequent ignition of volatiles released from heated coal powder are presented in Figure 2. The time interval τ_L makes up 21 s at 649 °C. Note that, without $C_{10}F_{18}$ $\tau_L = 2.8$ s at 653 °C. The time of combustion of this hybrid PGM in the presence of $C_{10}F_{18}$ also increases several times in comparison with combustion of the hybrid PGM in pure oxygen. It is illustrated in Figure 3, where the sequences of video images of ignition of hybrid PGM containing coal powder HV in the absence and in the presence of $C_{10}F_{18}$ are shown. As can be seen in Figure 3, in the presence of $C_{10}F_{18}$, the time of combustion of this hybrid PGM increases by a factor of 6. The addition of 6% CO_2 to oxygen at PGM producing on the basis of the most sensitive (Figure 4) coal powder A instead 6% $C_{10}F_{18}$ does not lead to an appreciable increase in τ_L , which is 3.3 s under these conditions. It was also shown⁵ that a 3% CCl_4 additive does not influence the value of τ_L . Thus, $C_{10}F_{18}$ acts as an inhibitor of PGM combustion.

It follows from the results obtained that $C_{10}F_{18}$ additive does not affect the ignition of separate particles of coal powder, but it inhibits the combustion of volatiles containing in coal powder.

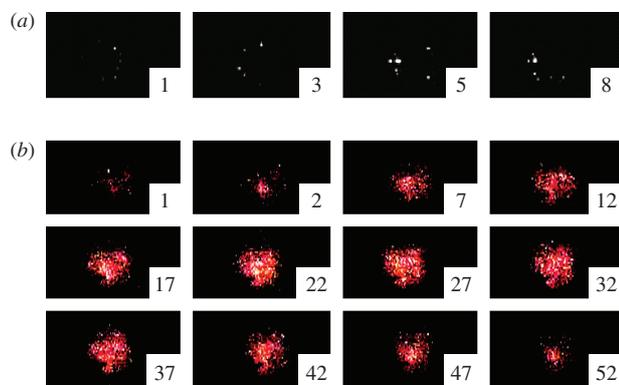


Figure 2 Sequences of video images of hybrid coal PGM ignition in oxygen at 85 Torr at the injection of coal powder A into the reactor with a stream of oxygen containing 6% $C_{10}F_{18}$, 1200 frames s^{-1} . Numbers in the picture correspond to the consecutive numbers of video images. The first shot number corresponds to the beginning of process registration. $T = 649$ °C. (a) The moment of injection of coal powder into the reactor; (b) ignition of hybrid PGM in 21 s after injection.

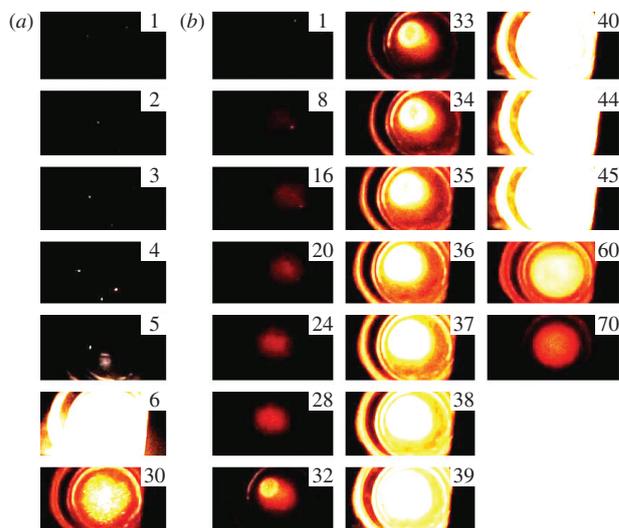


Figure 3 Sequences of video images of hybrid coal PGM ignition in oxygen at 85 Torr at the injection of coal powder HV into the reactor with a stream of oxygen containing 6% $C_{10}F_{18}$, 1200 frames s^{-1} . Numbers in the picture correspond to the consecutive numbers of video images. The first shot number corresponds to the beginning of process registration. $T = 649$ °C. (a) Ignition of hybrid PGM in the absence of $C_{10}F_{18}$, $\tau_L = 2.8$ s; (b) ignition of hybrid PGM in the presence of $C_{10}F_{18}$, $\tau_L = 4.4$ s.

Thus, in the presence of $C_{10}F_{18}$, τ_L corresponds to the sum $t_1 + t_2 + t_3$ and the time interval τ corresponding to the occurrence of combustible mixture into the area of spontaneous ignition at the expense of inhibitor consumption.⁸

One can assume that the lower the volatiles content of the gas phase, the more the relative (to fuel) concentration of the inhibitor $C_{10}F_{18}$. Hence, the smaller quantity of volatiles coal powder contains, the more τ_L values are at the expense of increase of the period τ for which the mixture enters into the area of spontaneous ignition as a result of inhibitor consumption.

Really, it has been experimentally established that, in the presence of 6% $C_{10}F_{18}$, τ_L increases for all types of coal powders; thus, relative τ_L increase (in comparison with ignition in pure O_2) depends on the type of coal powder. The least τ_L values correspond to hybrid PGM obtained from coal powder HV with the greatest content of volatiles (Figure 4). PGMs containing coal

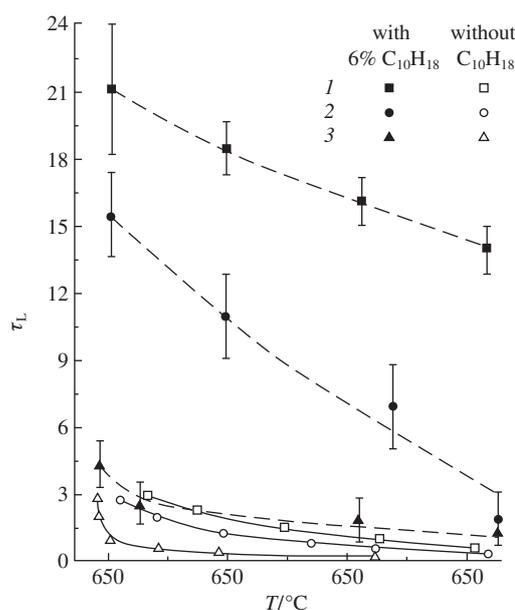


Figure 4 Dependence of τ_L values on temperature and type of coal powder in PGM in the absence and in the presence of 6% $C_{10}F_{18}$. (1) Coal HV, (2) coal C, (3) coal A.

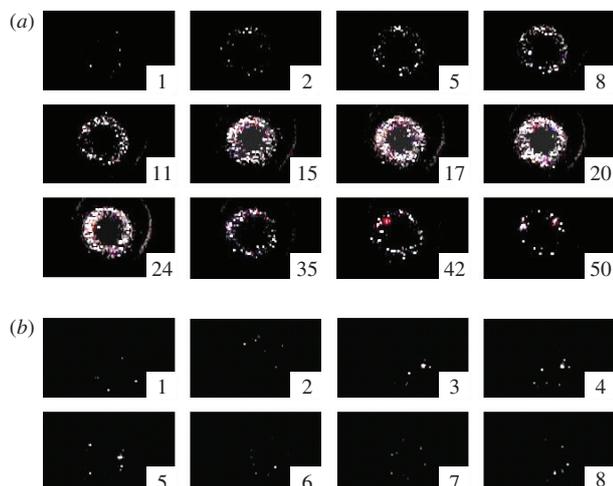


Figure 5 Sequences of video images of PGM ignition, arising at injection of soot powder into the reactor with a gas stream. Numbers in the picture correspond to the consecutive numbers of video images. The first shot number corresponds to the beginning of process registration. 1200 frames s^{-1} . (a) Simultaneous ignition of soot powder and stoichiometric mixture NG + O₂ (690 °C, 85 Torr);³ (b) ignition of soot powder particles right after injection with NG + O₂ stream containing 6% C₁₀F₁₈ (690 °C, 85 Torr).

powders C and A ignite less intensely with larger τ_L reaching 21 s (Figures 2, 4). Dependences of delay time τ_L on temperature and the type of coal powder in hybrid PGM in the absence and in the presence of C₁₀F₁₈ are shown in Figure 4.

To verify the assumption that the role of C₁₀F₁₈ is in inhibition of homogeneous ignition of the volatiles containing in coal powder, a series of experiments with soot powder without volatiles¹ has been performed. This powder was injected into the heated reactor with a stream of stoichiometric NG + O₂ mixture to a total pressure of 85 Torr. Right after injection along with

occurrence of sparks in the reactor, the intense ignition of NG (Figure 5) was observed.³ Thus, the presence of soot particles in hybrid PGM promotes the ignition of NG in oxygen. The promotion effect observed is most likely caused by the fact that the soot powder, according to results of sedimentation analysis, contains easily flammable fractions with the characteristic size of 0.1 μm .³ However, in the presence of 6% C₁₀F₁₈, the combustion of soot particles after injection is only observed; the ignition of NG does not occur. It means that a C₁₀F₁₈ additive inhibits methane combustion.⁹

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