The role of hydrogen in the kinetic mechanism of formation of a carbon fraction of dispersed particles in the combustion of hydrocarbon fuels

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Abstract. The issues of the scientific search for ways to limit emissions of dispersed particles are of particular importance within the context of socially important problem of environmental protection in the field of heat power during the operation of power plants for various purposes. The bulk of the dispersed particles are particles of the carbon fraction. These particles formed during the combustion of hydrocarbon fuel are among the most harmful substances. The high potential hazard of the particles of the carbon fraction is due to the fact that they contain a number of highly toxic mutagens and carcinogens. Moreover, the ultra-small particle sizes allow them to actively penetrate the human respiratory organs. An alternative version of the method for reducing carbon particles emission based on the use of an additive of a small fraction of free hydrogen to the working fluid of a power plant is considered. A number of scientific provisions on the role of hydrogen as a chemical reagent in the acts of formation and burning of carbon particles are substantiated, the validity of which is confirmed by the results of experimental testing.

1. Introduction

Objective: To study the effectiveness of the method of reducing the emission of carbon particles based on the use of an additive to the working fluid of a hydrogen power plant. Subject of research: Studying the role of hydrogen as a chemical reagent in the acts of formation and burning of carbon particles.

Dispersed particles (DP), containing mutagenic and carcinogenic components, are among the most harmful substances that are formed during the combustion of hydrocarbon fuel in power plants, which determines the relevance of the search for effective means to reduce their emission. More than 1000 substances were identified in the composition of such particles [1]. In the most general form, DP material is divided into 4 groups (fractions): carbon fraction; organic fraction; fraction of sulfates and nitrates; fraction of inorganic impurities. Due to the fact that the main fraction of the particles account for a carbon fraction [1] the most attention is paid to the study of the processes of formation of these particles.
A number of chemical agents are known (commercial fuel additives) that contribute to the reduction of the carbon fraction of DP in the composition of the products of combustion of hydrocarbon fuels [2, 3]. Hydrogen occupies a special place among the most effective means of chemical influence on the processes of formation of carbon particles. The data of numerous experiments [2-5] record a significant decrease in the content of carbon particles in the products of fuel combustion due to the utilization of hydrogen additives to the working fluid of the power plant.

At the same time, the reason for the decrease in particle emission and the detailed mechanism of the effect of hydrogen on this process have not had specific scientific explanations yet. To establish the possible nature of the manifestation by hydrogen of the reaction properties in chemical acts of the formation of dispersed carbon, we will use the already known provisions, which describe the kinetics of these events with varying degrees of certainty. Two independent acts can be distinguished in the mechanism of the resulting carbon black emission: the formation of a solid condensed carbon phase during the combustion of hydrocarbons and the heterogeneous combustion (oxidation) of a carbon particle (Fig. 1).

![Diagram](image-url)  
**Figure 1.** The structural scheme of the acts of formation and burning of dispersed particles of the carbon fraction in the process of fuel combustion.
The general scheme for the formation of carbon particles can be represented as a sequence of separate stages, each of which is carried out according to individual kinetic mechanisms [1]. At the first stage, the thermal decomposition of complex hydrocarbon fuel into low molecular weight components occurs. The second stage is accompanied by thermal decomposition of individual hydrocarbons with the formation of acetylene as the main raw material in the subsequent processes of formation of the carbon fraction. These processes proceed according to the kinetic scheme of cracking reactions of individual hydrocarbons. The third stage corresponds to the thermal explosive decomposition of acetylene with the formation of hydrocarbon radicals, which are the chemical nuclei of future carbon particles. The fourth stage is characterized by carburization of the radical and the formation of a physical nucleus of the particle. The fifth stage is accompanied by a heterogeneous process of surface growth of the particle to characteristic sizes determined by the residence time and the degree of supersaturation of the system with physical nuclei.

Such a representation of the carbon formation mechanism reveals a number of possibilities for implementation the targeted effect of free hydrogen on this mechanism. As noted above, the kinetic mechanism of surface growth of a particle is accompanied by the decomposition of an acetylene molecule, which is a donor of nuclei of carbon particles, and the capture of carbon atoms by the surface. The effect of a hydrogen reagent at this stage can manifest itself in a decrease in the intensity of surface growth of a carbon particle (the so-called ‘hydrogen inhibition’ effect, which was first established by Prof. Langmuir). This manifestation is due to activated adsorption of hydrogen molecules by the particle, which prevents the particle from contacting the reaction medium [6].

The decrease in the intensity of the surface growth of carbon particles in the presence of hydrogen creates favorable conditions for their subsequent rapid burning during the available time of the working cycle of the power plant. Note that among the known chemical agents, there are practically no ones that would contain hydrogen and exhibit a similar mechanism.

At the next stage of the fuel combustion process, the effect of hydrogen on the processes of the resulting carbon evolution can manifest itself in acts of initiation of its burning. Consider this question in more detail. Carbon burning is a complex multi-stage heterogeneous process of chemical reaction mainly on the outer surface of a carbon particle. This process is determined by both the kinetics of chemical reactions and the counter diffusion of the oxidizing agent and reaction products.

2. Materials and methods
The chemical mechanism of interaction of a carbon particle with an oxidizing agent includes heterogeneous oxidation reactions that occur on the surface of the particle, and homogeneous CO and \( \text{H}_2 \) after-combustion processes occurring in its boundary volume. For a detailed consideration of this mechanism, we use the well-known principles of the theory of catalysis [7, 8]. Considering the reaction of carbon oxidation as a first-order reaction with respect to oxygen, the particle burning rate can be expressed as:

\[
\omega_0 = X_{O_2} \frac{1}{1 + \frac{1}{\beta}}
\]

where \( X_{O_2} \) is the oxygen concentration; \( \kappa_1 \) is the reaction rate constant on the particle surface; \( \beta \) is the diffusion term. For the combustion conditions of hydrocarbon fuel in power plants, the Nusselt chemical criteria for the main soot oxidation reactions do not go beyond the kinetic region [1]. Therefore, the process of carbon burnout occurs in the kinetic region and the diffusion resistance of the process can be neglected. Physically, this is due to the very small size of the formed carbon particles, in which mass transfer does not limit the combustion process. Therefore, for the rate of carbon burnout, the above expression is simplified and takes the form:

\[
\omega_0 = X_{O_2} \cdot \kappa_1.
\]

Hydrogen added to the working fluid in the high-temperature phase of fuel combustion shows the ability to generate active particles [7]. According to the modern theory of combustion [8], this ability of
Hydrogen is manifested in the unique kinetics of the occurrence of branching and chain oxidation of \( \text{H}_2 \) in a mixture with \( \text{O}_2 \). The initiation reaction has the form:

\[
\text{H}_2 + \text{O}_2 \rightarrow 2\text{OH}^*.
\]

The continuation of the chain of this reaction:

\[
\begin{align*}
\text{OH}^* + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H}^*, \\
\text{H}^* + \text{O}_2 & \rightarrow \text{OH}^* + \text{O}^*, \\
\text{O}^* + \text{H}_2 & \rightarrow \text{H}^* + \text{OH}^*.
\end{align*}
\]

The overall reaction:

\[
2\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{H}^* + \text{OH}^*.
\]

As it can be seen, upon the implementation of the chain mechanism of hydrogen oxidation, the \( \text{H}_2\text{O} \) product is formed and the active reaction centers, the \( \text{O}^* \) chain carriers, are regenerated, and two more carriers of the \( \text{H}^* \) and \( \text{OH}^* \) chain arise. Each of the chain carriers can start a new link, with the formation of an even larger number of active centers.

In the presence of active centers, the oxidation reaction of particles (1) is implemented as a catalytic one. The rate constants of the normal \( (k) \) and catalytic \( (k)k \) reactions differ in the activation energies \( E \) and \( E_k \) and in the preexponential factors \( C \) and \( C_k \) in the Arrhenius equation:

\[
k_1 = C \cdot \exp \left( -\frac{E}{RT} \right); \quad k_{1k} = C_k \cdot \exp \left( -\frac{E_k}{RT} \right).
\]

where \( R \) is the gas constant; \( T \) is the temperature.

The relationship between the rate constant of carbon oxidation of the catalytic and normal reactions is denoted by \( \chi \), then:

\[
\chi = \frac{C_k}{C} \cdot \exp \left( -\frac{E - E_k}{RT} \right),
\]

where \( E - E_k = \Delta E \) – activation energy difference between normal and catalytic reactions.

Obviously, the rate of carbon oxidation during its catalysis at active sites increases as the relative amount of hydrogen \( \delta \) introduced into the reacting medium increases and its ability to generate active particles (we call this manifestation as an efficiency indicator \( \nu_k \)). Therefore, the ratio \( (C/C_k) \) can be replaced by the complex \( (\nu_k \cdot \delta_k) \). Then expression (2) can be rewritten in the following form:

\[
\chi = \nu_k \cdot \delta_k \cdot \exp \left( -\frac{E - E_k}{RT} \right),
\]

from which:

\[
\Delta E = R \cdot T \cdot \ln \left( \frac{\chi}{\nu_k \cdot \delta_k} \right).
\]

Here: \( \Delta E = (E - E_k) \). Thus, the efficiency of the reaction of hydrogen during heterogeneous catalysis of a carbon particle can be estimated by \( \Delta E \), which characterizes the decrease in the activation energy of the process. With a decrease in the activation energy of the process of carbon oxidation (burning), a more intensive increase in the reaction rate is observed. The dynamics of this growth is determined not only by the relative content of the hydrogen reagent in the reacting medium, but, first of all, by its ability to generate active particles — centers of nucleation of oxidative reactions. It should be noted that only the manifestation of such a chain mechanism can explain the unique ability of small doses of hydrogen to initiate acts of particle burnup so effectively [4, 5].
3. Results and Discussion

Based on the results of the analysis, it can be concluded that the addition of a hydrogen reagent to the working fluid of a power plant can be considered as an effective multi-functional means of reducing the resulting carbon emission during fuel combustion. In the low-temperature phase of the combustion process, hydrogen counteracts the formation of carbon nuclei (the effect of ‘hydrogen inhibition’), and in the subsequent high-temperature phase, it catalyzes the process of its accelerated burning.

The considered properties of the hydrogen reagent expand our understanding of its role in the kinetic mechanism of the resulting carbon emission, making it possible to develop methods of mathematical calculation for estimating the content of particles in combustion products with the participation of hydrogen additives.

As an example of the implementation of such an opportunity, we consider one of the variants of such a technique using the well-known model of H. Hiroyasu [9]. In this model, the current rate (in time $t$) of the formation of the mass of carbon particles ($m_c$) during fuel combustion is described by the equation:

$$\frac{dm_c}{dt}_{\text{form}} = A_f m_f p^{0.5} \exp \left( -\frac{E_f}{RT} \right),$$

and their burnup rate:

$$\frac{dm_c}{dt}_{\text{burn}} = A_c m_c X_{O_2} p^{1.8} \exp \left( -\frac{E_c}{RT} \right),$$

where $m_f$ is the mass of fuel; $A_f, A_c$ - preexponential factors for the processes of formation and burning of particles; $E_f, E_c$ - activation energy for the same processes, respectively; $p$ is the pressure in the combustion chamber.

The rate of change of the resulting particle mass $m_c$ in the cylinder is calculated as the difference between the speeds of two competing processes - formation and burnout:

$$\frac{dm_c}{dt} = \left( \frac{dm_c}{dt}_{\text{form}} \right) - \left( \frac{dm_c}{dt}_{\text{burn}} \right).$$

A distinctive feature of this model (as, indeed, of most other known models) is that in it the most important factor determining the intensity of the process of particle burning is the activation energy. This indicator ($E_c$) is included as quantity in the exponent, which determines its dominant significance in the calculation of the resulting carbon emission.

It is noteworthy that the exponent at pressure for the process of burning particles exceeds the same indicator by 3.6 times for the process of their formation. From this it follows that during the period of the active stage of the combustion process, when the pressure in the combustion chamber is high, by initiating the process of burning particles by reducing the activation energy and shortening the duration of this process, it is possible to provide the conditions for the most intensive reduction of the resulting carbon emission.

Given the properties of the hydrogen reagent discussed above, the acts of the current formation of particles during the combustion of hydrocarbon fuel in the presence of a hydrogen additive can be described as:

$$\frac{dm_c}{dt}_{\text{form}} = K_{H2} A_f m_f p^{0.5} \exp \left( -\frac{E_f}{RT} \right),$$

and acts of their burnup:

$$\frac{dm_c}{dt}_{\text{burn}} = A_c m_c X_{O_2} p^{1.8} \exp \left( -\frac{E_c - \Delta E}{RT} \right),$$

where $K_{H2}$ is a coefficient that takes into account the decrease in the total rate of surface growth of soot particles due to hydrogen inhibition; $\Delta E$ is a decrease in the activation energy of the process of burning of particles during heterogeneous catalysis of their burning (3).

The values of the $K_{H2}$ coefficient and the values of the decrease in the activation energy $\Delta E$ can be set in the process of model identification. Similarly, it is possible to ‘reconstruct’ many other well-known models for calculating carbon emission in power plants working with additives to the working fluid of a hydrogen reagent.
4. Conclusions

According to the research, it was found that hydrogen as a chemical reagent is an effective ‘chemical tool’ that can not only actively influence the processes of the resulting carbon emission during the combustion of hydrocarbon fuel but also optimize the kinetic parameters of its combustion in total [8].

The test results conducted confirmed the predicted analysis of the character position on the nature of the influence of the hydrogen reagent on the processes of carbon emission (in the form of soot particles) during the combustion of hydrocarbon (diesel) fuel. So, with the addition of hydrogen of 1.25% with respect to the fuel consumed by the diesel engine, a decrease in the carbon black content in the combustion products is observed over the entire range of changes in engine load conditions. At the nominal regime, the content of soot in the combustion products decreases from 3.2 to 1.8 units in the Bosch instrument, i.e. by 45%.

The results of the study stimulate the further development of research aimed at expanding the use of hydrogen as a highly effective chemical reagent in order to improve environmental safety in the environment of operation of energy facilities of modern heat power engineering.

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