

HYDROGASDYNAMICS IN TECHNOLOGICAL PROCESSES

INFLUENCE OF THE ADDITION OF HYDROGEN AND OF A SYNTHESIS GAS ON THE CHARACTERISTICS OF THE PROCESS OF COMBUSTION OF GASOLINE–AIR MIXTURES UNDER CONDITIONS TYPICAL OF INTERNAL COMBUSTION ENGINES

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The influence of the addition of hydrogen and of a synthesis gas on the basic parameters of combustion of gasoline–air fuel mixtures is investigated theoretically. The possibility of feeding gasoline internal combustion engines with lean fuel mixtures with a concentration of 5–10 vol.% hydrogen is shown; this will greatly improve their ecological purity.

Introduction. Over the course of time, questions connected with the development of technologies aimed at increasing the ecological purity of vehicles equipped with internal combustion engines have become more and more topical. The increase in the abundance of motor vehicles inevitably has led to a substantial deterioration of the ecological situation in large cities. Under such conditions, even a small decrease in the amount of harmful emissions by each vehicle may considerably decrease the harm done to the surrounding medium. Leaders in the world's, automobile industry have already begun the production and selling of small batches of ecologically pure cars that use hydrogen as a fuel for internal combustion engines (ICE) or a fuel element; however, their cost and maintenance charges substantially exceed those for the cars with classical engines.

In publications on the problems of hydrogen power engineering, great attention is paid to the study of the effect of the addition of hydrogen on the kinetics of the combustion of hydrocarbons. In particular, improvement of the ecological characteristics of classical ICEs on addition of a small amount of hydrogen has been established experimentally [1].

The present work is devoted to finding the main trends in the influence of the addition of hydrogen on the parameters of the process of combustion of a mixture in the chambers of internal combustion engines. Since such kind of experimental investigations are expensive and cannot provide the detailed information needed for a deep understanding of the process, a detailed numerical simulation is used as a method of investigation.

Kinetic Mechanism. In order to investigate the kinetic specific features of the combustion of gasoline in the presence of additives, a corresponding kinetic mechanism is needed. In the open literature, one can only find several complex kinetic mechanisms that describe the kinetics of basic hydrocarbons contained in gasolines. Most of this has been developed at the University of California and its departments [2–5]. Of promise seems to be the use of the results of [5], where a full list of elementary chemical reactions is given and a comparison with experimental data is made. With the aid of the mechanism described in [5] one may consider homogeneous combustions of practically all saturated hydrocarbons — from methane to isooctane, which is sufficient for the combustion of gasolines to be simulated, but without account for the kinetics of interaction of nitrogen with other components of a gas mixture. It is known that nitric oxides are the by-products of the operation of internal combustion engines that negatively affect the surrounding medium but that practically do not exert a direct effect on the very process of combustion. In order to

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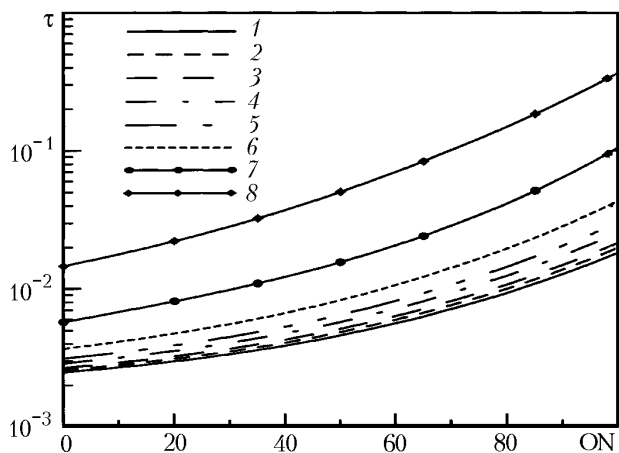


Fig. 1. Dependence of the time of gasoline ignition on the octane number for different additions of hydrogen: 1) $[H_2] = 0$; 2) 0.5; 3) 1; 4) 2; 5) 3; 6) 5; 7) 10; 8) 20. τ , sec.

adequately describe the formation of NO_x of compounds in burning of gasolines, the above-mentioned kinetic mechanism has been further improved and supplemented with some blocks from the mechanism described in [6], where the fullest kinetics of nitrogen-containing compounds has been implemented. The thus-formed mechanism contains 1078 chemical components and 4393 elementary chemical reactions. Its description is not given here because of its unwieldiness. To exclude incorrectly given velocity constants, this mechanism has been checked by the method described in [7] and corrected appropriately. The data on the time of delay in thermal ignition (TDI) calculated with the aid of the mechanism developed were compared with the experimental data of [8, 9] and were in good agreement.

We note that the kinetic scheme of such a dimension is difficult for processing even on modern PCs. For example, simulation of chemical conversions in a 0-dimensional adiabatic reactor with the aid of such a kinetic mechanism takes almost 4 h on a computer with an Intel Pentium 42.8 GHz processor.

Initial Conditions. Compression of a fuel mixture in an internal combustion engine is accompanied by its heating. In the absence of ignition, the maximum values of pressure and temperature are attained at the top dead point of the engine. For gasoline engines usually operating at a compression ratio between 7 and 11, the pressure to the end of the compression stroke amounts to about 15–25 atm and the temperature rises up to 680–780 K. Present-day gasoline ICEs operate at a compression ratio not lower than 9; therefore, as the initial conditions for subsequent simulation we take a gas pressure of 20 atm and a temperature of 730 K.

Real gasoline is a complex mixture of hydrocarbons, the composition of which is usually not known exactly and may vary from one batch to another; in the present work, calculations were done for model mixtures of normal heptane and isooctane. The octane number of gasoline was specified by the volumetric concentration of isooctane in a mixture with normal heptane in the generally accepted manner.

Influence of the Addition of Hydrogen on the Time of Delay in Thermal Ignition. Calculations of the time of delay in ignition were performed for stoichiometric mixtures in the isochoric-adiabatic approximation. Figure 1 presents the dependence of the time of delay in the ignition of a fuel mixture on the octane number of gasoline for different additions of hydrogen. It is seen from the figure that an increase in the octane number is accompanied by an increase in the time of delay in the thermal ignition of the mixture, which is due to the increased content of isooctane in the fuel, which, by virtue of the more compact structure of the molecule, possesses higher stability against disintegration as compared to the long molecule of normal heptane. The addition of hydrogen leads to a lag in the thermal ignition of the mixture, with this effect being slightly increased on increase in the octane number of the gasoline. For the most abundant A-76 gasoline, the addition of hydrogen in the ratio of 5 hydrogen to 1 gasoline leads to about a sixfold increase in the time of ignition, whereas a 10:1 ratio delays ignition by more than an order of magnitude as against a mixture without hydrogen.

We note that the 5:1 ratio corresponds to 4.2 vol.% hydrogen in a fuel mixture and 20:1 to 10.2 vol.%, whereas a stoichiometric mixture of hydrogen with air contains approximately 29% hydrogen.

TABLE 1. Values of the Volumetric Fraction of Hydrogen Relative to Gasoline Needed for a Corresponding Increase in the Effective Octane Number of Gasoline

Gasoline quality	Needed effective octane number				
	80	92	95	98	100
A-76	0.84	3.5	4.75	4.96	5.45
A-80	0	2.64	3.33	4.07	4.55
A-92	—	0	0.68	1.38	1.84
A-95	—	—	0	0.7	1.16
A-98	—	—	—	0	0.47

The observed increase in the time of delay in thermal ignition on the addition of hydrogen is associated with the fact that the latter reacts actively with radical OH, forming water and atomic hydrogen which is transformed into HO₂ by the reaction of fast chain breakage. The sequence described substantially decreases the concentration of the OH radical, thus increasing the time of delay in thermal ignition of the mixture.

As is known, the octane number characterizes the detonation stability of gasoline. At the same time, the detonation occurring in an internal combustion engine is usually associated with spontaneous ignition of the unburnt mixture on its compression by a moving flame front. Therefore, an increase in the time of delay in thermal ignition points indirectly to an increase in the detonation stability of a mixture and, consequently, to an increase in the effective octane number. Table 1 lists calculated data on the addition of hydrogen that lead to an increase in the effective octane number of the mixture which was estimated from the corresponding increase in the time of delay in thermal ignition. Each value in the table corresponds to the volumetric fraction of hydrogen needed for the desired increase in the effective octane number of a fuel mixture. For example, to increase the octane number of gasoline A-76 up to 92, it is necessary to ensure that the hydrogen/gasoline ratio in a mixture be equal to 3.5.

We note that an increase in the effective octane number of a fuel mixture gives a positive effect, since it allows one to design internal combustion engines with an increased compression ratio and, consequently, an increased efficiency.

Influence of the Addition of Hydrogen on the Ecological Parameters of the Combustion of Gasolines.

Investigation of the yields of nitric oxides and carbonic oxide was performed by modeling combustion of a fuel mixture under isochoric–adiabatic conditions. It has been found that the quality of gasoline exerts little effect on the concentration of nitric oxides and carbonic oxide at the outlet. Figure 2 presents the results of calculations of the yield of nitric oxides (Fig. 2a), mixture temperature (Fig. 2b), and carbonic oxide (Fig. 2c) depending on the equivalent relationship between A-76 gasoline and air in a mixture for different additions of hydrogen. In the given case, the determining factors of the accumulation of NO_x (Fig. 2a) are the availability of free oxygen in the mixture and a high temperature. On the one hand, a maximum gas temperature is attained when the equivalent ratio of a mixture is equal to about 1.1, which should be attributable to the highest concentration of nitric oxides, and, on the other hand, the amount of free oxygen is inversely proportional to the degree of mixture enrichment. The result of the competition between these factors is that a maximum of the yield of nitric oxides is observed at an equivalent ratio equal to about 0.9.

It is seen from Fig. 2b that, on the addition of hydrogen, the temperature of the process is noticeably increased and, consequently, the outlet concentration of nitric oxides is increased for depleted mixtures, which, however, does not influence the yield of nitric oxides in combustion of rich mixtures. We note that the values of the equivalent ratios 0.7 and 1.0 are practically the extreme limits of the accumulation of nitric oxides for the combustion conditions considered, beyond which the concentration of NO_x in combustion products is severalfold lower than the maximum one.

Figure 2c presents the results of simulation of the yield of CO depending on the equivalent ratio of the mixture of A-76 gasoline with air. An analysis has shown that the increase in the concentration of CO at the outlet with an increase in the equivalent ratio of a mixture occurs for two reasons: disappearance of free oxygen in lean mixtures prevents oxidation of CO to CO₂, whereas an excess of hydrocarbons in rich mixtures blocks the main channel of oxidation of CO [8].

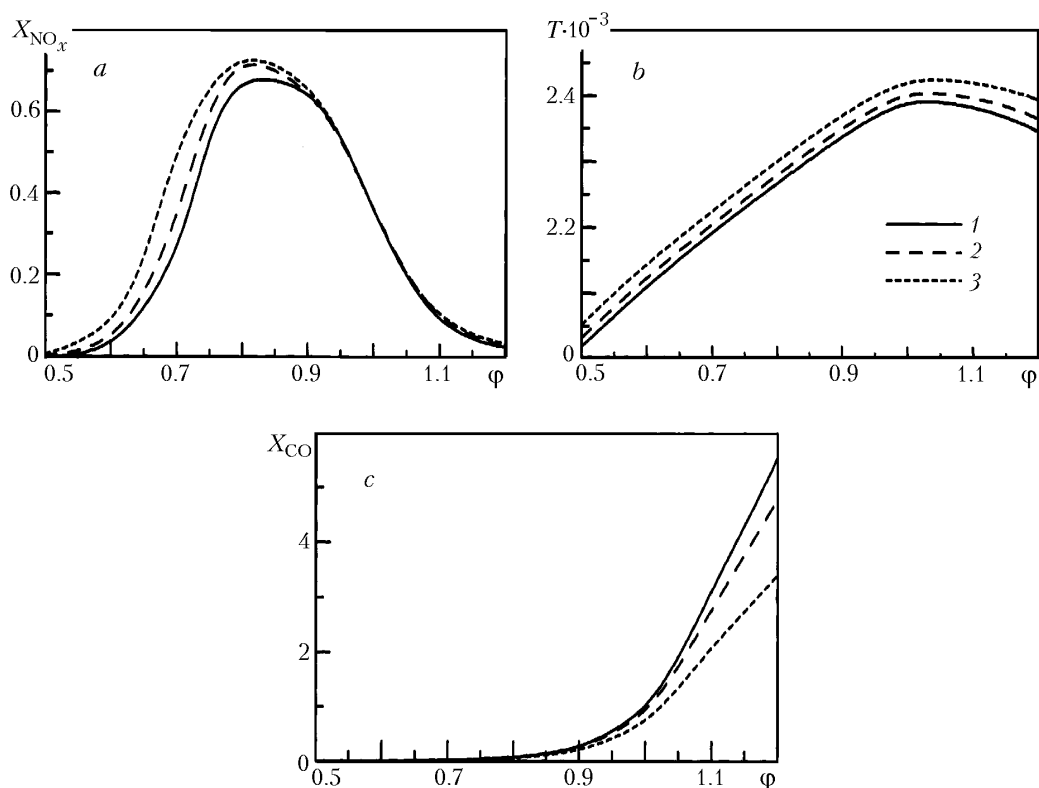


Fig. 2. Dependence of the yield of nitric oxides (a), temperature of combustion products (b), and yield of carbon monoxide (c) on the equivalent ratio of a mixture of A-76 gasoline with air for different additions of hydrogen: 1) $[H_2] = 0$; 2) 10; 3) 20. X_{NO_x} , %; T , K; X_{CO} , %.

Addition of hydrogen to the initial fuel leads to a reduced yield of CO due to both an increase in the temperature of the process (see Fig. 2b) and acceleration of the process of oxidation of CO. Moreover, on addition of hydrogen the balance between carbon and hydrogen is redistributed, and this reduces the amount of carbonic oxide produced in the case of complete combustion.

Thus, the addition of hydrogen practically does not change the yield of NO_x of compounds and somewhat reduces the yield of CO in the region of equivalent ratios (0.9–1.2) typical of internal combustion engines. A comparison of the results obtained shows that to increase the ecological purity it is worthwhile to change the operating conditions of an internal combustion engine by shifting the working range to the side of lean fuel mixtures with an equivalent ratio not higher than 0.7, which will ensure a low level of both carbon monoxide and nitric oxides. However, it is known that stable operation of classical gasoline-based internal combustion engines on such lean mixtures is impossible.

Influence of the Addition of Hydrogen on the Velocity of Propagation of a Laminar Gasoline–Air Flame. To investigate the influence of the addition of hydrogen on the laminar-flame propagation velocities, a special program has been worked out making it possible to calculate the speed of the front of laminar combustion in a preliminarily mixed mixture of a fuel with an oxidant in a one-dimensional approximation with allowance for the complete chemical kinetics and thermal conductivity of the gas. In order to accelerate the calculations, the program ignored the diffusion of chemical components, since its account would lead to the retardation of calculations at least by an order of magnitude, which would amount to about 50 h of machine time for calculating one point of combustion of a gasoline–air mixture. At the same time, preliminary calculations have shown that the error in calculation of the rate of laminar combustion in the absence of diffusion depends on the type of fuel, and it decreases with increase in the weight of the fuel molecule. Thus, for example, the error in calculation of the rate of combustion of an isooctane–air mixture under normal conditions does not exceed 10%. With increase in pressure, the influence of diffusion on the

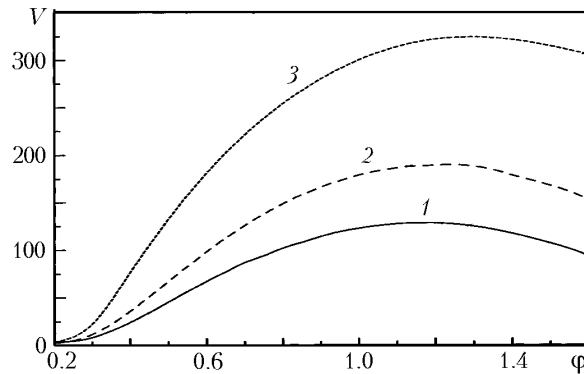


Fig. 3. Dependence of the velocity of the laminar front of combustion on the equivalent ratio of a mixture of A-76 gasoline with air. Designations of 1–3 are the same as in Fig. 2. V , cm/sec.

rate of combustion decreases substantially; this improves the agreement between calculated and experimental data and justifies the application of the program developed to investigate the limits of ignition and rate of laminar combustion of mixtures under the conditions typical of internal combustion engines.

Figure 3 demonstrates the dependence of the rate of laminar combustion of a preliminarily prepared mixture of A-76 gasoline with air on the equivalent ratio of the mixture for different additions of hydrogen. It is seen from the graph that the addition of hydrogen leads to a severalfold increases in the rate of the laminar combustion of the mixture in the entire range of equivalent ratios. Such a change in the propagation velocity also points to the extension of the limits of stable combustion of the mixture. The shift of the maximum on the combustion rate curve to the region of richer mixtures on increase in the amount of hydrogen added is attributable to the fact that the maximum of the rate of combustion of pure hydrogen with air occurs at the equivalent ratio 2.0, whereas the maximum for A-76 gasoline occurs at a ratio of about 1.15. The addition of hydrogen in the ratio 5:1 into a mixture with the equivalent ratio 0.7 yields a rate of combustion which is approximately equal to the maximum rate of combustion of a mixture without hydrogen, which allows one to judge the possibility of displacing the operating range of an internal combustion engine to the region of lean mixtures, which cannot be done when using purely gasoline mixtures. We note that in the real combustion chamber of an engine, combustion has a turbulent character, which leads to a thirtyfold acceleration in flame propagation in comparison with a laminar rate of combustion. This acceleration depends to a greater extent on the scale of turbulence (in the given case, on the frequency of crankshaft rotation) than on gas composition [9]. Therefore, the behavior of the real velocity of flame propagation in the chamber of an internal combustion engine depending on the mixture composition and additions of hydrogen will be analogous to the behavior of the laminar rate of combustion.

Characteristic Features of the Influence of the Additions of a Synthesis Gas on Combustion of Gasoline–Air Mixtures. From the practical viewpoint, the addition of a synthesis gas seems to be most convenient, since then it is possible to organize conversion of a hydrocarbon fuel into a synthesis gas directly aboard a vehicle. In this connection, estimations of the possibility of applying a synthesis gas, produced by partial oxidation of gasoline, as an addition to a gasoline–air fuel mixture were performed.

The quantity of the synthesis gas added was calculated from the volume of the gasoline vapors subjected to partial oxidation by air aboard a vehicle in percent of the total quantity of gasoline entering into the combustion chambers of an engine in the form of gasoline vapors and synthesis gas. Here, the maximum fraction of the fuel converted into the synthesis gas β was taken equal to 20%, which corresponds to 10% of the synthesis gas in a stoichiometric fuel mixture.

It has been established that small additions of a synthesis gas ($\beta < 3\text{--}5\%$) decrease the time of delay in thermal ignition by 3–7%. A further increase in the amount of additives leads to an increase in the time of delay in thermal ignition up to 50% for the greatest of the additives considered, $\beta = 20\%$, in the entire range of equivalent ratios.

In analyzing the influence of the addition of a synthesis gas on the ecological characteristics of combustion products, it has been revealed that the temperature of the process is decreased by about 50 K depending on the quan-

tity of the addition. This entails a certain decrease in the yield of nitric oxides (by 7%) and carbon monoxide (by 20%), which is indicative of the increase in the ecological purity of combustion products.

Calculations of the laminar flame propagation velocity in preliminarily prepared gasoline–air mixtures have shown that the addition of a synthesis gas just as the addition of hydrogen accelerates free propagation of a flame. However, the influence of the synthesis gas is many times smaller than that of hydrogen. Indeed, while for the maximum considered addition of the synthesis gas the increase in the velocity is equal to about 5%, on the addition of 5% hydrogen the velocity increases by more than 50%.

Conclusions. The investigations carried out have shown that additions of hydrogen and synthesis gas practically do not improve the ecological parameters of gasoline combustion in the chamber of an internal combustion engine without a change in the conditions of its operation. However, the addition of hydrogen substantially accelerates the propagation of a flame and makes the operation of an internal combustion engine on lean mixtures possible ($\varphi \leq 0.7$). In this case, displacement to the region of lean mixtures leads to a considerable decrease (practically to the disappearance) of the yield of harmful substances. Thus, it seems worthwhile to design ecologically pure internal combustion engines operating on lean mixtures and using small admixtures of hydrogen as an addition to a traditional fuel.

NOTATION

P , gas pressure, atm; T , gas temperature, K; T_0 , initial gas temperature, K; V , flame-propagation velocity, cm/sec; X , molar fraction of a substance, %; β , volumetric fraction of gasoline subjected to partial oxidation to generate a synthesis gas relative to the total amount of fuel entering into the combustion chamber of an internal combustion engine, %; φ , equivalent ratio; τ , time of ignition delay, sec; ON, octane number.

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