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Knock Characteristics of Gas Fuels in the Light of the Kinetics of Hydrogen and Methane Oxidation

Vladimir Arutyunov[1,2*], Artem Arutyunov[1,3], Andrey Belyaev[1], Liudmila Strekova[1]

[1]N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Kosygina 4, Moscow, 119991, Russia
[2]Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia
[3]Shenzhen MSU-BIT University, Shenzhen, 518172, China

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ABSTRACT

Understanding and operational assessment of the knock behavior of environmentally friendly gas engine fuels is very important for expanding their practical application. Recent studies of the autoignition of hydrogen and methane at temperatures typical for this process in internal combustion engines (800<T<1000 K) have shown that near 900 K, fundamental changes occur in the mechanisms of their oxidation associated with a change in the role of peroxide compounds in them. This leads to very abrupt changes in the autoignition dependence of mixtures containing them on temperature, pressure, and composition. In particular, near this temperature, depending on the composition of methane-hydrogen mixtures, such an important characteristic of their ignition as the activation energy of the ignition delay time can vary almost 4 times. Based on the analysis of the published data, this paper analyzes the nature of these changes and the related problem of assessing the knock resistance of gas fuels. It has been shown that the Methane Number, a common indicator of the knock resistance of gas fuels, is principally inapplicable for hydrocarbon gas fuels. The reason for this is the fundamental difference between the effect on ignition and combustion of methane, the main component of hydrocarbon gas fuels, admixtures of its heavier homologues, and hydrogen. An important reason is also some peculiarities of low-temperature hydrogen ignition. Although a theoretical assessment of the knock resistance of gas fuels containing methane and hydrogen is possible, it is of little use in practice. Thus, the development of a practically applicable scale for assessing the knock resistance of gas fuels remains an acute problem.

1. Introduction

The stabilization of world oil production [1], and its inevitable reduction in the future, as well as the need to reduce greenhouse gas emissions, declared the goal of the Paris Climate Agreement [2], have sharply increased interest in the use of gas fuels. The lower carbon content in natural gas and secondary gaseous energy carriers, such as syngas and hydrogen, makes them an attractive alternative to traditional liquid fuels.

Optimization of methods for the use of methane and hydrogen-containing gases in technological processes, as well as ensuring safe operation conditions, require reliable information on their ignition and combustion, primarily in the temperature range of 500–900 K, characteristic of internal combustion engines (ICE) [3], power plants and various technological processes. However, most of the experimental data on the ignition of methane and hydrogen has been obtained from shock-tube experiments, typically at temperatures of at least 950 K (see, e.g. [4–8]). Even in the few experimental studies of the ignition of gases containing methane and hydrogen using Rapid Compression Machines (RCM) [9, 10],

*Corresponding author.
E-mail address: v_arutyunov@mail.ru

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the researchers practically did not descend significantly below this temperature.

The kinetic mechanisms of the ignition and combustion of hydrogen and methane at T>1000 K have been well-known for a long time [11] and do not raise any principal questions. The general conclusions of almost all known works in this region are in good agreement with each other and are that all methane-hydrogen fuel compositions exhibit a linear correlation of log(t) to 1/T, that is, they satisfy the Arrhenius equation, and even small additions of H_2 to CH_4 enhanced the ignition process [10]. At the same time, near 900 K, serious changes occur in the oxidation mechanisms of both hydrogen and methane associated with a change in the role of peroxide compounds in them [12, 13], which significantly affect the ability of these gases and mixtures containing them to ignite [14–16].

In addition to ensuring the safety of syngas and hydrogen production [17, 18] and their subsequent domestic and industrial use [19], an important practical consequence of the complex behavior of hydrogen, methane and containing them gases near 900 K is the problem of determining the knock resistance of gaseous engine fuels. The fact is that the experimental determination of the main motor characteristic of gaseous fuel, its knock resistance, is technically much more complicated than that of traditional liquid fuels.

The common characteristic of knock resistance of a fuel for internal combustion engines (ICE) with spark ignition is its Octane Number (ON), which is determined on a standard single-cylinder engine with a variable compression ratio. Usually, a fuel is characterized by two Octane Numbers.

The Research Octane Number (RON) is determined on a single-cylinder engine at a crankshaft rotation speed of 600 rpm, intake air temperature of 52 °C, and ignition-timing angle of 13°. It shows how the fuel behaves in the modes of low and medium loads.

The Motor Octane Number (MON) is determined at a crankshaft rotation speed of 900 rpm, intake mixture temperature of 149 °C and a variable ignition-timing angle. MON usually has lower values than RON and characterizes the behavior of fuel under heavy loads.

However, many gas fuels have a very high ON (Table 1), noticeably exceeding this value for iso-octane, which corresponds to 100 points of the octane scale, which makes this scale unsuitable for testing the knock resistance of Compressed Natural Gas (CNG) and even Liquefied Petroleum Gas (LPG). In addition, it is technically difficult to compare the knock rating of fuels in different aggregate states. Therefore, a mixture of hydrogen and methane as a standard reference fuel was proposed to assess the knock resistance of gas fuels [20–22], which expands the measured range beyond the traditional range of octane numbers. The measure of knock resistance corresponding to this scale is Methane Number (MN), which is defined as the volume percentage of methane in a mixture with hydrogen corresponding to the knock intensity of the test gas mixture at specified engine operating conditions.

The addition of any inert component, such as N_2 or CO_2, increases the specific heat capacity of the system, thereby increasing the ignition delay and, accordingly, the knock resistance of gas mixture [23]. Therefore, for MN above 100 points, methane–

Table 1. Octane and methane numbers of some fuels.

Fuel	RON	MON	MN
Sewage or landfill gas (70% CH_4+30% CO_2)	-	-	129.8
CH_4	107.5	110	100
C_2H_6	107.1	108	43.7
C_3H_8	105.7	100	35
n-C_4H_{10}	93.6	91.0	11
n-C_5H_{12}	61.7	61.7	9.5
n-C_6H_{14}	24.8	26.0	9.5
n-C_7H_{16} (*n*-heptan)	0	0	9.5
n-C_8H_{18} (*n*-octane)	-19	-17	9.5
iso-C_8H_{18} (*iso*-octane)	100	100	-
Naphtha	43-58	41-56	-
H_2	>130	60	0

carbon dioxide mixtures are used as reference mixtures. In this case, according to the definition, the MN is 100 plus the volume percentage of CO_2 in the reference methane–carbon dioxide mixture [24]. In 1999, a consortium of European gas industry leaders decided on the preference of using this method for determining the knock resistance of gas fuels [24]. Currently, a number of calculators are available [25, 26] for evaluating the Methane Number of a gas mixture based on its composition.

However, there is neither universal standard procedure for determining the Methane Number of gaseous fuels as for gasoline motor tests, nor a generally accepted method for calculating the Methane Number based on the fuel composition. Almost every engine manufacturer has developed its own proprietary method for calculating MN, therefore, the values obtained by different methods may differ greatly [21]. The purpose of this work is to analyze the causes of the complex dependence of ignition of gas fuels containing methane and hydrogen on temperature and other conditions [13] and to draw attention to the problem of accessing the knock resistance of gaseous motor fuels related to the fundamental features of the complex kinetics of ignition of hydrogen, methane and gas mixtures containing them.

2. Kinetic analysis of the problem

2.1 Ignition delay time as an indicator of the knock resistance of a fuel

Motor tests are the most objective indicator of fuel properties. However, in academic studies of the ignition of various fuels, in addition to the ignition concentration limits [27], the most frequently determined indicator characterizing the ability of the fuel to ignite under specified conditions is their ignition delay time (IDT), as well as its dependence on the temperature, pressure, and fuel composition. This is the most objective physical parameter reflecting the knock resistance of the fuel, and any practical indicator of the knock resistance should theoretically be related to the IDT. A large number of papers have been devoted to studying this parameter for methane and hydrogen, with a significantly smaller number of studies on the ignition of various gas mixtures and real hydrocarbon gases, e.g. [4–10, 14–16]. However, the vast majority of them were carried out using shock tubes, which impose significant restrictions on the temperature range of studies, since at temperatures below 1000 K, the time of existence of relatively stable conditions in the reflected shock wave is close to the ignition delay time, so that serious errors are possible [28]. Even in a few experimental works using RCM [9, 10], the authors do not analyze the ignition at T<900 K.

One of the real consequences of this is a serious discrepancy between the extrapolation of the experimental results to the region of lower temperatures and the results of the kinetic simulation of the ignition at these temperatures [29]. This is especially important because it is in this temperature range that dramatic changes occur in the temperature dependence of the ignition delay time of methane and hydrogen. While at temperatures above 1000 K, a regular Arrhenius dependence is observed for both methane and hydrogen, at lower temperatures, this dependence for both of them has a complex character with a significant change in the activation energy of IDT [29]. Since the ignition of the fuel mixture in ICEs occurs at 500–900 K [3], it is determined by the kinetics of processes occurring at these temperatures. Therefore, to analyze the applicability of any scale as a benchmark characterizing the motor properties of hydrocarbon gas fuels, it is necessary to study their ignition at temperatures below 900 K, which are practically inaccessible to the shock-tube experiments. The main component of gas engine fuels in the vast majority of cases is compressed natural gas, that is, methane, which has a high knock resistance (Table 1). However, such fuels always contain an admixture of heavier hydrocarbons, inert components, and in some cases additives of hydrogen or syngas. Therefore, to assess the knock properties of gas fuels, first of all, it is necessary to understand the effect of these compounds on the knock resistance of methane.

2.2 The effect of alkanes on the ignition of methane

There are very few experimental studies on the effect of individual alkanes on methane ignition at T<1000 K [6–8, 14, 30]. A series of studies performed in a static reactor at temperatures of 523 to 1000 K [30] showed a sharp difference between the ignition delay time of methane and that of its closest homologues C_2–C_6. For all these alkanes, the observed ignition delay time under similar conditions was almost the same, with almost the same dependence of this value on the alkane concentration for all methane–alkane–air mixtures. Moreover, despite significant differences in the length of the carbon chain of these alkanes and in their reactivity, the same concentration of the additive, the values of the IDT at ~900 K

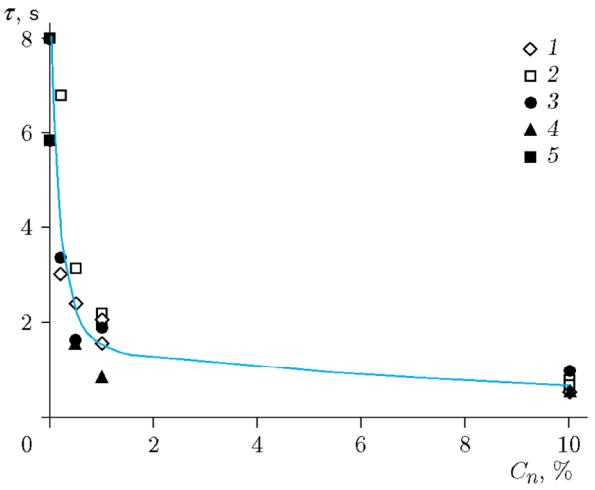

Fig. 1. Ignition delay time of methane–alkane–air mixtures versus the concentration of added alkane [C_n]: symbols 1–5 refer to ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively; T = 900 K, P = 1 atm, equivalence ratio φ = 1 [14].

were nearly identical. Addition of any of the C_2–C_6 alkanes even in a concentration of 1% reduces the IDT by a factor of two to three, whereas at their concentration of 10% the IDT of the mixture is practically indistinguishable from that of the added hydrocarbon itself (Fig. 1).

Thus, the effect of the length of the carbon chain of the added hydrocarbons in the first approximation can be considered insignificant, which, given the large difference in the reactivity of these light alkanes, is quite unexpected. This is evidently due to a relatively high temperature, significantly exceeding that of their autoignition. Under these rigid temperature conditions, the effect of the individual features of the oxidation of these alkanes on the ignition of methane seems to become insignificant. With such an identical influence of all C_2–C_6 alkanes, it is no surprising that the influence of their multicomponent admixtures practically does not depend on the composition and is determined only by their total concentration [30], which greatly simplifies the assessment of the knock characteristics of complex gas mixtures.

The above experimental results on the effect of the homologues of methane on its ignition delay time are not only qualitatively, but also quantitatively, within typical experimental error of ~30%, described by modern kinetic mechanisms [31], for example, this one, presented in [32]. A completely adequate level of theoretical description of these processes makes it possible to use computational methods not only to analyze the behavior of systems based on the oxidation of light alkanes, but also to justify the use of analytical expressions for an assessment of the ignition delay time of complex hydrocarbon mixtures [8, 31].

2.3 Ignition of methane-hydrogen mixtures

The possibility of using hydrogen as a carbon-free energy carrier is widely discussed in connection with the observed climatic processes [2]. A large number of related problems [33] and the absence of non-carbon sources of hydrogen adequate to the needs of the world's energy [34] make it more likely to use methane–hydrogen mixtures [35], known as Hythane. Using such mixtures makes it possible to evade many complex problems of hydrogen production, storage, transportation and distribution [35–38]. Such mixtures can be used to power traditional ICEs [39–46], where hydrogen is only slightly inferior to the efficiency of its use in fuel cells [40]. For the time being, the use of hydrogen or its mixtures in ICEs is technically more advanced and cheaper as compared to fuel cells.

The tests carried out on the engines showed that the use of hydrogen-enriched natural gas expands the combustion limits of lean mixtures suitable for practical use while reducing the level of emissions of unburned hydrocarbons and carbon dioxide [47]. Due to progress in the development of ICEs, it is expected that by 2045 their fuel efficiency will almost reach the efficiency of fuel cells [48]. Therefore, the use of hydrogen and methane–hydrogen fuel blends in ICEs can become a natural transition link between modern internal combustion engines running on liquid or gas fuel and future fuel cell-based transport [49].

Although the basic features of the combustion of hydrogen and methane have been determined a long time ago [11], there are still quite a lot of white spots and a large field for research that needs to be carried out in order to ensure the possibility of widespread practical use of methane–hydrogen mixtures. From the point of view of using hydrogen as a reference point for assessing the knock properties of fuels, an important problem is a significant difference in the temperature dependence of the IDT of hydrogen at high and low temperatures. While at temperatures above 1000 K, a regular Arrhenius dependence of IDT is observed, at temperatures below 900 K, which lie outside the range covered in shock tube experiments, hydrogen exhibits a complex behavior with a significant change in the activation energy of the IDT [13, 29].

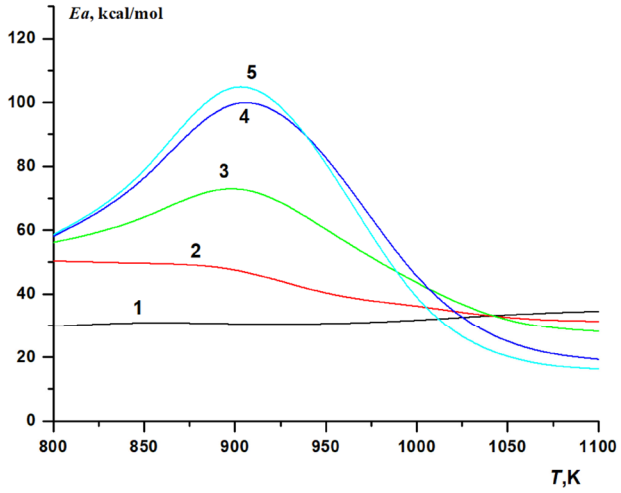

Fig. 2. Calculated temperature dependence of the effective activation energy E_a for the ignition delay time of stoichiometric CH_4–H_2–air mixtures on the initial temperature at various hydrogen concentrations (%): 0 (1), 40 (2), 70 (3), 90 (4), and 100 (5); P_0 = 1 atm [15].

The IDT of methane–hydrogen mixtures with hydrogen content from 0 to 50% was experimentally determined in [15]. In the high-temperature part of the studied range, the ignition delay time reduces significantly with increasing hydrogen content in the mixture, i.e., hydrogen promotes the ignition of methane. However, at a lower temperature T ~ 850 K, the promotion effect was weak if any. An increase in pressure reduces the range of variation of the effective activation energy of the ignition delay as the concentration of hydrogen changes. Simulation of ignition of methane-hydrogen mixtures in [15] showed that at a hydrogen concentration in the mixture of up to 40%, the temperature dependence of the ignition delay exhibited a nearly Arrhenius behavior with activation energy for methane itself (Fig. 2, curve 1) remains almost constant, ~30 kcal mol^{-1}. However, at higher H_2 concentrations, the dependence ceases to be the Arrhenius, revealing a well-pronounced maximum in the effective activation energy of the IDT at ~900 K (Fig. 2, curves 3–5). The effective activation energy of the IDT of hydrogen and mixtures with its high content increases at T ~900 K up to ~3–4 times compared to the effective activation energy of the IDT at lower and higher temperatures (Fig. 2, curves 4, 5). A similar effect was observed in [10], where the apparent increase in activation energy with increasing H_2 content was noted.

The influence of pressure on the ignition of methane–hydrogen mixtures is also complex due to its opposite influence on the ignition of hydrogen and methane. According to numerous data, obtained mainly from shock tube experiments at temperatures above 1000 K, an increase in pressure reduces the ignition delay time of hydrocarbons, including methane. But in some works, the opposite trend is observed at the lower end of this range. The results of [50] show that, at T = 1093 K, the IDT of hydrogen at a pressure of 20 atm is ten times longer than at 5 atm. A complex dependence on pressure was also observed in [51]. The results of kinetic modeling of the IDT of methane–hydrogen mixtures in the considered temperature range at a pressure range of 1–15 atm are shown in Fig. 3.

These results show that, in the entire temperature range covered, at a hydrogen concentration of $[H_2]$ = 20% and all the pressures considered, the temperature dependence of the IDT of stoichiometric methane–hydrogen–air mixtures obeys the Arrhenius equation. In the entire temperature range, an increase in pressure promotes ignition (Fig. 3a).

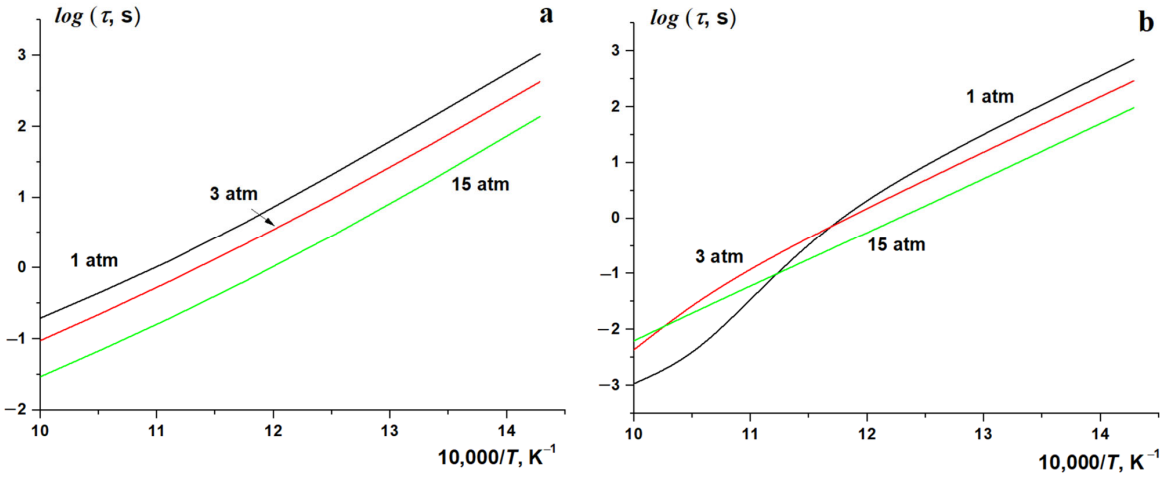

Fig. 3. Calculated temperature dependence of ignition delay time for stoichiometric methane–hydrogen–air mixtures at various initial pressures and hydrogen concentrations: (a) $[H_2]$ = 20%; (b) $[H_2]$ = 80% [15].

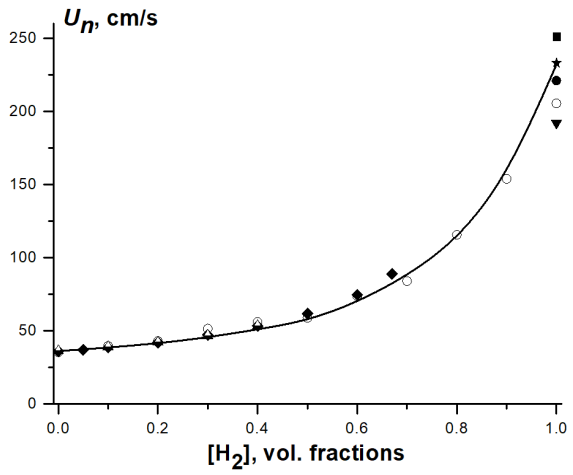

Fig. 4. Dependence of the laminar flame speed U_n of stoichiometric mixtures of methane–hydrogen–air on the concentration of hydrogen in them at T_0 = 293 K. The line represents the calculation results; the symbols, experimental data from different studies [13].

This confirms the conclusion that the oxidation of methane–hydrogen mixtures with low hydrogen content is mainly controlled by the methane oxidation mechanism. However, the ignition behavior changes significantly for mixtures with a high hydrogen content [H_2] = 80%, being controlled, according to [50, 29], by the hydrogen oxidation mechanism. While at P_0 = 15 atm, the Arrhenius dependence persists, at P_0 = 3 atm, it is markedly distorted, being clearly violated at P_0 = 1 atm (Fig. 3b). At the same time, while in the low-temperature part of the considered range an increase in pressure promotes ignition, reducing its delay time, in its high-temperature part it inhibits ignition. A fundamental change in the character of the influence of pressure on the ignition process occurs at T ≈ 900 K. These results are quite consistent with the results of [50], which show that, for hydrogen, with increasing pressure, the temperature dependence of the IDT approaches to the Arrhenius behavior.

The most important feature in combustion behavior of methane–hydrogen mixtures is the dependence of the laminar flame speed on the hydrogen concentration [52]. In [52] and the works cited therein, it was demonstrated that, at a concentration of hydrogen below 40%, it weakly affects the flame speed of such mixtures. By contrast, at higher concentrations, the influence of hydrogen increases exponentially with concentration (Fig. 4). In the same way, the concentration of H_2 affects the oxidation kinetics and ignition limits of methane–hydrogen mixtures [53].

2.4 Kinetic interpretation of the observed features of methane and hydrogen ignition

Complex behavior of hydrogen and methane during their ignition near 900 K, which strongly affects their knock characteristics, is due to the peculiarities of the kinetics of their oxidation in this region. These features are well demonstrated by the obvious deviation of the effective activation energy of the IDT of methane from the general dependence of this value on the number of carbon atoms in alkane molecules (Fig. 5).

The kinetic explanation for this is quite obvious. At T<900 K, the $CH_3^\bullet$ radicals formed during methane oxidation are highly likely to attach to oxygen, forming in an equilibrium reaction

$$CH_3^\bullet + O_2 <=> CH_3OO^\bullet \quad (1)$$

methyl peroxide radicals $CH_3OO^\bullet$, whose interaction with various hydrogen–containing molecules, including methane, leads to the formation of methyl hydroperoxide CH_3OOH with a relatively weak O–O bond, followed by the chain-branching step

$$CH_3OOH => CH_3O^\bullet + OH^\bullet \quad (2)$$

Therefore, at 800<T<900 K, methane oxidation is a branched-chain process. At higher temperatures, T>900 K, the equilibrium of reaction (1) shifts to the left. The rate of formation of methyl peroxide radicals, and hence, the rate of oxidation decreases, and the process is now ceases to be branched-chain.

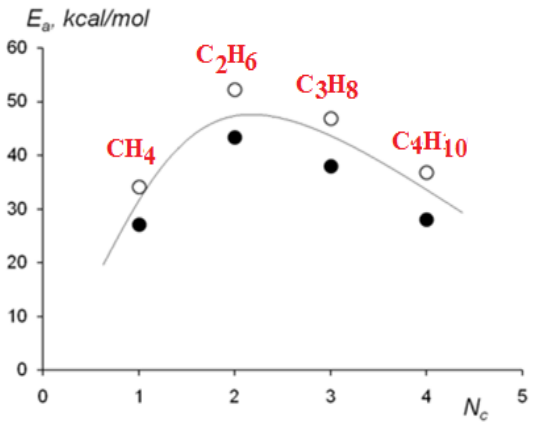

Fig. 5. Dependence of the activation energy of the ignition delay time of alkanes C_1–C_4 on the number of N_c atoms in the molecule. The filled and unfilled symbols represent two different series of experiments; the line approximates the averaged values; adapted from [14].

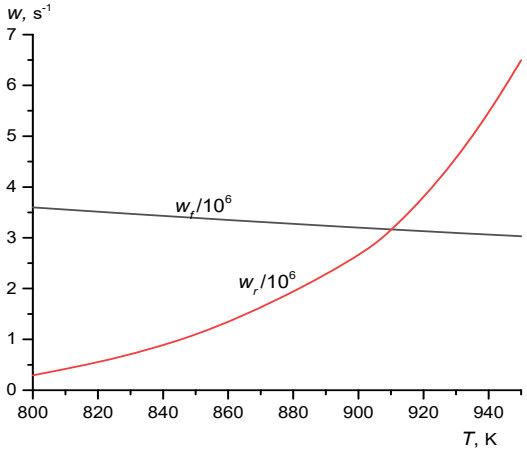

Fig. 6. Temperature dependence of the radical removal rate (in s^{-1}) in the forward W_f and reverse W_r reactions (1) during oxidation of a stoichiometric mixture of $CH_4 + O_2$. P = 1 atm. Calculations based on the mechanism from [54].

Only a further significant increase in temperature leads to an increase in the rate of methane oxidation, but now via the high-temperature mechanism with the chain-branching reaction

$$CH_3^{\bullet} + O_2 => CH_3O^{\bullet} + O^{\bullet\bullet} \quad (3)$$

Simulation using the mechanism from [54], which, despite being small in size, adequately describes the yields of the products of the direct oxidation of methane to methanol [55], a process in which reaction (1) plays a key role, showed that at a pressure of 1 atm, the rates of forward and reverse reactions (1) become equal at temperatures just above 900 K (Fig. 6). Thus, the region of transformation of methane oxidation mechanism near 900 K is critical for all methane-containing gas mixtures.

For other alkanes, a similar low-temperature branched-chain mechanism is not realized due to the rapid isomerization of the corresponding alkyl peroxide radical, followed by decomposition into an olefin $Q^{=}$ and the weakly reactive radical $HO_2^{\bullet}$ (Fig. 7),

$$R^{\bullet} + O_2 <=> RO_2^{\bullet} \quad (4)$$

$$RO_2^{\bullet} => Q^{=} + HO_2^{\bullet} \quad (5)$$

This means that at temperatures of 750–900 K, the oxidation of other alkanes occurs without chain-branching, that is, slower than the oxidation of methane. Similarly, at these relatively low temperatures, the oxidation of hydrogen deprived of chain-branching, proceeds more slowly than methane oxidation. One of the striking consequences of these differences in the low-temperature oxidation mechanisms of methane and hydrogen is the possibility of inhibiting the ignition of methane by hydrogen additives. In Fig. 8, this effect manifests itself in both simulation and experimental results.

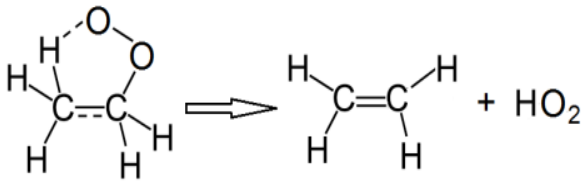

Fig. 7. Isomerization of the ethyl peroxide radical $CH_3CH_2OO^{\bullet}$ followed by decomposition into ethylene and radical $HO_2^{\bullet}$.

The kinetic interpretation of such a seemingly unexpected effect is self-evident. Below 900 K, molecular hydrogen is oxidized by a radical mechanism, while the branched-chain mechanism in which low-active $HO_2^{\bullet}$ radicals play an important role remains inoperative. At these temperatures, the main channel of their consumption is self-recombination

$$HO_2^{\bullet} + HO_2^{\bullet} => H_2O_2 + O_2 \quad (6)$$

Although the characteristic dissociation time τ_v of hydrogen peroxide,

$$H_2O_2 => OH^{\bullet} + OH^{\bullet}, \quad (7)$$

is lower than the IDT of hydrogen τ_i (Fig. 9), the addition of hydrogen to methane can lead to inhibition of the branched-chain oxidation of methane due to the conversion highly active methyl radicals into $H^{\bullet}$,

$$CH_3^{\bullet} + H_2 => CH_4 + H^{\bullet}, \quad (8)$$

with their subsequent transformation into low-active $HO_2^{\bullet}$ radicals

$$H^{\bullet} + O_2 + M => HO_2^{\bullet} + M, \quad (9)$$

followed by reaction (6). At the same time, as a sensitivity analysis of this process shows, at 900<T <1000 K, the rate of reactions leading to the formation of hydrogen peroxide significantly exceeds the rate of its decay or transformation into other products. This is what significantly increases the effective activation energy of the ignition delay time with increasing hydrogen concentration in methane–hydrogen–air mixtures near T = 900 K [13, 15].

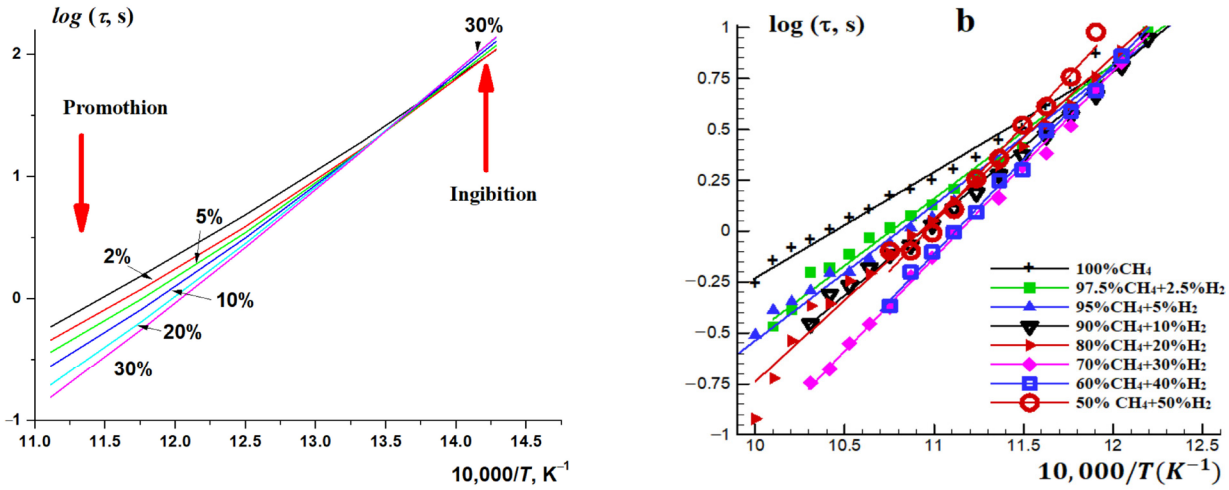

Fig. 8. Calculated (P_0 = 15 atm) (a) and experimental (P_0 = 3.0–3.2 atm) (b) temperature dependence of the ignition delay time of stoichiometric mixtures of CH_4–H_2–air at different concentrations of H_2 (%). Adapted from [15].

The contribution of the chain-branching reaction in the mechanism of hydrogen oxidation

$$H^{\bullet} + O_2 \Rightarrow OH^{\bullet} + O^{\bullet\bullet} \quad (10)$$

at these relatively low temperatures is too low to ensure the branched-chain character of the process. Although the rate of this reaction increases sharply at T>900 K (Fig. 9), another factor interferes with the processes in this temperature range, preventing a rapid increase in the rate of the oxidation process with temperature. At 950–1000 K, the characteristic decay time of hydrogen peroxide becomes higher than the ignition delay time of hydrogen. Thus, reaction (6) of recombination of $HO_2^{\bullet}$ radicals, leading to the formation of hydrogen peroxide, during the ignition delay period actually becomes a chain termination reaction, slowing down the hydrogen ignition. To illustrate this, the temperature dependence of the concentration of $H^{\bullet}$ atoms was calculated upon ignition of stoichiometric mixture of hydrogen and air at the time of pre-explosive heating of the mixture, when its temperature exceeds the initial temperature by 100 K, with a standard and an order of magnitude increased rate constant of reaction (7) of hydrogen peroxide decomposition (Fig. 10). This comparison shows that at T<900 K, the reaction (7) significantly affects the ignition process, reducing the concentration of $H^{\bullet}$ atoms.

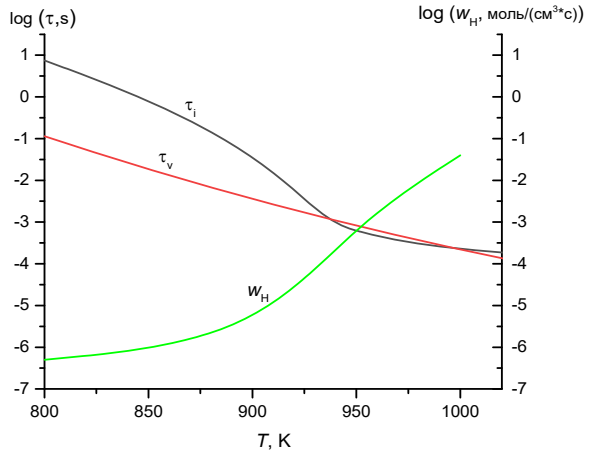

Fig. 9. Temperature dependence of the characteristic dissociation time of hydrogen peroxide τ_v, characteristic ignition delay time of hydrogen τ_i, and rate of reaction (10) W_H (mol/(cm³·s)). Calculations based on the mechanism from [54].

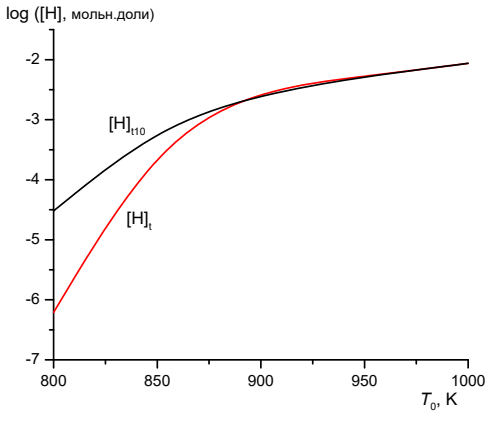

Fig. 10. Calculated temperature dependence of the concentration of $H^{\bullet}$ atoms during ignition of a stoichiometric hydrogen–air mixture at the moment of its pre–explosive heating, when its temperature exceeds the initial one by 100 K. $[H]_t$ and $[H]_{t+10}$ are, respectively, the $H^{\bullet}$ concentrations, calculated with the standard and 10–fold-increased rate constant of reaction (7).

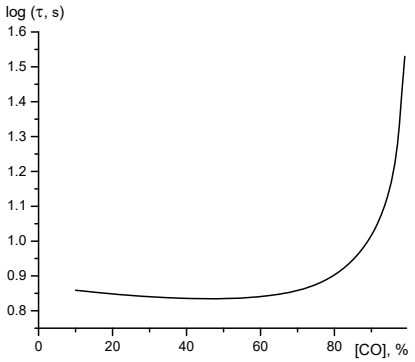

Fig. 11. The calculated dependence of the ignition delay time of the syngas on the concentration of CO for the conditions of a constant volume reactor. T_0 = 800 K, P = 1 atm, equivalence ratio ϕ = 1.0; adapted from [13].

A complex interplay of the two substantially different mechanisms, branched-chain low-temperature methane oxidation and low-temperature hydrogen oxidation, give rises to unconventional dependencies of the IDT for these mixtures not only on temperature, but also on pressure. As shown in [15], at concentrations of hydrogen in the mixture <50%, the temperature dependence of the ignition delay time for stoichiometric CH_4–H_2–air mixtures obeys the Arrhenius equation, with an increase in pressure reducing this time. By contrast, at a high concentration of hydrogen and low pressures (1–3 atm), the temperature dependence of the ignition delay time ceases to be of Arrhenius type. At low temperatures, an increase in pressure promotes the ignition, while at high temperatures inhibits it.

In view of these features of hydrogen ignition near 900 K, it is also worthwhile to discuss briefly syngas ignition, which can also be used as a gaseous engine fuel. The main parameter determining the ignition characteristics of a syngas is the H_2-to-CO ratio, the effect of which strongly temperature-dependent. At T>900 K, in the region of high-temperature branched-chain mechanism of hydrogen oxidation, an increase in the carbon monoxide concentration leads to a monotonous increase in the ignition delay time due to an increase in the specific heat capacity of the mixture because of its dilution with low-active CO, as well as due to the contribution of the chain termination reaction

$$CO + O^{\bullet\bullet} + M => CO_2 + M \quad (11)$$

However, at temperatures T<900 K, in the region of low-temperature hydrogen oxidation, an increase up to 60% in the concentration of low-active carbon monoxide, which in principle is not able to be oxidized by a chain mechanism in the absence of hydrogen-containing molecules due to the absence of chain carriers [56], promotes the ignition of hydrogen, noticeably reducing the delay time of its ignition (Fig. 11).

The reason for such an unexpected phenomenon as the promotion of ignition of hydrogen, a highly reactive reactant, by additives of carbon monoxide, a low-active reactant, is also related to $HO_2^{\bullet}$ radicals, which play an essential role in low-temperature hydrogen oxidation. The interaction of $HO_2^{\bullet}$ radicals with carbon monoxide via the reaction

$$CO + HO_2^{\bullet} => CO_2 + OH^{\bullet} \quad (12)$$

converts these low-active radicals, otherwise consumed by chain-termination reaction (6), into highly active $OH^{\bullet}$ radicals, participating in chain-propagation, and thereby turns of this channel of chain termination.

3. Discussion

The above-discussed ignition features of methane and hydrogen are very important for the practical application of gaseous hydrocarbon fuels. Firstly, they show the need for keeping the total content of all C_2+ alkanes in gas engine fuel at a level of less than 1%. Secondly, since the ignition delay of multicomponent gas mixtures depends only on the total concentration of heavier alkanes in fuel, while being practically independent of their component composition, there is no need to know the detailed component composition of the hydrocarbon fuel, but only the total content of heavier alkanes in it, which significantly facilitates the assessment. In addition, the activation energy of the ignition delay time for such complex mixtures is practically independent of the specific fractions of these alkanes in methane at their constant total concentration [14, 30]. Thirdly, they show a very strong temperature dependence of the ignition delay time of methane–alkane and methane–hydrogen mixtures on their composition, caused by the transition from the low- to high-temperature mechanism of methane and hydrogen oxidation at T ~900 K.

The mechanism of this transition is strongly influenced by the change in the dissociation time of H_2O_2 in the range 800<T<1000 K (H_2O_2 turnover [57]). In the low-temperature part of this range, the characteristic lifetime of hydrogen peroxide can be very

close to the duration of the ignition processes, which makes the recombination of low-activity $HO_2^•$ radicals into hydrogen peroxide actually the chain termination stage. However, at T>1000 K, the characteristic dissociation time of H_2O_2 becomes lower than the ignition delay time of these gases, and the recombination of $HO_2^•$ radicals to form hydrogen peroxide, which rapidly decays at these temperatures to active hydroxyl radicals (reaction (7)). Therefore, at these temperatures the recombination of $HO_2^•$ radicals ceases to be chain termination.

Thus, the temperature interval near T ≈ 900 K separates regions with fundamentally different mechanisms of methane and hydrogen oxidation, the complex interaction of which determines the unusual features of the ignition of gas mixtures containing these gases. These features, including a significant change in the activation energy of the ignition delay of hydrogen-containing gases near T ≈ 900 K, as well as the complex influence of pressure on this process, cannot be ignored when assessing the ignition behavior of such gas mixtures. They also impose serious restrictions on the choice of methods for assessing the knock resistance of such gaseous fuels, in particular, showing the fundamental inadequacy of the Methane Number, although it is widely used for this purpose.

Other important issue that determines the problems of using the methane–hydrogen scale as a benchmark for assessing the knock resistance of hydrocarbon fuels is the character of the influence of hydrogen concentration on the flame speed of methane [52]. The Methane Number is actually based on the assumption that the motor characteristics (flame speed, ignition limits, ignition delay) of methane–hydrogen mixtures are close to the linear dependence on the concentration of both components, that is, on the additive nature of the dependence of these characteristics on the composition of such mixtures, which does not correspond to reality.

It is also necessary to pay attention to the very sharp dependence of the ignition delay time of natural gas on the content of methane homologues, observed only in a very narrow range of their concentrations (Fig. 1), fundamentally different from the effect of hydrogen on this parameter (Fig. 4). This fundamental difference in the effect of hydrocarbons and hydrogen on the ignition delay time of natural gas alone calls into question the expediency of assessing knock resistance of hydrocarbons based on any scale with a much less drastic dependence on the concentrations of reference components. Comparing Figs. 1 and 4 shows that the influence of alkanes C_2–C_6, which are the main components of all gaseous hydrocarbon fuels, and hydrogen on the ignition and combustion of methane, is substantially different. This is a fundamental disadvantage of the Methane Number.

Despite the zero value ascribed to hydrogen in the Methane Scale, hydrogen has a MON of 60, and a RON above 130 [39] (Table 1), being quite successfully used as a motor fuel in ICEs [39, 41, 58]. Thus, depending on the test mode, hydrogen additives, apparently, can lead to both a decrease and an increase in the knock resistance of methane, which is another reason of the inapplicability of the MN to characterizing the knock properties of hydrocarbon fuels.

The almost identical effect on methane ignition of all C_2–C_6 alkanes [14, 30], makes it promising for practical assessment of the knock resistance of at least hydrocarbon gaseous fuels of any scale based on methane and one of its heavier homologues. The idea of replacing the methane–hydrogen scale in assessing the knock resistance of gas fuels with a methane–butane scale was first put forward in [59]. Subsequently, it was proposed to use the Propane Knock Index (PKI) for this purpose [60], which is currently used to compare the fuel properties of LNG of various compositions and origins [61]. The PKI is a characteristic of the knock resistance of a gas mixture defined as the percentage of propane in a mixture with methane having the same knock resistance under the same engine operation mode as the tested mixture. An almost identical effect of individual C_2–C_6 alkanes on the ignition delay time of methane [14, 30] suggests that the PKI can adequately qualify the knock resistance of at least methane–alkane gas fuels, i.e., real Compressed Natural Gas, if instead of the propane concentration the total concentration of all alkanes C_2+ presented in a mixture with methane is used.

The identical effect of the admixture of all C_2–C_6 alkanes on the ignition delay of methane not only simplifies the possibility of rapid assessment of the knock resistance of hydrocarbon gas fuel, but also opens up the possibility of using analytical formulas to calculate their knock resistance. In [62], based on experimental results on the effect of ethane, propane, and n-butane additives on methane ignition, a generalized dependence was proposed for all types of hydrocarbon additives taken into account in the form of their total concentration [HC],

$$\tau_{ign} = 1.77\times10^{-14}[CH_4]^{0.66}[O_2]^{-1.05}[HC]^{-0.39}\exp(37100/RT),$$

for temperatures from 1300 to 2000 K, pressures from 3 to 15 atm, and an equivalence ratio of ϕ = 0.43–1.25 with a general pressure dependence of ~P−0.78. A number of other dependencies of a similar type are considered in [8, 52, 63].

The change in the mechanism of hydrogen oxidation near 900 K, associated with a change in the role of peroxide compounds in this process, suggests that this is the reason for the unusually high difference between the RON and MON as applied to hydrogen. At low and medium loads, at which the RON is determined, hydrogen oxidation occurs at relatively low temperatures, at which the formation of peroxide compounds leads to chain termination and a low rate of their branching. This explains the high knock resistance of hydrogen in this mode, which corresponds to RON values of >130. At high loads corresponding to the definition of the MON, hydrogen oxidation occurs at higher temperatures, at which hydrogen peroxide decays at a high rate, and the process proceeds in the branched-chain mode, which corresponds to a significantly lower octane number, MON = 60 (Table 1).

It can be assumed that the situation with methane, having a higher MON (110) than RON (107.5), which is not typical for traditional fuels, is also associated with changes in the mechanism of its oxidation [12], leading to a decrease in the reactivity of methane with an increase in temperature near 900 K with increasing engine load.

In conclusion, it is worth shortly mentioning the influence of other compounds on the knock resistance of hydrocarbon gaseous fuels. Addition of inert components increases the specific heat capacity of gas mixtures per unit volume of the fuel component, thereby increasing their knock resistance [23]. Of the other classes of compounds, only light olefins, ethylene and propylene, components of refinery gases, may be of real interest in this regard. Ethylene can also be considered as a product of the selective oxycracking of heavier homologues of methane C_2+ in order to reduce their concentration to increase the knock resistance of natural and associated gases [64]. Their influence is also interesting because in the literature on the knock resistance of motor fuel, it is usually pointed out that alkenes, as well as cycloalkanes, have higher octane numbers compared to alkanes with the same number of carbon atoms [65]. Alkenes are part of the products of catalytic cracking, which is one of the main processes of oil refining used to produce high-octane components of motor fuels. However, as the literature data and experiments [66] show, the conclusion about higher motor characteristics of alkenes is valid only for those with at least four carbon atoms. For C_2–C_3 hydrocarbons, the octane numbers of the saturated hydrocarbons are even slightly higher than those of the corresponding alkenes and, apparently, the effect of the addition of alkanes and corresponding alkenes on the autoignition of methane is practically the same.

From other classes of compounds, oxygenates, which are widely used to increase the octane number of liquid hydrocarbon fuels, may be of real interest [67]. However, given high octane numbers of the gas fuels and the difference in the aggregate state with liquid oxygenates, it is still difficult to decide on the feasibility of their practical application. Experimental data and kinetic modeling show that DME is a more reactive component than methane, the addition of which reduces its knock resistance [68]. It can be surely assumed that the effect of other oxygenates will be similar.

4. Conclusions

Understanding and operational assessment of the knock behavior of environmentally friendly gas engine fuels is very important for expanding their practical application. While modern kinetic mechanisms of oxidation of light alkanes and hydrogen provide a fully adequate understanding of the features of these processes, the problem of a practically acceptable operational assessment of the knock resistance of gas fuels does not yet have an acceptable solution. Methane Number commonly used for this purpose is fundamentally unsuitable for evaluating of knock resistance of hydrocarbon gas fuels due to specific fundamental features of the ignition of methane and hydrogen. Thus, the development of a practically applicable scale for assessing the knock resistance of gas fuels remains an acute problem.

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