

The Influence of Small Additives of Alcohol Vapors on Combustion of Hydrogen and Methane in Air

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Abstract

The results of investigation of combustion of hydrogen-air and methane-air mixtures in the presence of small additives of ethanol, isopropanol, propenol in horizontal tubes are presented. The additives reduce the upper limits of flame propagation and the rate of flame propagation. The difference of inhibiting efficiencies of these alcohols corresponds to their ability to break the reaction chains of hydrogen and methane combustion processes. In the mixtures, containing less than 15% of hydrogen the suppression of combustion does not occur.

Introduction

Until recently the utilization of chemical additives in regulation features of gas phase combustion and explosion processes has limited application. The action of such reactants is based on reaction chain termination by their participation. While it was generally accepted for a long time, that the branching chain mechanism plays any significant role in gas phase combustion only at very low pressures, tens or hundreds times lower than atmospheric pressure (see for example, [1-6]). Up to nowadays only the two lower limits of self-ignition of combustible gas mixtures are considered to be the limits of chain ignition; plots for only these limits were included in the graphical depiction of chain combustion areas (*e.g.* [1,4-10]). Attempts were made in [11] even to disclaim one of the basic principles of the theory of chain processes, *viz.* the statement that self-heating is not obligatory for chain ignition to occur [1-3]. It was shown however, experimentally that the chain ignition proceeds even when the reacting system is monotonically cooled providing the chain branching faster than the chain termination [10].

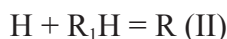
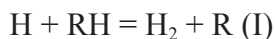
Macrokinetic features of combustion at atmospheric pressure were considered only in terms of competition of heat release by the reaction and the

heat removal from the reaction system (*e.g.* [2,5,13-15]). One of frequent forms of negation of the role of avalanche-like chain propagation in combustion accompanied by self-heating is the statement that calculations made without considering the chain mechanism are in good agreement with experimental data. Indeed, such a statement is equivalent to the negation of the role of chain factor not taken into account. Note that such an agreement is attained when any feature is considered in isolation from others and under quite restricted conditions. Besides, a great number of inputted parameters having restricted accuracy are used in such calculations. This facilitates the attending of agreement but does not make it convincing.

It was pointed as a motivation of negation of chain character of combustion at not very low pressures to that the temperature dependence of the reaction rate follows the Arrhenius law which is much stronger than the dependence on the reactant concentrations, which is merely a power function [2,5]. This statement is repeated latter (*e.g.* [16]). However, it was shown that the rate of a branching-chain reaction increases with temperature dramatically: as a double exponential function [17,18]. A great number of characteristic features of combustion processes at atmospheric and elevated pressures have been established which can be explained only by taking into account the predominant role of competition of reaction chain bran-

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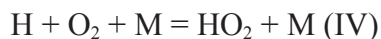
ching and termination. The sensitivity to small contaminations of a number of compounds is an example of such features. Combustion, explosion and detonation of hydrogen-air mixtures, containing more than 12-15% of H₂, are suppressed by hydrocarbons both at low and high pressures [18,20-24]. It was shown that such an action is caused mainly by reactions:



leading to replacement of atomic H by a significantly less active hydrocarbon radicals. Here RH and R₁H are aliphatic and olefinic hydrocarbons respectively. These reactions compete with the chain branching step:



Chain termination occurs also by the reaction:



because HO₂ radical as a chain carrier is substantially less active than H, O atoms and OH radicals.

The reactions (I) and (II) increase the total rate of chain termination and thus reduce the reaction rate. If the regeneration of H, O and OH by radicals R_i formed from the additive molecules is slower than by CH₃ radicals, then such additives will suppress the combustion of methane as well.

The present paper is devoted to reveal the role of reactivity of special functional groups in the molecules of inhibitors in their action on flame propagation in mixtures of hydrogen and methane with air. Propanol and propenol containing the same numbers of C-atoms were chosen for this purpose. Propenol was expected to be more efficient suppressant due to π-bond in its molecule.

Experimental

The reactions were carried out in stainless steel tubes: 200 cm length, 5.0 cm diameter and 250 cm length, 8 cm diameter. The initial conditions of the gas mixtures of reactions were room temperature and atmospheric pressure. Gaseous mixtures were prepared by admission of components into the evacuated tube, partial pressures being measured by means of sensitive manometers. After a time interval that necessary for perfect mixing of the components the gas mixture was ignited by an electrical spark near the tube end. The propagating flame was detected by its chemiluminescence which was recorded with a photomultiplier through three quartz windows located

along the reactor tube axis and a branched light guide. The average visible flame velocities were determined for four intervals located between the windows. For this reason the time intervals for flame propagation between the windows were recorded. The average value of the flame velocity along the whole tube was also determined. Repeated measurements were specially carried out to examine the reproducibility of the results. Characteristics of flame propagation in the absence of additives and in the presence of different amounts of propanol and propenol were compared in other conditions being kept unchanged.

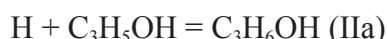
Results and Discussion

It is seen in Figs. 1 and 2 that the additives of vapors of alcohols reduce considerably the upper flammability limits of both hydrogen-air and methane-air mixtures *i.e.* prevent the ignition of mixtures containing relatively high contents of fuel. It can be seen as well that alcohol vapors substantially reduce as well the flame velocity in mixtures containing more than 15 vol.% of hydrogen and more than 7 vol.% of methane. The observed reduction of hydrogen flame velocity by alcohol additives correlates with the data on their action on the upper inflammability limits. The suppression of flame propagation can not be explained by the assumption of increase in heat capacity, because the efficiencies of the action of the same small additives of propanol and propenol are different. Assumption on independent consumption of oxygen with the additive as a reason of suppressing action of hydrocarbons on combustion of hydrogen was made *e.g.* in [25] as an explanation of the suppression of organic compounds on hydrogen combustion. While it is quite evident, that as the ignition of hydrogen – air mixtures is prevented by small additives *i.e.* the combustion does not start at all, then the action of alcohols is not caused by any consumption of oxygen in any reaction. This experimental fact is an indication as well that the reduction of flame velocity under the action of the additives is not caused by consumption of oxygen in any reaction with the additive occurring independently on hydrogen oxidation. It is well known on the other hand that H atom which is formed during the processes of combustion of methane and hydrogen intensively reacts with alcohol vapors similarly to reactions (I) and (II) (*e.g.* [27,28]). The formed alkyl and alkoxy radicals are less capable to propagate the reaction chains of hydrogen combustion than atomic hydrogen. This is

confirmed *e.g.* by the known much less flammability of vapors of propanol and propenol as compared with that of hydrogen [5]. The reactions which are responsible for prevention of ignition evidently occur as well in conditions of developed combustion. The independent combustion of alcohol vapors in the present experiment both in hydrogen-oxygen and methane-oxygen mixtures is excluded also by the reason that the concentrations of these additives in the mixtures under consideration are lower than their well known lower limits of combustibility [5].

Thus, the observed suppression of hydrogen combustion is resulted in additional termination of reaction chains occurring by participation of alcohol molecules similar to reactions (I) and (II).

The fact that the efficiencies of the action of propanol and propenol vapors on flame propagation of methane-air mixtures are different is an indication that the observed suppression effect is not caused by dilution of the named combustible mixture. The obtained data show as well, that the influence of propenol both on the flame velocity and the upper limit of ignition is more profound than that of aliphatic alcohols, *e.g.* C_3H_7OH . This difference is caused by the known fact, that the reaction of joining of atoms to π -bond occurs almost without any energetic barrier. For example, the activation energy of H atom joining to propylene is less than 6500 kJ/mol [29], *i.e.* is less than average heat energy RT . This reaction is not limited by stabilizing ternary collisions at pressures exceeding some kPa and so occurs by second kinetic order. Its rate constant is greater than that of the chain branching reaction (III) even at high temperatures. The structure and properties of C–C bond in propenol molecule are quite similar to those propenol. Therefore the value of the rate constant of the reaction of atomic hydrogen with propenol is as great as the value of that of its reaction with propylene. Therefore chain termination caused by participation of propenol proceeds via joining of atomic hydrogen to the π -bond:



The ability of the radical C_3H_6OH to continue the reaction chains is very low. Due to this, the reaction (IIa) successfully competes with chain branching and reduces the branching factor.

The reaction (IIa) due to its low energetic barrier is substantially faster than the reaction



Thus, the π -bond in propenol molecule is respon-

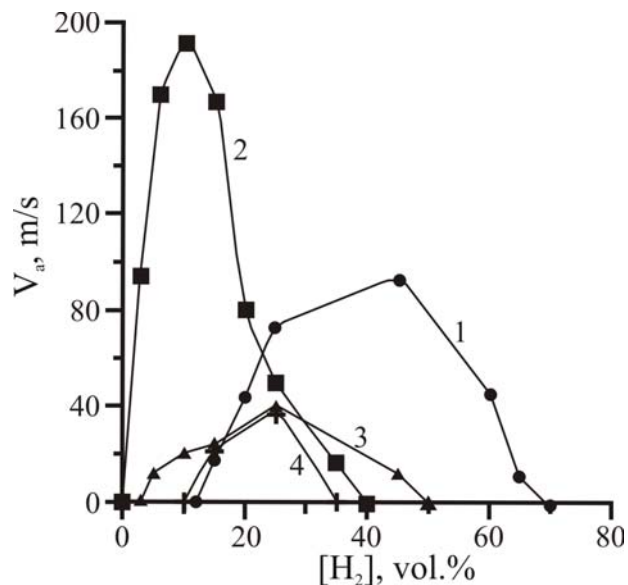


Fig. 1. Influence of additive alcohol vapors on average flame velocity of hydrogen-air mixtures. 1 – hydrogen-air mixture without additives; 2 – addition of 3 vol.% of C_3H_7OH ; 3 – addition of 3 vol.% of C_2H_5OH ; 4 – addition of 2 vol.% of C_3H_5OH .

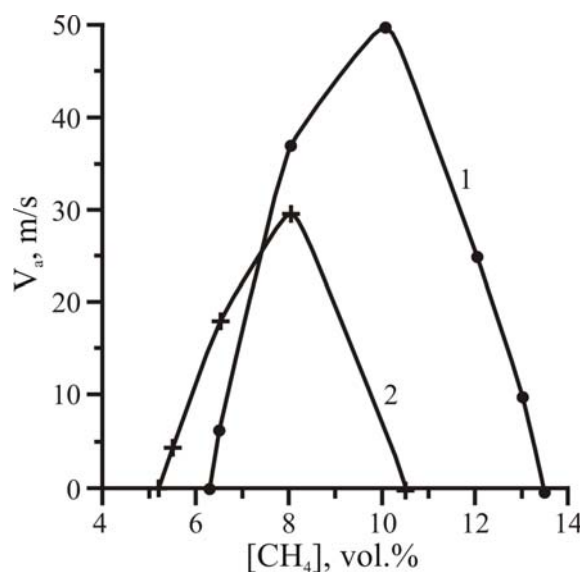


Fig. 2. Influence of additives of alcohol vapors on the average flame velocity of methane-air mixtures. 1 – methane-air mixture without additives; 2 – additive of 2 vol.% of C_3H_5OH .

sible for its greater suppressing activity of as compared with propanol. The difference of the efficiencies of these two alcohols as suppressants is a direct indication, that the main factor determining the suppression effect is not the consumption of oxygen by the additive, but is the ability of the inhibitor to break reaction chains.

Let us now consider the action of the additives on the flame propagation. As it can be seen from Fig. 3, in mixtures containing 20 to 60% hydrogen in the absence of any inhibitor the flame propagation is self-accelerating. The presence of 1 vol.% of propenol significantly reduces the concentration range for self-acceleration. In the presence of more than 2% of propenol the flame in any mixture of

hydrogen in air never accelerates and the flame slows down. Taking into account that the transition of deflagration into detonation is realized via self-acceleration of the flame, we come to conclusion that at concentrations of propenol exceeding 2% in mixtures of hydrogen and air the transition from deflagration to detonation will be prevented similarly to the action of olefins [18,23].

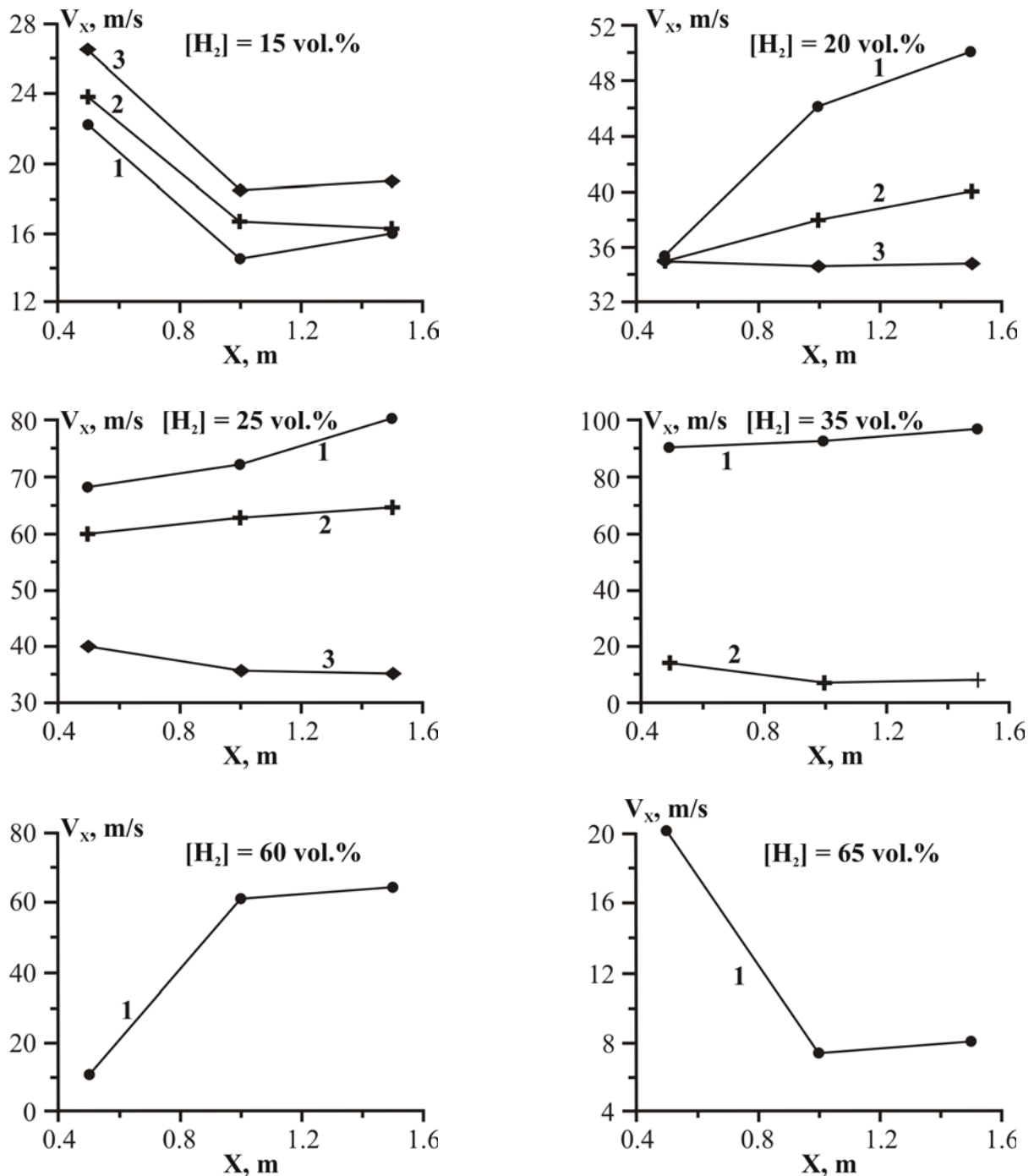


Fig. 3. Average velocities (V_x) of hydrogen-air flames at various distances (X) from ignition point. 1 – hydrogen-air mixture without any additive; 2 – addition of 1 vol.% of C_3H_5OH ; 3 – addition of 2 vol.% of C_3H_5OH .

The results obtained for the combustion of methane (Fig. 4) are similar to those for hydrogen-air mixtures. In the mixtures containing between 8 and 12% of CH_4 , the flame propagates in the accelerating mode. With 2 vol.% of propanol in the mixture there

is no flame acceleration and consequently one may expect that transition such an additive will prevent the transition of deflagration to detonation similarly to the observed effect in experiments with additions of hydrocarbons in hydrogen-air mixtures.

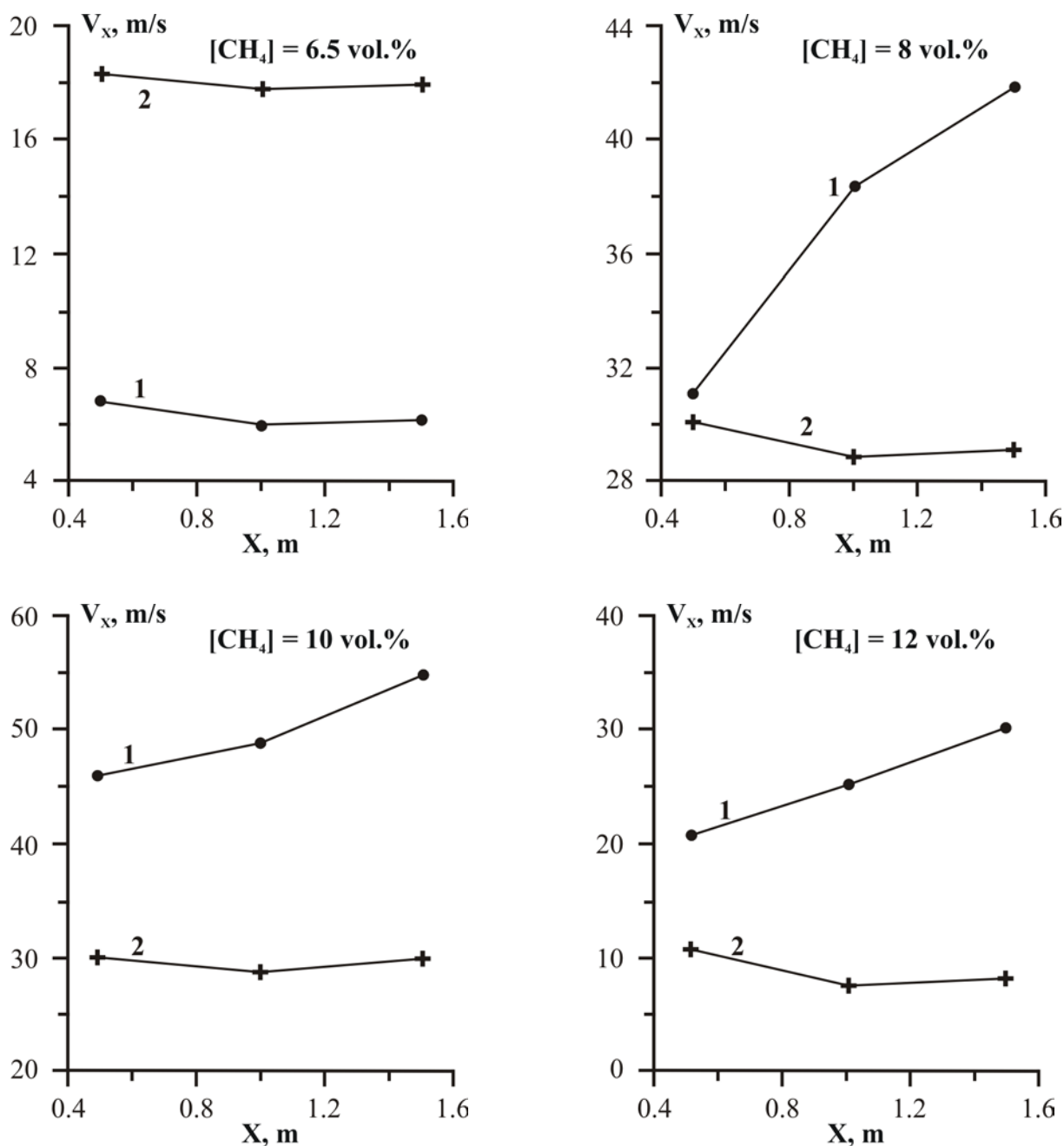


Fig. 4. Average velocities (V_x) of methane-air flame at various distances (X) from ignition. 1 – methane-air mixture without any additive; 2 – addition of 2 vol.% of $\text{C}_3\text{H}_5\text{OH}$.

It should be noted that the flame in the hydrogen-air mixtures containing more than 85% air is accele-

rated, if the concentration of propanol lies between 3 and 7% (Fig. 5). The reason is that because in such

mixtures concentrations of alcohol vapors are inside their ignition limits and consequently they are able to ignite and burn themselves. The combustion of alcohol vapors is promoted by hydrogen.

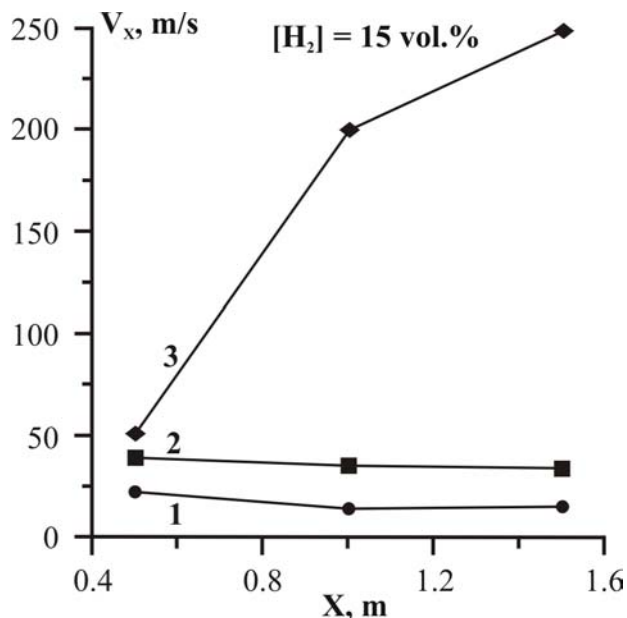


Fig. 5. Average velocities (V_x) of hydrogen-air flame at various distances (X) from the ignition point. 1 – hydrogen-air mixture without any additive; 2 – addition of 1 vol.% of C_3H_7OH ; 3 – addition of 3 vol.% of C_3H_7OH .

Conclusions

It was shown experimentally that alcohol vapors reduce the upper concentration limits of hydrogen-air mixtures, slow down flame propagation rate of hydrogen-air and methane-air mixtures. The flame suppression is resulted in additional chain termination occurring with molecules of additives. The inhibiting action of propenol is substantially greater than that of propanol. This is due to the presence of a π -bond in the propenol molecule. These results are the additional indication of the dominant role of chain avalanche, of competition of reaction chain branching and termination at atmospheric pressure unlike commonly accepted views. If the content of alcohol vapor is inside the concentration area of their ignition, they accelerate flame propagation in mixtures with a high concentration of oxidant. Hydrogen promotes the combustion of alcohol vapors.

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