

1. PRESSURE AND TEMPERATURE DEPENDENCE OF FLAMMABILITY LIMITS AND BURNING VELOCITY OF GASEOUS MIXTURES
2. THE DEPENDENCE OF PRESSURE INDEX OF BURNING VELOCITY OF GASEOUS MIXTURES ON CHEMICAL KINETICS IN THE FLAME FRONT

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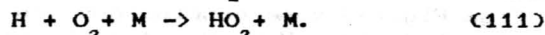
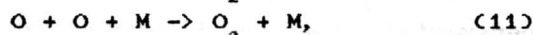
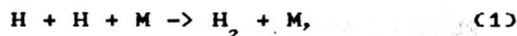
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ABSTRACT

Results of theoretical and experimental investigations of flammability limits and burning velocity of gaseous mixtures under increased pressures and temperatures are presented.

Flammability limits were investigated at temperatures from 20 to 250°C and pressures from 0.1 to 2.0 MPa. Gaseous mixtures included the following components: hydrogen, oxygen, air, steam, nitrogen, argon, carbon dioxide, helium.

The burning velocities of gaseous mixtures, containing hydrogen, air and steam, were defined experimentally at temperatures from 20 to 200°C and pressures from 0.1 to 6.0 MPa. The effect of sign change of pressure index n of burning velocity S_u for values of S_u much greater, than 0.5 m/c, was found. It means, that the violation of Lewis-Elbe rule for the pressure index of burning velocity occurs. Numerical modelling of flame propagation in stoichiometric methane-air and hydrogen-air mixtures was executed with detailed chemical kinetics under room temperature and pressure in the range 0.1-2.0 MPa. The variation of rate constants k_i of following reactions was made :



Rate constants k_i were reduced by a factor K , where K was 0.1, 1, 10, 100, 1000. The dependence of burning velocity and its pressure index on a factor K was investigated.

INTRODUCTION

The combustion characteristics of hydrogen-air-diluent mixtures at elevated pressures and temperatures are often needed for fire- and explosion safety in the process industry. The data for normal pressures P and temperatures T are rather complete, but the data for elevated P and T are rather poor. The values of upper flammability limit (UFL) of hydrogen-oxygen-diluent (He, Ne, Ar, CO) at room temperature and pressure from 0.1 to 3.0 MPa were determined in⁴. In⁵⁻⁸ the lower flammability limit (LFL) of stoichiometric hydrogen-oxygen mixture in diluents (steam, nitrogen, helium etc.) were determined at temperatures from 20 to 200°C and pressures from 0.1 to 2.0 MPa. But, more complete data for combustion characteristics of hydrogen- contained mixtures at elevated pressures and temperatures are not sufficiently presented in literature. The purpose of this

work is the investigation of combustion processes in hydrogen-oxygen-diluent mixtures (flammability limits, burning velocity) at pressures from 0.1 to 2.0 MPa and temperatures from 20 to 250°C. Theoretical interpretation of experimental results was made.

EXPERIMENTAL

Experiments for determination of flammability limits were performed in closed reaction steel vessel, which had the cylindrical form (diameter 300 and height 800 mm).⁷⁻⁸ The mixtures were created by partial pressures after vacuum-pumping of the reaction vessel and mixed by means of convective flows appearing due to slow temperature differences of reaction vessel walls. The ignition was made in the lower part of vessel by means of nichrim wire fusion due to electrical heating. The ignition energy was equal 10 J. Flame registration was made by means of thermocouples near the top of vessel and pressure transducer.

The burning velocity S_u for hydrogen-air-steam mixtures at high pressures and temperatures was measured in constant volume bomb, which had spherical form and volume of 4.2 l. The mixture obtained by partial pressures was initiated by means of nichrom wire fusion with the energy 1-2 J in the center of sphere. The pressure in the vessel during explosion was registered by means of pressure transducer "Sapphire-22" with time constant of the order of $3 \cdot 10^{-3}$ s. The burning velocity dependence from pressure and temperature was calculated according to method described elsewhere.⁹ This method is based on comparing of experimental and calculated (by means of closed vessel explosion model) dependence of pressure in the vessel during mixture explosion. This method gave a good agreement with the available experimental data for initial pressure of 0.1 MPa and room temperature.

RESULTS AND DISCUSSIONS

The experimental data for flammability limits are shown in Fig.1-3. From Fig.1-3 some conclusions can be made. Among the diluents investigated (CO_2 , H_2O , N_2 , Ar) the most efficient is the gas with the largest molar heat capacity (CO_2). But the behavior of lower flammability limits for hydrogen-oxygen-helium mixtures is unusual the dependence of hydrogen concentration at low flammability limit on diluent concentration is sufficiently nonlinear. This effect is due to the bubble character of flame propagation in very lean (from 4 to 8% (vol.)) hydrogen-oxygen respect with oxygen and other diluents investigated and high thermoconductivity coefficient for helium.

Some experimental data for lower flammability limits of hydrogen-oxygen-composite diluent (helium + steam, helium + carbon dioxide, nitrogen + carbon dioxide) are presented in Fig.4.

It is evident that additive empirical rule for flammability limits in the case of composite diluent contained helium is disturbed. This effect is caused by high thermoconductivity coefficient of helium and bubble character of combustion of very lean hydrogen-air mixtures mentioned above.

The dependence of burning velocity of hydrogen-air-steam mixture on pressure at various temperatures is shown in Fig.5. It can be seen that addition of a small quantity of steam (5% (vol.))

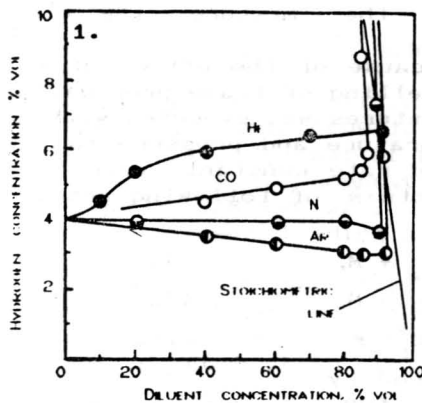


Fig. 1. Flammability limits of hydrogen-oxygen-diluent mixtures at temperature 20°C and pressure 0.1 MPa.

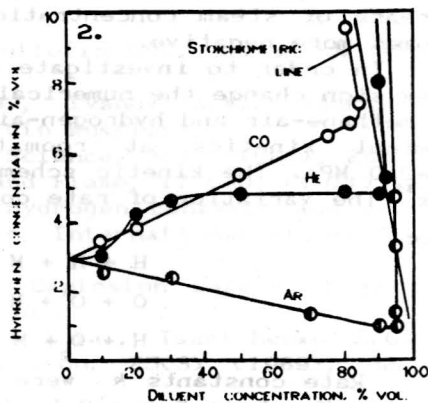


Fig. 2. Flammability limits of hydrogen-oxygen-diluent mixtures at temperature 250°C and pressure 0.1 MPa.

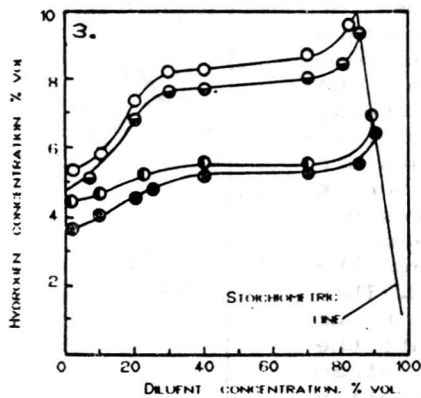


Fig. 3. Flammability limits of hydrogen-helium-diluent mixtures at temperatures T and pressures P :

- - $P_0 = 20 \text{ MPa}$, $T = 20^\circ\text{C}$; ● - $P_0 = 0.6 \text{ MPa}$, $T = 20^\circ\text{C}$;
- ⊙ - $P_0 = 2.0 \text{ MPa}$, $T = 250^\circ\text{C}$; ● - $P_0 = 0.6 \text{ MPa}$, $T = 250^\circ\text{C}$.

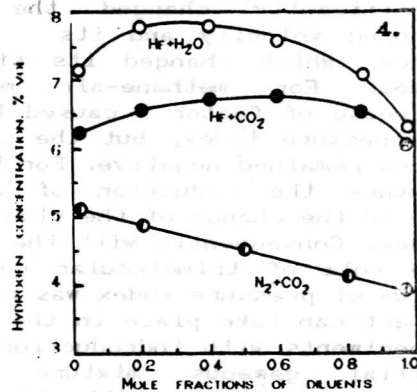


Fig. 4. Lower flammability limits as a function mole fractions the first diluent component in diluent mixtures at temperatures and pressures :

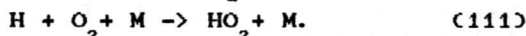
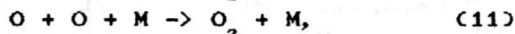
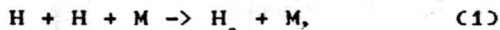
(He-H₂O) - $P_0 = 0.6 \text{ MPa}$, $T = 250^\circ\text{C}$;

(He-CO₂) - $P_0 = 0.1 \text{ MPa}$, $T = 20^\circ\text{C}$;

(N₂-CO₂) - $P_0 = 0.1 \text{ MPa}$, $T = 70^\circ\text{C}$.

causes change of sign of pressure index n in the expression for pressure dependence of burning velocity $S_u = S_{u0}(P/P_0)^n$. With the increase of steam concentration in the mixture the value of n becomes more negative.

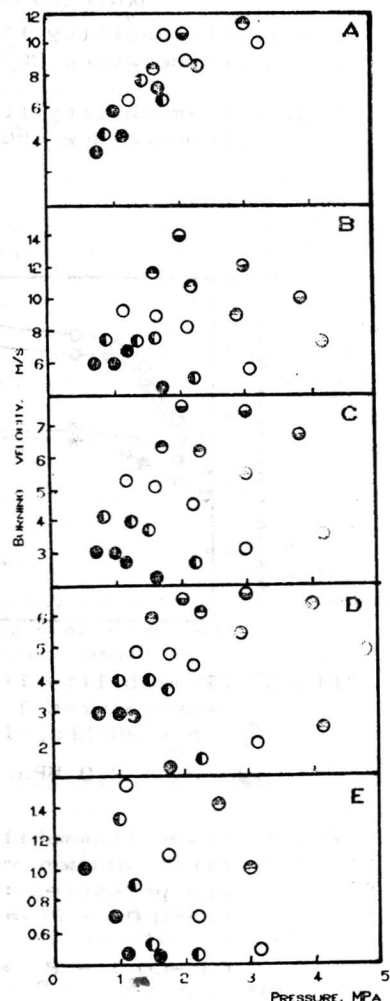
In order to investigate the cause of the effect of pressure index sign change the numerical modelling of flame propagation through the methane-air and hydrogen-air mixtures was executed with detailed chemical kinetics at room temperature and pressure in the range 0.1-2.0 MPa. The kinetic scheme and rate constants were taken from work¹¹. The variation of rate constants k of following reactions was made:



Rate constants k were reduced by a factor K , where K was 0.1, 1, 10, 100, 1000. The dependence of burning velocity and its pressure index on a factor K was investigated. It was found that the variation of k for the reaction (1) and (11) in pointed range had relatively small influence on burning velocity. In this case the sign of pressure index was not change, but the change of rate constant of reaction (111) significantly changed the value of burning velocity and its pressure index, which changed its sign in some cases. For methane-air mixture the increase of factor K caused the increase of pressure index, but the sign of this index remained negative. For hydrogen-air mixture the reduction of a factor K caused the change of the sign of pressure index. Consequently with the increase of the role of trimolecular reactions the value of pressure index was reduced. This effect can take place in the case of our experiments with introduction into the initial gaseous mixture the steam molecules, which catalysed recombination reactions¹².

Fig.5. The dependence of burning S_u from pressure P at various temperatures T and concentrations of steam C_{H_2O} :

- a) $C_{H_2O} = 0\%$ vol.; b) $C_{H_2O} = 5\%$ vol.;
 c) $C_{H_2O} = 10\%$ vol.; d) $C_{H_2O} = 20\%$ vol.;
 e) $C_{H_2O} = 30\%$ vol.
 ● - $T = 200^\circ C$; ○ - $T = 250^\circ C$; ○ - $T = 300^\circ C$;
 ⊙ - $T = 350^\circ C$; ⊙ - $T = 400^\circ C$



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