

# Hydrogen Fire and Explosion Safety Ensuring by Application of Passive Catalytic H<sub>2</sub>-Recombiners

YU.N. SHEBEKO, I.A. BOLODIAN, A.V. TRUNEV, V.YU. NAVZENYA and V.A. SHEPELIN

All Russian Scientific Research Institute for Fire Protection

Balashikha-3, Moscow Region, 143900, Russia

## ABSTRACT

Hydrogen recombination on a catalytic surface for various configurations of catalytic elements has been investigated both experimentally and theoretically. The proposed H<sub>2</sub>-recombiners were collections of rods coated by Al<sub>2</sub>O<sub>3</sub> film with catalytic platinum centers. The rod's surface was additionally coated by a porous teflon film, which prevents a contact of catalytic centers with liquid water but is penetrable for gases and steam. Operation characteristics of such H<sub>2</sub>-recombiners in various regimes have been determined. The relationship between a rate of hydrogen recombination and temperature of the catalytic surface has been revealed. It has been found, that an availability of helium in a gaseous mixture causes a sufficient reduction of a hydrogen oxidation rate on the catalytic surface due to a decrease of temperature of the catalytic surface because of a high thermoconductivity coefficient for helium. A simple mathematical model of a hydrogen recombination on the catalytic surface has been proposed which describes the main peculiarities of this process. It has been found that an allocation of catalytic rods into vertical metal tubes with internal diameter of 20 mm increases significantly an efficiency of each catalytic element by means of a formation of convective flows from the hot catalytic surface of the rod.

Keywords: hydrogen, catalytic recombination, fire and explosion safety.

## INTRODUCTION

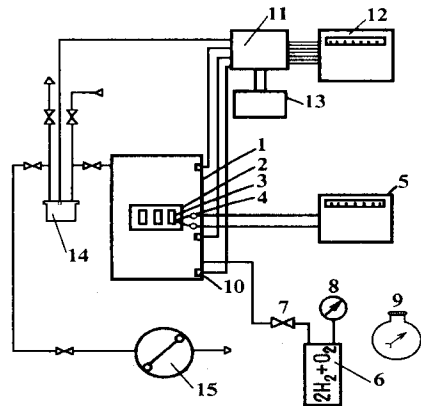
Hydrogen is often used or produced in various branches of industry. At accidents with a hydrogen leakage combustible H<sub>2</sub>-air mixtures can be formed in the equipment or industrial rooms. For prevention of formation of such combustible mixtures passive catalytic H<sub>2</sub>-recombiners can be used, in which non-flame hydrogen combustion on a catalytic surface takes place. Results of some investigations of gaseous non-flame combustion on catalytic surfaces have been published elsewhere.

Trevino (1992) [1], Bruno et al. (1983) [2], Griffin et al. (1989) [3] and Rangel et al. (1986) [4] have explored a possibility and conditions of gaseous mixtures ignition by catalytic surfaces. Sherbakova et al. (1986, 1988) [5, 6] have presented a description of an operation of a recombiner of hydrogen in mixtures with steam. The main feature of such recombiner is an availability of a porous teflon film on the catalytic surface which provides an effective recombiner operation in a moist environment. Investigations of a non-flame hydrogen combustion on the surface of such catalyzer have been described by Keller et al. (1989) [7], Trunev et al. (1992) [8] and Baronov et al. (1993) [9]. The following parameters have been determined: ignitability of catalytic surface, specific hydrogen recombination rate and their

dependence on mixture composition, temperature and pressure. Results of investigations of an operation of many-layers hydrogen recombiners have been described by Chakraborty (1986, 1988) [10, 11]. Data characterizing an influence of various components of gaseous mixtures on a recombiner operation are presented. But at the same time the investigations of an operation of collection of catalytic elements, dynamics of this process, relationship between temperature of the catalytic surface and specific hydrogen oxidation rate are not presented in literature. This work is aimed on a decision of these questions.

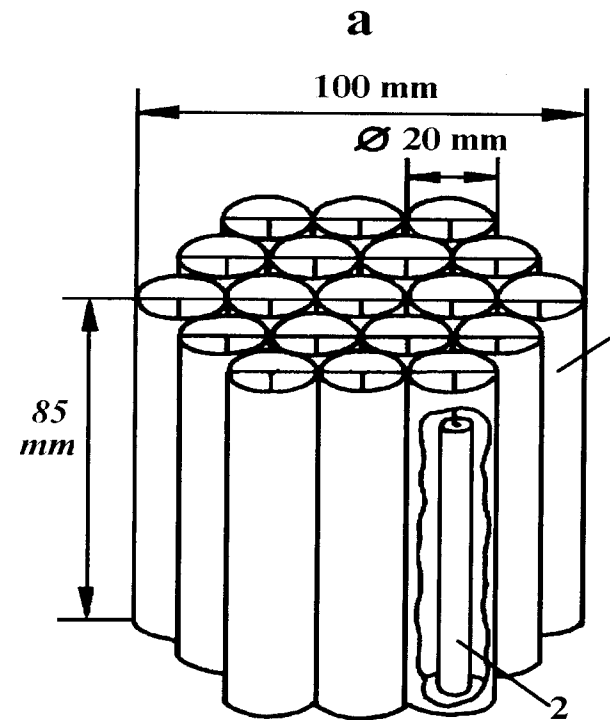
## EXPERIMENTAL

Experiments have been executed on a set-up which diagram is presented in Fig. 1. The main part of the set-up is a reaction vessel with a volume of  $50 \text{ dm}^3$ , which has a form of a closed vertical cylinder with a diameter of 300 and a height of 800 mm. A catalytic hydrogen recombiner which is a definite collection of catalytic rods was placed inside the reaction vessel in its middle part. A stoichiometric hydrogen-oxygen mixture ( $2\text{H}_2 + \text{O}_2$ ) was prepared in a special high pressure mixer by partial pressures and then was introduced into the lower part of the reaction vessel. A gas flow rate was measured by a continuous pressure registration in a mixer during the whole experiment. Three hydrogen concentration detectors were placed in the lower, middle and upper parts of the reaction vessel. Signals from these detectors were registered on a many-channel oscillograph. The reaction vessel was connected by a tube with an intermediate cavity, which had a hydrogen concentration detector. A gaseous mixture from the reaction vessel was supplied into this intermediate vessel and then was rejected into atmosphere through a flow rate detector. Because of non-flame hydrogen and oxygen recombination on the catalytic surface and condensation of steam formed due to the chemical reaction, the gas flow rate on the entry of the reaction vessel is greater than the one on its exit.



**Fig. 1.** The experimental set-up diagram.  
1 - reaction vessel; 2 - hydrogen recombiner; 3 - catalytic rod; 4 - thermocouple; 5, 12 - oscillograph; 6 - mixer; 7 - valve; 8 - manometer; 9 - timer; 10 - hydrogen concentration detector; 11 - logic apparatus; 13 - direct current source; 14 - intermediate vessel; 15 - flow rate detector.

Three catalytic recombiner structures were investigated (Fig. 2). The structure 1 represents a collection of combined metal tubes with internal diameter 20 and height 75 mm (Fig. 2a). The catalytic rods were placed along the axis of the tubes. The catalytic surface has been made from  $\text{Al}_2\text{O}_3$  with platinum centers and coated by a porous teflon film penetrable for gases and steam. A diameter and a height of the rods were 5.8 and 63 mm respectively. Each rod had an axis channel with a diameter of 1 mm. The more detail description of a catalyzer has been given by Sherbakova et al. (1986, 1988) [5, 6]. Diameters and heights of the tubes have been justified in preliminary experiments (Trunev et al., 1992 [8]; Keller et al., 1991 [12]). The total number of rods in the structure 1 was equal to 19.



**Fig. 2 a.** The diagrams of catalytic recombiner structures.  
Structure 1. 1 - cylindrical cell; 2 - catalytic rod;

The structure 2 (Fig. 2b) represents a collection of cells each in the form of equilateral triangle with a side of 21 mm, placed along a perimeter of a rectangle with sides of 70 and 140 mm. The catalytic rods were placed in centers of these cells. There were 32 rods in this structure.

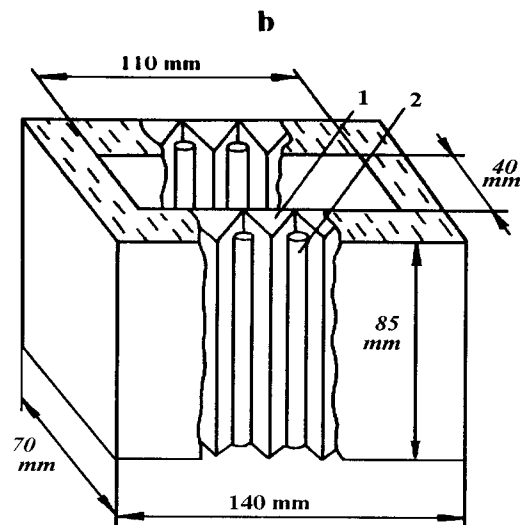


Fig. 2b. The diagrams of catalytic recombiner structures. Structure 2. 1 - triangular cell; 2 - catalytic rod.

The structure 3 was quite the same as the construction 1 except the number of rods which was equal to 7.

There was a one rod in each structure, for which temperature of the catalytic surface was measured by a thermocouple. These rods were placed in the centers of the structures 1 and 3 and near the side surface of the structure 2. Signals from the thermocouples were registered on a many-channel oscillograph.

Some experiments with the structure 3 have been executed for initial reaction vessel atmosphere which is not air but an inert gas (nitrogen, carbon dioxide, helium). In these experiments only temperature of the catalytic surface was measured.

The relative errors in determination of parameters of recombination process (hydrogen concentration, gas flow rates, temperature) did not exceed 10%.

## RESULTS

The typical experimental data obtained for the structures 1 and 2 are presented in Figs. 3, 4. Despite of the rate of the stoichiometric hydrogen-oxygen mixture at the entry of the reaction vessel is constant, the flow rate at the exit of the reaction vessel after approximately 5 min from the experiment beginning drops to a zero value. This fact is due to the total hydrogen-oxygen mixture recombination and steam condensation. Simultaneously with the drop of the exit flow rate hydrogen concentration in the reaction vessel decreases. The time dependences obtained for the structures 1 and 2 are qualitatively the same.

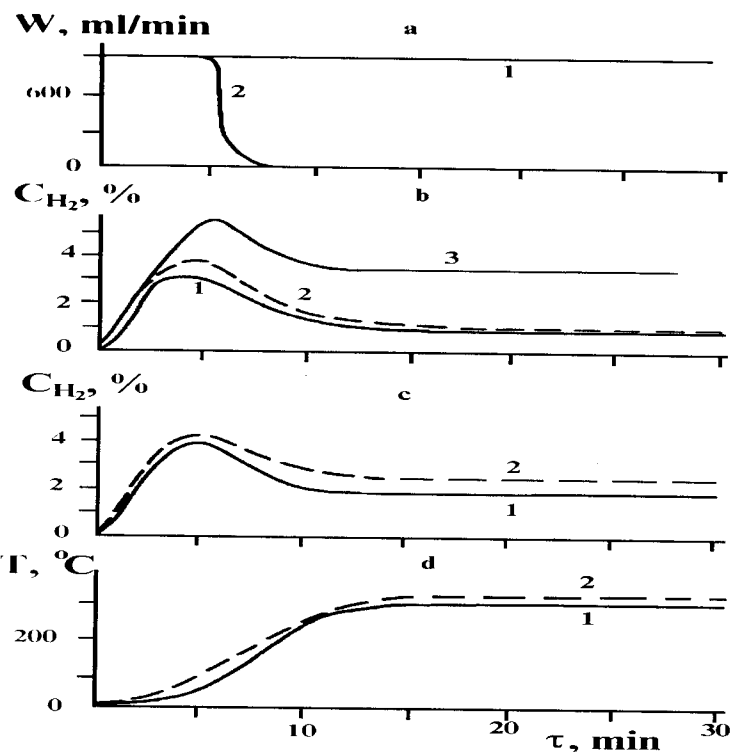


Fig. 3. The typical time dependencies of a gas flow rate  $W$  (a, 1 - at the reaction vessel entry, 2 - at the reaction vessel exit), hydrogen concentrations at various parts of the reaction vessel (b, 1 - in the upper part, 2 - in the middle, 3 - in the lower part), mean hydrogen concentration across the reaction vessel volume (c, 1 - experiment, 2 - theory) and catalytic surface temperature  $T$  (d, 1 - experiment, 2 - theory) for the structure 1.

Hydrogen concentration in the upper part of the reaction vessel (near the exit) is some lower than in the lower part of the reaction vessel (near the entry in it). But the differences in hydrogen concentrations in various parts of the reaction vessel are rather low because of a strong mixing by convective flows created by the hot catalytic surface. Practically simultaneously with the decrease of the gas flow rate at the reaction vessel exit a rapid increase of temperature of the catalytic surface takes place, which indicates on a chemical reaction.

At high gas flow rates temperature of the catalytic surface becomes high enough in order to ignite the gaseous mixture. Critical values of these flow rates were 5000 and 2000  $\text{cm}^3/\text{min}$  for the structures 1 and 2 respectively, or 260 and 62.5  $\text{cm}^3/\text{min}$  for one rod of the mentioned above structures.

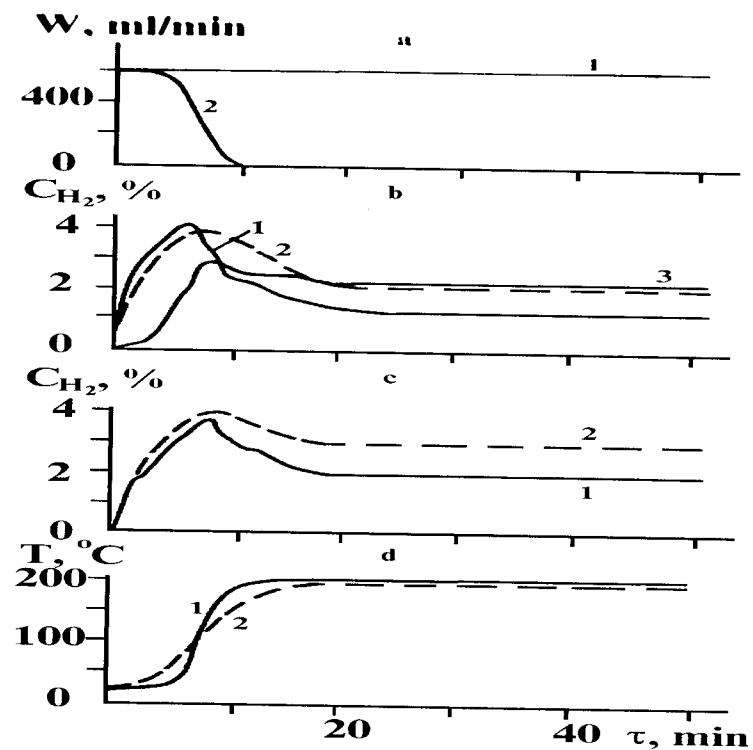


Fig. 4. The typical time dependencies of a gas flow rate  $W$  (a, 1 - at the reaction vessel entry, 2 - at the retain vessel exit), hydrogen concentrations at various parts of the reaction vessel (b, 1 - in the upper part, 2 - in the middle, 3 - in the lower part), mean hydrogen concentration across the reaction vessel volume (c, 1 - experiment, 2 - theory) and a catalytic surface temperature  $T$  (d, 1 - experiment, 2 - theory) for the structure 2.

Figure 5 shows results of measurements of temperature of the catalytic surface for the structure 3 at various initial gaseous atmospheres. Data for air, nitrogen and carbon dioxide are qualitatively close to each other. Practically simultaneously with the stopping of hydrogen-oxygen mixture flow a reduction of temperature begins. The maximum temperature value depends on both molar heat capacity of gaseous mixture (for nitrogen this value is lower, than for carbon dioxide) and oxygen concentration in the reaction vessel volume (for air the maximum temperature is higher, than for nitrogen, because an oxidation rate of hydrogen on the catalytic surface depends on oxygen concentration).

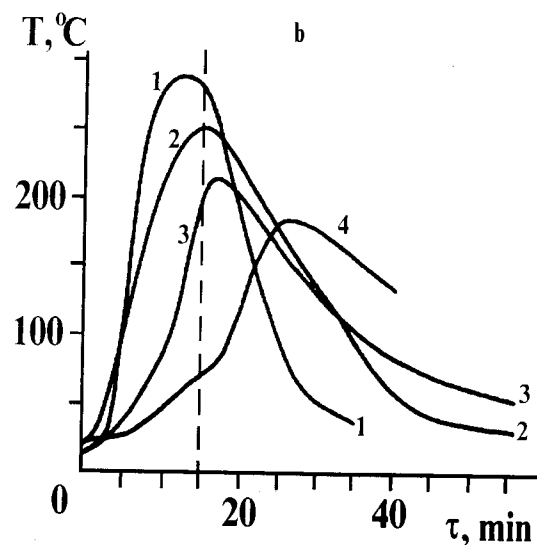
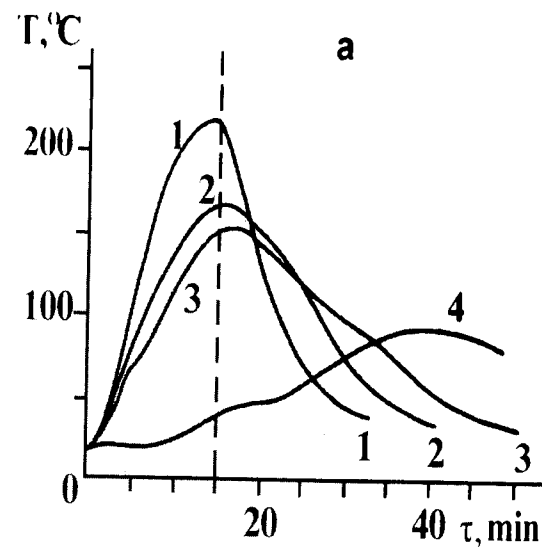


Fig. 5. The typical time dependencies of a catalytic surface temperature  $T$  at various initial gaseous mixture compositions at the hydrogen-oxygen mixture flow rates 300 (a) and 600 (b)  $cm^3/min$ . The hydrogen-oxygen mixture flow stops after 15 min.

1 - air; 2 - nitrogen; 3 - carbon dioxide; 4 - helium.

The time dependence of temperature of the catalytic surface for the helium atmosphere differs sufficiently from the analogous dependencies for air, nitrogen and carbon dioxide by a more slow temperature rise rate. A temperature increase continues after stopping of the hydrogen-oxygen mixture flow. For our opinion this effect is caused by a high thermoconductivity coefficient of helium. In this case a heating of the catalytic surface with an appropriate elevation of hydrogen oxidation rate occurs more slowly than for other gases considered. Therefore even after stopping of a hydrogen-oxygen mixture flow a rather large amount of hydrogen remains in the reaction vessel, and its oxidation after stopping of the combustible mixture flow caused the further increase of temperature of the catalytic surface. The maximum value of the temperature is however much lower than for other gases considered.

In Fig.6 the typical curves are presented which characterize the hydrogen recombiner operation in the regime of an impulse repeated flow of hydrogen-oxygen mixture. After the stopping of the hydrogen-oxygen mixture flow hydrogen concentration drops rapidly to a value of 0,3% (vol.). At the second and following impulses of combustible mixture flow the qualitative picture of the process repeats. But because temperature of the catalytic surface at the second and following impulses beginning is greater than for the first one (because the rods have not sufficient time for cooling), the maximum hydrogen concentrations are lower than for the first impulse.

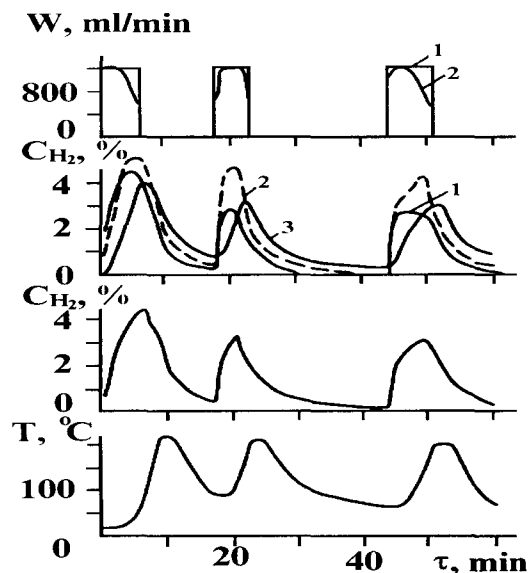


Fig. 6. The typical time dependencies of a gas flow rate  $W$  (a, 1 - at the reaction vessel entry, 2 - at the reaction vessel exit), hydrogen concentrations at various parts of the reaction vessel (b, 1 - in the upper part, 2 - in the middle, 3 - in the lower part), mean hydrogen concentration across the reaction vessel volume (c) and a catalytic surface temperature  $T$  (d) for the impulse flow of a hydrogen-oxygen mixture in the case of the structure 1.

## DISCUSSION

Figs. 3 and 4 shows that hydrogen concentration variations with time are nonmonotone. This fact and time dependence of temperature of the surface demonstrate a sufficient temperature dependence of the hydrogen recombination rate. Taking this fact into account we have proposed a simple mathematical model of non-flame hydrogen combustion on the catalytic surface. This model is based on the following propositions:

- hydrogen concentration in a reaction vessel volume is uniform, that is a rapid gas mixing takes place;
- recombiner structure is considered as a "black box" with the known dependence of a hydrogen oxidation rate on temperature and hydrogen concentration;
- hydrogen recombination rate, according to data Keller et al. (1989) [7] and Trunev et al (1992) [8], is proportional to  $H_2$  concentration;
- dependence of a hydrogen recombination rate on temperature of the catalytic surface is described by Arrhenius formula;
- gaseous temperature is constant during the whole process.

Equations which describe dependences of hydrogen concentration and temperature of the catalytic surface on time are the following:

$$\frac{dC_H}{d\tau} = \frac{100}{V}(W_0 - G_0 C_H), \quad (1)$$

$$\frac{dT}{d\tau} = \frac{1}{C_{eff}} [G_0 G_H Q - \alpha(T - T_a)], \quad (2)$$

where  $C_H$  is hydrogen concentration in the reaction vessel, % (vol.);  $\tau$  is time, s;  $V$  is volume of the reaction vessel,  $m^3$ ;  $W_0$  is hydrogen flow rate at the reaction vessel entrance,  $m^3/s$ ;  $G_0$  is specific hydrogen recombination rate,  $m^2/(s \cdot \% \text{vol.})$ ;  $T$  is temperature of the catalytic surface, K;  $C_{eff}$  is effective thermocapacity coefficient, J/K;  $Q$  is hydrogen volumetric heat of combustion, J/ $m^3$ ;  $\alpha$  is effective heat exchange coefficient, J/K;  $T_a$  - gaseous temperature, K.

The  $G_0$  value is described by the formula:

$$G_0 = G_{m0} \exp(-E/RT), \quad (3)$$

where  $G_{m0}$  is constant;  $E$  is an effective activation energy for hydrogen recombination on the catalytic surface;  $R$  is the universal gas constant.

The  $G_{m0}$ ,  $E$ ,  $C_{eff}$  and  $\alpha$  values were determined on the basis of experimental data obtained in this work. It has been found, that the  $E$  value is independent on a recombiner construction and is equal to 4.2 kJ/mole. The  $G_{m0}$ ,  $C_{eff}$ ,  $\alpha$  parameters depend on a recombiner construction.

The typical calculated results for the  $C_H$  and  $T$  are presented in Figs.3 and 4. A relatively satisfactory agreement is observed between experimental and theoretical data, that is the proposed simple model describes the main features of the process investigated.

In Fig.7 an comparison of dependences of stationary mean hydrogen concentrations in the reaction vessel  $C_s$  on a specific hydrogen-oxygen mixture flow rate on a one rod  $W_s$  for the structures 1 and 2 is made. Though the structure 1 contains sufficiently less catalytic rods than the structure 2 (19 instead of 32), it is more effective from both the viewpoint of the lowest stationary hydrogen concentration

and the viewpoint of an operation possibility at more high flow rates of combustible mixtures without the gas ignition. This effect is accounted by a more effective supply of a hydrogen contained gaseous mixture to the catalytic surface because of formation of the convective flows from the heated catalytic surface through metal tubes. Earlier it has been shown by Trunev et al. (1992) [8] and Keller et al. (1991) [12], that such tubes significantly increase hydrogen recombination rate on the catalytic surface. At the same time the characteristic size and form of cells in the case of the structure 2 are not sufficient to obtain the optimum hydrogen flow rate to the catalytic surface.

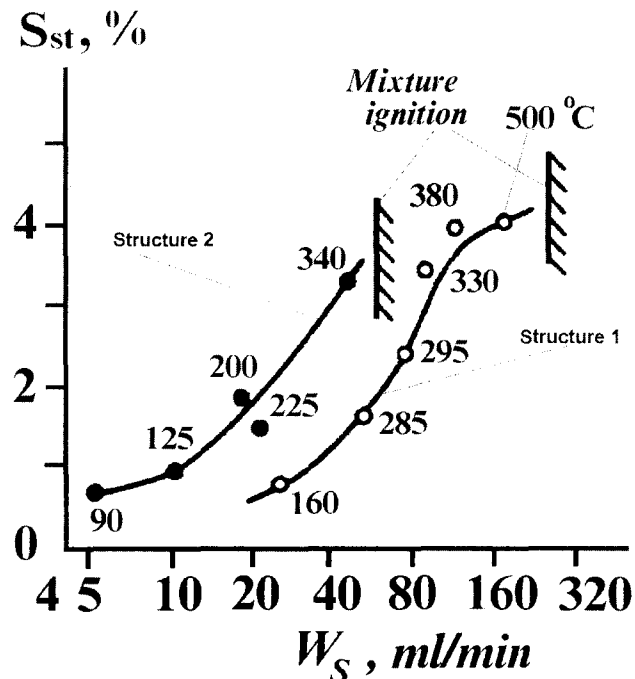


Fig. 7. The dependence of stationary hydrogen concentration on specific gas flow rate for one rod for structures 1 (o) and 2 (•). In parenthesis the stationary values of rod temperatures are indicated.

## CONCLUSIONS

On the basis of the carried out investigations the following conclusions can be made.

1. A process of a non-flame hydrogen combustion on the catalytic surface for various recombiner structures has been investigated both experimentally and theoretically.

2. The quantitative relationship between a hydrogen catalytic recombination rate and temperature of the surface has been revealed.

3. It has been shown, that the availability of helium in a gaseous environment causes a sufficient reduction of the hydrogen recombination rate on the catalytic surface because of a high thermoconductivity of helium.

4. A simple mathematical model of the non-flame hydrogen combustion on the catalytic surface has been proposed, which describes the main characteristics of this process.

5. It has been found, that a placement of catalytic rods into metal tubes with an internal diameter of 20 mm increases sufficiently the effectiveness of each catalytic element by means of formation of convective flows from the catalytic surface.

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