# PURE HYDROGEN GENERATOR FOR PLASMA DEVICES


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Laboratory model of the pure hydrogen generator was created and studied (hydrogen generation capacity about 1 $Ncm^3$ ($H_2$)/s (3.6 l ($H_2$)/hour). Hydrogen is produced from the flame of combustion of hydrocarbons (ethyl alcohol, gas, benzene) with help of Pd membrane. The temperature dependence of hydrogen flow through membrane was measured. High level of generated hydrogen purity (better than 99.999 % vol.) has been confirmed by mass-spectrometric investigations. The physical-chemical mechanisms are discussed to explain pure hydrogen generation from the flame of combustion and its inlet to high-vacuum systems.



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## INTRODUCTION

High purity hydrogen is required for scientific investigations in many plasma devices. Also it is used in chemical, electronic and others industries. Most of present technologies for making of high pure hydrogen consists, per se, from two main technological processes: making of technical hydrogen with low purity and its cleaning up to high level of purity [1]. The essential power input is required for both processes. Then produced pure hydrogen is compressed in balloons and it is not excluded that hydrogen from balloon has the same purity as produced hydrogen. Besides in some cases the use of hydrogen balloons may not be preferred, e.g., for safety reasons. The scheme combining the processes of hydrogen generation and admission was suggested in the work [2] where pure hydrogen was generated by means of thermal decomposition of alcohol vapor on the palladium membrane surface. But in the last case Pd catalyst deterioration is possible due to carbon release on its surface during work process. It leads to hydrogen production decrease and the procedure of so-called "activation" of palladium is required [3, 4]. Recently the new technology was developed for pure hydrogen production (purity is 99.999 % vol. and higher), when pure hydrogen is generated in only one technological process - generation of hydrogen as coproduct during hydrocarbons utilization, e.g. during combustion of hydrocarbon materials (such as natural gas, benzene, gasoline, alcohol, etc.) [5]. In this paper the laboratory model of pure hydrogen generator, working on above mentioned principle, is tested and investigated.

## 1. EXPERIMENTAL AND RESULTS

The scheme of the experiment is presented in Fig. 1. The principle of hydrogen generator operation is clear from Fig. 2. Hydrogen generator includes source of the flame of hydrocarbons combustion (1) and diffusion-catalytic membrane (2). The diffusion-catalytic membrane was a palladium (Pd-99.98 grade) pipe, 6 mm in diameter, 19 cm in length and 0.25 mm in thickness, which was hermetically brazed at one end and the another one was connected through leak valve (3) to high vacuum system (4) for hydrogen flow measurements and mass-spectrometric investigations of hydrogen purity. During the generator work at first, the inner volume of the membrane was pumped by the special pump to pressure about $10^{-4}$ Torr. Then membrane was placed in the flame (gas-stove as flame source was usually used) and it was heated up to 300…700ºC temperature (in dependence on a zone in a flame or on the flame intensity). Membrane temperature was controlled by a chromel-copel thermocouple located on the membrane surface. Flames of combustion of such hydrocarbons as ethyl alcohol and benzene were used in these experiments, too. Hydrogen from the flame and formed on the catalytic active surface of Pd membrane diffuses through it according to Fick's law and is inputted into high vacuum system.

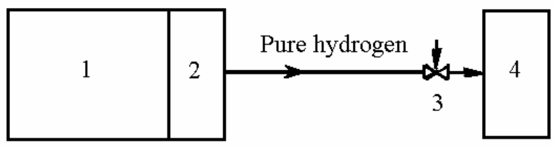


*Fig. 1. The experiment scheme for pure hydrogen generator investigations: 1 – source of the flame of hydrocarbons combustion; 2 – Pd/Ni membrane; 3 – leak valve; 4 – high vacuum system*

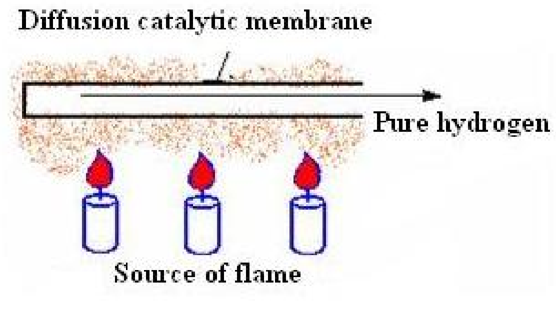


*Fig. 2. Principle of work of pure hydrogen generator*

The measurement of hydrogen flow through membrane and calculation of a specific hydrogen flow was carried out by the constant pressure method, similar to that as described in the work [6]. With membrane temperature increase the hydrogen pressure $p$ in the vacuum chamber also increases. When the pressure value is steadied on the stationary (highest possible) level, it was measured. Considering this pressure and pumping speed of hydrogen $S$, it is possible to calculate specific hydrogen flow $q$ through membrane due to equation $q=(p-p_0)\cdot S/F$ [7], where $F$ is the effective area of the membrane surface, $p_0$ is the initial pressure in the vacuum chamber and $S$ is the pumping speed (1 l/s). At the membrane temperature of 700ºC specific hydrogen flow $q$ from the flame through membrane is about 0.07 $Ncm^3/s \cdot cm^2$. The total hydrogen flow $Q$ was about 1 N $cm^3$ ($H_2$) /s (0,036 g. $H_2$/h). For all kinds of hydrocarbons hydrogen flow through membrane was practically the same (Fig. 3). Besides, as carbon combines with oxygen during the combustion process forming $CO_2$, it is not deposited on the membrane surface and, as the result, the degradation of membrane permeation properties was not observed in contrast to method described in [2]. A purity of hydrogen was estimated with help of mass-spectrometer MX-7304 and was better than 99.999 vol.%. Note, that when nickel membranes were used instead of palladium, hydrogen flows decreased more than in one order of magnitude and for stainless steel membrane hydrogen flow in high vacuum system was not observed.

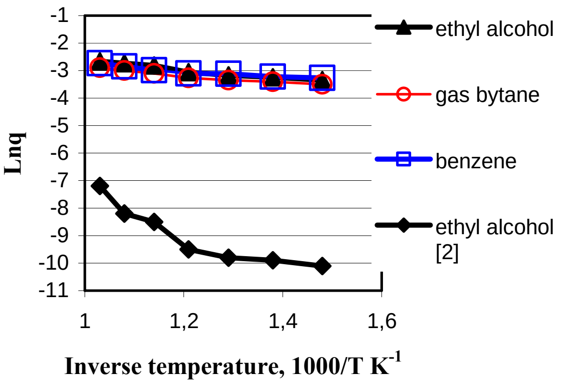


*Fig. 3. Temperature dependences of hydrogen generation for various hydrocarbons*

## 2. DISCUSSION

The possibility of essential hydrogen flow generation and permeation from the flame of combustion of hydrocarbons is not so evident fact. Really, hydrogen in a flame can be consumed, to combine with carbon, etc. During the combustion of hydrocarbons materials, e.g. spirits, natural gases, benzene etc. the chemical oxidation reaction of carbon by oxygen takes place. For example, in the case of ethyl alcohol it is :

$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O + 1386,87$ *kJ/mole.*

Physical-chemical processes in the flame of combustion are not sufficiently studied and for their clarification the additional investigations are needed. But it is known [8], that behind of reaction products $CO_2$ and $H_2O$, also $H_2$, H, CO, hydroxyls etc. are presented in the flame. So the ways of hydrogen admission to the membrane surface could be various: thermal hydrocarbons decomposition on the membrane surface (similar to mechanisms described in [2]), molecular and atomic hydrogen, water molecules decomposition on the heated, catalytic active surface of membrane, etc. The process of hydrogen permeation through Pd membrane is studied very good. It includes such main stages: hydrogen molecules adsorption and dissociation, hydrogen atoms solution in metal, penetration through membrane, hydrogen atoms recombination and hydrogen molecules desorption. The minimum activation energy of hydrogen permeation through so-called "activated" Pd with clean surface is about 15.5 kJ/mole [3]. The activation energy of alcohol vapor dehydration process on the Pd membrane surface is essentially lower (about 6.2 kJ/mole [2]). The slopes of the experimental curves of temperature dependences for hydrogen generation from the flames of combustion of alcohol, gas and benzene indicates the similar low values of activation energy (≈6.5 kJ/mole). So, the processes on the Pd membrane surface could be the limiting stages of hydrogen permeability. But to more clarify the situation with the limiting stage the additional experiments are needed.

It could be noted that only small part of the heat which escapes from the flame is used for membrane heating. Really, the estimation shows that only 4 kJ are needed to heat Pd membrane of 12 g weight to the temperature of 700ºC. The main heat from the flame one could use in another technological process, e.g., heating of water. In this case the consumption of fuel on hydrogen production will be only small part in comparison with fuel consumption for the main function (water heating). It will provide low prime cost of generated pure hydrogen.

Note, that the hydrogen capacity of described generator (1 $Nсм^3$ ($H_2$) /s ) is enough to provide pure hydrogen for such large plasma device as torsatron Uragan-2M in both work and discharge cleaning regimes. Really, if to put U-2M pumping speed even about 1000 l/s, according to equation $p=Q/S$ we will obtain the work pressure in U-2M vacuum chamber of $7.6 \cdot 10^{-4}$ Torr.

In conclusion briefly review the possible scheme of pure hydrogen generator with capacity about 16 $Ncm^3$ ($H_2$)/s (or about 80 standard 40 l volume balloons per year, Figs. 4, 5). The diffusion-catalytic membrane (2) of this generator is made of 16 Pd pipes with the dimensions of each similar to the one used in laboratory model. All pipes is hermetically brazed at one end and the others is connected to collector which is connected, in turn, to high vacuum system (4) for hydrogen flow and pressure measurements and with hydrogen accumulator (5). The membrane is placed in flame of gas-jet (1) in such a way to get the maximum hydrogen flow through it. To provide this the possibilities exist to change the flame intensity and membrane position. The thermal irradiation from heated the flame, which partially flows through gaps between the pipes, are used for water heating in the heat exchanger (3). At the membrane temperature of 700°C the pure hydrogen flow from the flame to vacuum system will be 16 $cm^3$/s or 13.8 g $H_2$ per day or, 5 kg/year. This hydrogen capacity can provide the production of about 80 standard balloons per year.

The main advantages of proposed scheme is the fact that it includes only one technological process: generation of super pure hydrogen, which is carried out at the same time with hydrocarbon materials utilization (during water heating). As the result, the power inputs are saved on the maintenance of necessary parameters of the hydrogen generation process. It will provide low prime cost of generated hydrogen.

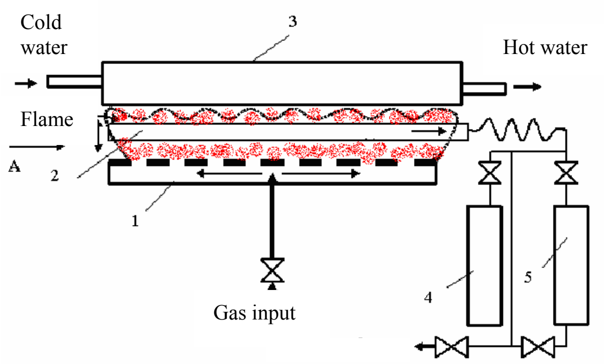


*Fig. 4. Scheme of pure hydrogen generator with ≈16 Ncm$^3$ ($H_2$)/s hydrogen capacity*

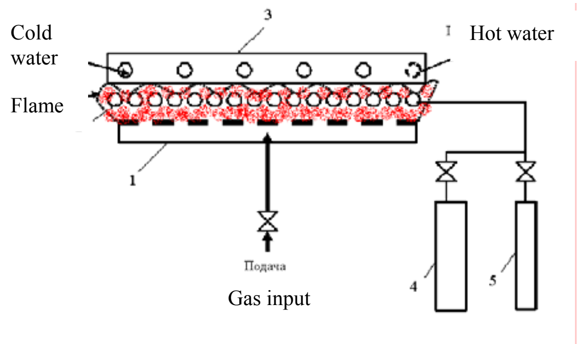


*Fig. 5. Left-side view of the generator*

## CONCLUSIONS

The model of laboratory pure hydrogen generator was created and examined (hydrogen capacity about 1 Ncm$^3$ ($H_2$)/s). The possible scheme of pure hydrogen generator with pure hydrogen capacity of about 16 Ncm$^3$ ($H_2$)/s is suggested and discussed. In contrast to the most pure hydrogen generators in this case hydrogen is produced in one technological process from the flame of combustion of hydrocarbons (ethyl alcohol, gas, benzene) with help of Pd membrane. The temperature dependence of hydrogen flow through membrane was measured and activation energy of the generation process was calculated as ≈6.5 kJ/mole. It was shown that the most probable limiting stage of hydrogen generation is the processes on the Pd membrane surface. High level of generated hydrogen purity (better than 99.999 % vol.) has been confirmed by mass-spectrometric investigations.

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## ГЕНЕРАТОР ЧИСТОГО ВОДОРОДА ДЛЯ ПЛАЗМЕННЫХ УСТАНОВОК

***Г.П. Глазунов***

Создана и исследована лабораторная модель генератора чистого водорода с производительностью около 1 Ncм$^3$ ($H_2$)/с (3.6 л ($H_2$)/ч). Водород генерировался из пламени горения углеводородов (газ, спирт, бензин) при помощи мембраны из Pd. Измерена температурная зависимость потока водорода через мембрану. Высокий уровень чистоты генерируемого водорода (лучше, чем 99.999 об. %) подтвержден масс-спектрометрическими исследованиями. Обсуждаются физико-химические механизмы, объясняющие процессы генерации водорода из пламени и его напуск в высоковакуумные системы.

## ГЕНЕРАТОР ЧИСТОГО ВОДНЮ ДЛЯ ПЛАЗМОВИХ УСТАНОВОК

***Г.П. Глазунов***

Створена і досліджена лабораторна модель генератора чистого водню з продуктивністю близько 1 Ncм$^3$ ($H_2$) /с (3.6 л ($H_2$) /год). Водень генерувався з полум'я горіння вуглеводнів (газ, спирт, бензин) за допомогою мембрани з Pd. Виміряна температурна залежність потоку водню через мембрану. Високий рівень чистоти водню (краще, ніж 99.999 об. %), що генерується, підтверджений мас-спектрометричними дослідженнями. Обговорюються фізико-хімічні механізми, що пояснюють процеси генерації водню з полум'я і його напуск у високовакуумні системи.