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The Prospect of Producing Hydrogen by Electrolysis of Idle Discharges of Water from Reservoirs and Recycling of Waste-Gas Condensates

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Abstract**—**The results of the studies for the hydrogen production by the application of water electrolysis and plasma-chemical processing of gas condensate-waste of natural gas production methods are presented. Thin coating covers the electrode surfaces in the process of water electrolysis. Therefore, water for electrolysis was first exposed to electrosedimentation. The threshold voltage is shifted to a lower value compared with the use of electrodes made of stainless steel. At electrolysis of electrosedimented water by use of electrodes from stainless steel, a significant amount of hydrogen is formed. Pyrolysis of gas condensates in the atmosphere of a nitrogen was followed by the formation of acetylene (3-7 vol.%), ethylene (4-8 vol.%), and pyrolysis carbon (10-15 wt.%).

Keywords**—**Electrolyze, gas condensate, hydrogen, pyrolysis.

I. Introduction

ALTHOUGH hydropower in total energy resources of the Central Asia is 96%, but its share is less than 2%. According to the Program of the United Nations for economy of the Central Asia, the renewed hydropotential in the Central Asia is 460 bln. kWt·h per year, and only 10% is used now. The basic volume of hydropotential is concentrated in Tajikistan (69%) and Kyrgyzstan (22%) [1].

In the formation of water-energy resources of Central Asian region, the Republic of Tajikistan which occupies the leading place is characterized by more than 25 000 rivers with a total length of about 90,000 km and 8500 glaciers that correspond to 6% of the country [2], [3].

The total hydropower potential of the Republic of Tajikistan is 527 bln. kWt·h from which more 40% are technically possible for production of the electricity. Water resources focus on the large rivers – Vakhsh, Pyanj, Obikhingou and the others. The specific saturation of potential water resources makes up a significant size – 3682.7 kWt·h on 1.0 km^2 territories (the first place in the world) and per capita 87800 kWt·h per year [4].

Nowadays, one of the actual problems of the modernity is the global climate change characterized by a series of abnormal climate and emergencies. The concentration of greenhouse gases in atmosphere is considered as a key factor of the global climate change [5]-[8].

The main pollutants of the atmosphere of the Central Asia are the heavy particles (35%) and SO_2 (31%), CO_2 (14%), and nitrogen oxides (10%) [9]. Problem of environmental protection and reduction of dynamics of global warming stimulates research for alternative and clean energy. In this plan, hydrogen power can be considered as a potential applicant to fill the energy sector with cheaper and clean fuel.

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II. Production of Hydrogen by Electrolysis of Water

Electrolysis of water is one of the known methods for the production of pure hydrogen (99.6–99.9% H_2) in one technological stage. The efficiency of the process of hydrogen production by electrolysis is primarily determined by the cost of electricity (85%).

Electrolysis can successfully be realized directly at the hydropower, thermal, and nuclear power plants when excess capacity can be used for the production and storage of hydrogen. The electrolysis of water on a large plant with capacity of 450 tons per day and its power consumption for 1 m^3 hydrogen can be finished by capacity of up to 4 – 4.5 kWt·h. At such expense, electricity that is necessary for the electrolysis of water can become a competitive method for hydrogen production even under modern conditions. Electricity consumption for the production of 1 m^3 H_2 and 0.5 m^3 O_2 under normal conditions and the theoretical equilibrium voltage of water decomposition (1.23 V) will be:

$$W_T = 1.23(2 \cdot 26.8 : 0.0224) = 2.95 \text{ kWt·h} \quad (1)$$

where 26.8 is the Faraday's number (A·h) on mole, 2 is the number of capacitance (in Faraday) spent for allocation 1 mole H_2, 0.0224 is the volume of 1 mol hydrogen at normal conditions.

At thermo-neutral voltage of 1.48 V, for the production of 1 m^3 H_2, about 3.54 kWt·h electropower is consumed. The real expense of the electric power on modern electrolysis makes up to 5.5 kWt·h on 1.0 m^3 H_2. At normal conditions, for the production of 1.0 m^3 H_2 and 0.5 O_2, it is necessary to possess 805 gallons of water.

The Republic of Tajikistan is a mountainous country (93% of the territory is mountains). While all regions are connected to a single power supply system, transmission equipment is often destroyed transmission equipment due to the extreme climatic events in the mountains. Every year in the summer months, idle water which is equivalent to 6 billion. kWt·h of electricity discharges from reservoirs.

According to the preliminary calculations, the transportation of hydrogen is almost four times cheaper than that of electricity. It gives the basis and prerequisite for the

development of hydrogen power engineering in the Republic of Tajikistan [1].

For us, the hydrogen electrolyser concept that is shown in Fig. 1 was used. Electrolysis of water was held at a voltage stamps from 2.4 to 4.4 V.

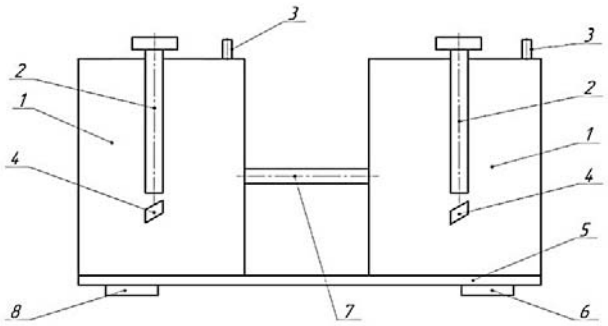

Fig. 1 Schematic diagram of electrolysis cell (1-cell, 2-electrode holder, 3–pipe, 4-electrodes, 5-cell basis, 6-feet, 7-connecting tube)

The stainless steel and copper electrodes at electrolysis were used. The current-voltage characteristic of the cell by stainless steel and copper differed significantly. For electrolysis, river water was used before and after the purification process. It should be noted that the deposition of complex composition conglomerates on the electrodes at electrolysis of water without purification.

Monitoring the formation of hydrogen qualitatively is determined by the formation of bubbles on the electrode surface and is quantified by using manometer connected to the cell (Fig. 1). It is known that formation of bubbles on a surface of electrodes influences the electrostatic field and reduces intensity of the field between plates and current in a chain. Eliminating this effect is achieved by vibration of the electrodes using an external oscillating device. For the removal of bubbles from a surface of electrodes, mechanical vibration was used. Fig. 2 shows the current-voltage characteristic of cell with electrodes by stainless steel at the electrolysis of river water and after the electrosedimentation.

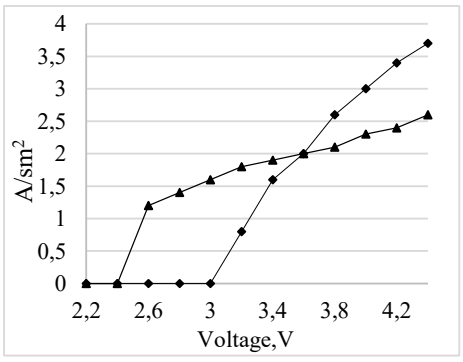

Fig. 2 Volt-Ampere characteristic of the electrolyze cell by electrodes from stainless steel at electrolysis of river water (▲) and after its electrosedimentation (■)

Existence of ions and cations of chemical elements in water generated electrolysis at lower of voltage (Fig. 2).

For the purpose of establishment of deposits of components of water to shift the values of voltage at electrolysis, complex physical and chemical analyses were carried (Fig. 3). The composite chemical composition of river water explains the observed process of accumulation of conglomerates on a surface of electrodes and specifies about the need of their preliminary cleaning for electrolysis implementation.

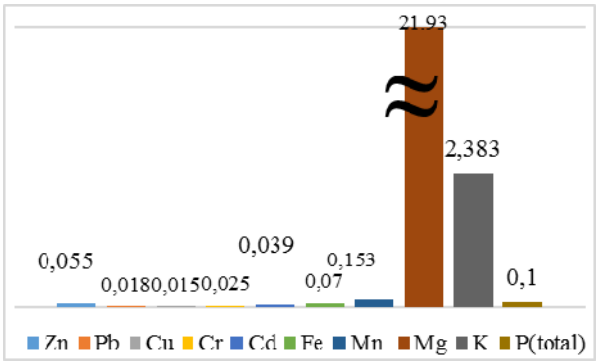

Fig. 3 (a) Cation content of the Vakhsh river water

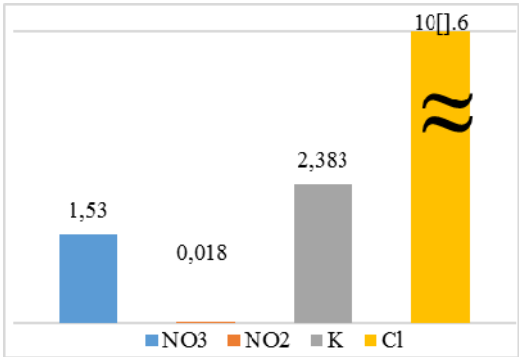

Fig. 3 (b) Anion content of the Vakhsh river water

III. Plasmochemical Treatment of Gas Condensate

The present work is devoted to research of the gas condensate treatment in low temperature plasma for production of no-limiting hydrocarbons. The gas condensate exists in the nature as in the form of liquid fraction taken of natural gas (2-6% weight at rate of 1.0 t gas production) and in independent deposits. Gas condensate depending on the content of the light and heavy fractions is characterized by a boiling point of 60-350 °C. In our investigation, natural gas condensate deposits of "Kanibadam" of Republic Tajikistan have been used with molecular weight of 140 ($C_{10}H_{20}$) and average value of temperature of boiling about 55 °C.

Plasmochemical pyrolysis of the gas condensate is spent on plasmochemical equipment. The plasma generator “EDP 104” works on a direct current and provides a necessary regime of heating of a plasma stream as in nitric and air environments. The mode of combustion of a plasma arch in near electrode space was provided by means of turbulence stabilization of an arch. In turn, the turbulent stream of gas was created by means

of the chamber in coupling sleeve through a ring having four apertures, tangentially directed to an axis. For this reason, the cylindrical flowing and cooled reactors with internal diameters of 8-10 mm, length from 20 to 120 mm, with a radial supply of raw materials to the heat-vehicle have been used.

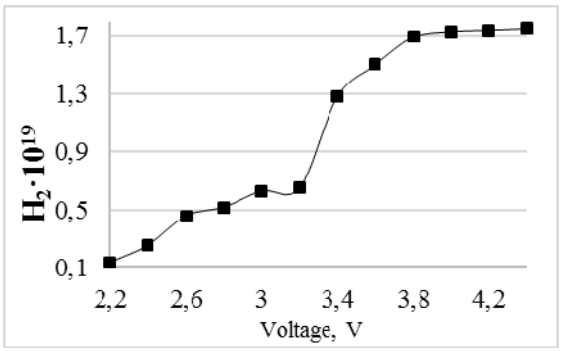

Fig. 4 Amounts of hydrogen at electrolysis of water by use of stainless steel electrodes

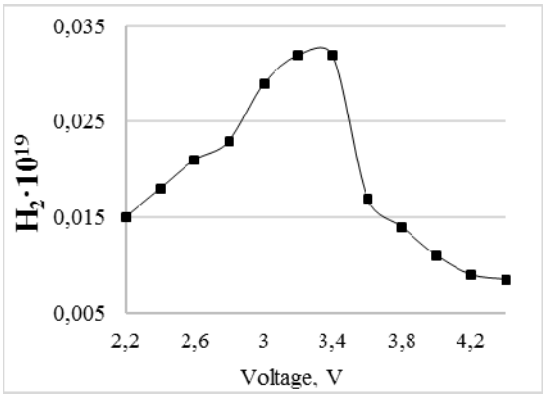

Fig. 5 Amounts of hydrogen at electrolysis of water by use of coper electrodes

IV. Result and Discussion

The composition and the amount of the products of the gas condensate plasmochemical pyrolysis were held on the chromatograph "Gazohrom". The determination of the ethane, ethylene, acetylene, propylene and homology impurity concentrations was held on the chromatograph UX-2 by use of INZ-600 sorbent. The analysis of cyanic hydrogen was carried out on chromatograph PAXV-07 by use of Zeolite – 545 sorbents. The reaction products which are cooled in a heat exchanger are accompanied by deposition of soot on the walls of pipes. As a result, it increases the pressure and violation of steady work of plasmochemical installation [10]. The results of plasmochemical processing of gas condensates in the nitrogen plasma are presented on the Table I. The reaction products cooled by the initial gas condensate vapors were used to prevent of the soot deposition (Table II).

From Table II, it is seen that forced cooling of the reaction products with use of initial raw materials leads to increase of content of unsaturated hydrocarbons. It was revealed that the system works permanently, and the process submits to management on exits of products.

TABLE I
Results of the Plasmochemical Treatment of Gas Condensate in Nitric Plasma

Parameters	Experiments				
	1	2	3	4	5
P, kWt	7.6	8.0	9.2	8.8	9.8
G $\cdot 10^{-3}$,m^3/sec	6.7	6.7	6.7	7.0	7.0
M$\cdot 10^{-1}$, g/sec	6.67	5.67	5.00	5.03	7.67
T, K	1800	2000	2200	2100	2100
Gas products, % vol.					
Nitrogen	50.0	46.7	47.0	46.7	45.0
Hydrogen	26.0	25.0	23.0	26.6	26.1
Methane	1.39	0.80	0.40	0.10	0.20
Ethane	-	-	0.20	0.20	0.40
Ethylene	9.20	9.60	5.00	4.60	6.80
Acetylene	10.70	13.00	14.40	12.00	13.60
Propylene	1.91	1.40	1.10	0.20	0.40
Cyanic hydrogen	3.40	4.40	8.00	9.20	6.90
Total conversion of raw materials to gas form products, %	92.8	94.4	88.9	89.6	94.2

Note: P–useful power, G–expense of plasma forming gas, M–expense of gas condensate, T-temperature of reaction.

TABLE II
Results of the Plasmochemical Treatment of Gas Condensate in Nitric Plasma and Training of Products by Stream of Initial Gas Condensate

Parameters	Experiments				
	1	2	3	4	5
P, кВт	6.9	7.2	8.4	9.2	9.8
G $\cdot 10^{-3}$, m^3/sec	7.0	7.0	7.0	6.7	6.7
M$\cdot 10^{-1}$, g/ sec	5.83	6.67	5.00	5.00	5.30
m$\cdot 10^{-1}$, g/ sec	2.50	1.70	1.70	2.00	2.00
T, K	1900	2000	2200	2200	2300
Gas products, % vol.					
Nitrogen	50.0	49.0	44.0	47.0	48.0
Hydrogen	14.4	15.2	20.7	20.5	18.1
Methane	4.3	4.1	2.8	2.1	2.0
Ethane	0.4	0.5	0.4	0.3	0.2
Ethylene	12.2	13.2	10.0	9.8	10.6
Acetylene	9.1	8.1	12.2	12.6	11.9
Propylene	2.8	3.2	2.8	2.0	2.1
Cyanic hydrogen	3.0	3.5	4.2	3.6	4.8
Total conversion of raw materials to gas form products, %	78.0	71.0	86.0	82.0	89.0

Note: P–useful power, G–expense of plasma forming gas, M–expense of gas condensate, m-expense of raw materials on training, T-temperature of reaction.

At change of the energy density of the plasma flow from 1.8 to 10.8 MJ/m^3 and φ = 0.5 (N_2/initial gas condensate) output of hydrogen cyanide is accompanied with hydrocarbons C_2H_2 (12% vol.) and C_2H_4 (10 vol. %). Thus, its maximum value is reached at specific energy of plasma 7.2 MJ/m^3. The hydrogen content, the amount of other homologous impurities, and pyrolytic carbon in the pyrolysis products were 20-22% vol., 1.5-2.5% vol., and 25-30% by weight, respectively. The increase φ up to units at the same specific energy of the plasma leads to increase output of HCN to 9% vol. and to reduce of the concentration of unsaturated hydrocarbons C_2H_4

and C_2H_4 to 8% vol. and 10% vol., respectively. The increase of the HCN concentration to 10-12% and the decrease of unsaturated hydrocarbons at using uncooled reactors were observed. On Fig. 6, results of the present study on influence of the plasma stream specific energy on the target products exit of the gas condensate pyrolysis are presented.

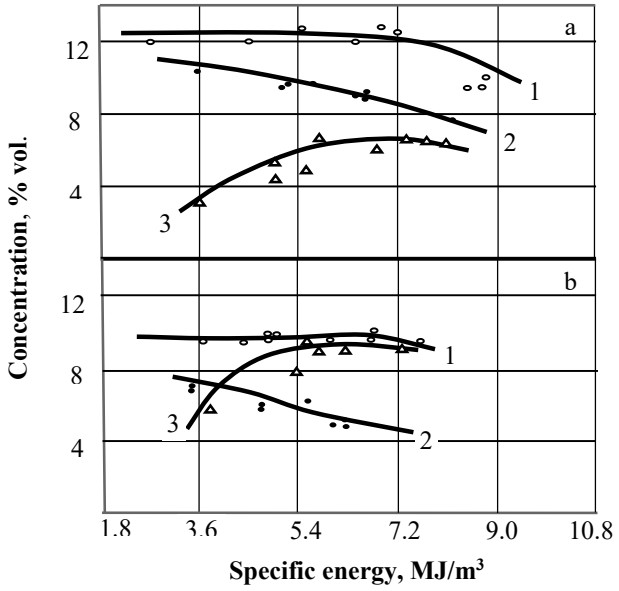

Fig. 6 Influence of the plasma jet specific energy on output of the reaction products: a - φ =0.5; b - φ =1 (0; 1- C_2H_2; 2-C_2H_4; 3-HCN)

Fig. 6 demonstrated that at φ =0.5 proportional growth of concentration HCN with increase of specific energy and reduction of exit C_2H_2 and C_2H_4 is observed. Besides, if at φ =0.5 maximum concentration HCN corresponds at higher values of specific energy (7.2 MJ/m^3), the increase φ leads to displacement of maximum exit HCN on lower value of the plasma stream specific energy (5.4 MJ/m^3). At energy density of a plasma stream 5.4-7.2 MJ/m^3 and when using of the cooled and uncooled reactors, an exit of pyrolysis carbon was made by 23-28 and 30% weight, respectively.

The great influence of the raw materials (τ) stay time in the reactor on the target products exit is observed. At increase in time of stay of raw materials in the reactor, concentration of HCN increases, and the exit of the pyrolysis carbon grows, but decreases of no-limiting products at the same time are observed. On the contrary, at reduction of time of stay of raw materials in the reactor, concentration of the cyanic hydrogen decreases, and the exit of ethylene and homologies impurity grow. Besides, if pyrolysis of gas condensate is accompanied by compulsory training with hydrocarbon raw materials, exits of acetylene and ethylene together with homologies of acetylene impurity increase.

Due to intensive soot and deposition on the cooled reactor walls, the use of uncooled reactor is more preferably. In uncooled reactors, the optimal conditions of distribution of temperature and high-speed fields are created. Thus, based on the received results, it is possible to assert that for maintenance of the maximum exit of no-limiting products (C_2H_2 and C_2H_4), pyrolysis of gas condensate should be spent in cooled reactors and cyanic hydrogen in uncooled reactors.

V. Conclusion

The rich hydropower potential of the Republic of Tajikistan opens a wide perspective for the development of alternative and ecological source of energy - hydrogen energy. The possibility of processing of waste of the gas industry by using of low-temperature plasma is established.

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