Research Article

Production of Hydrogen by Electrolysis of water and Plasmochemical Treatment of the Gascondensates-Waste of the Gas Industry

Inom Sh Normatov, Makhmadrezbon T Idiev, Nurmakhmad Shermatov, Abdulnosir Zokirov, Davlat Q Solikhov

Tajik National University, 17 Rudaki Ave., Dushanbe, Tajikistan,

Abstract Present the results of research on water electrolysis and plasma-chemical processing gascondensate–waste of gas industry to produce hydrogen. The electrolysis was subjected to the river water and after it electro-sedimentation. Found that due to the complex chemical composition of river water the surface of the electrodes during electrolysis is covered by conglomerates consisting of a set of chemical elements. 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 number of hydrogen is formed. The principal possibility of the application of low temperature plasmas for the processing of condensates. The pyrolysis of gascondensate with a molecular weight of 140 ($C_{10}H_{20}$) with an average boiling point of about 55 °C, it was observed that in case use of nitrogen as agents for turbulences of plasma stream, pyrolysis of a gascondensates was accompanied by an acetylene (3÷7 vol. %), ethylene (4÷8vol. %), pyrolysis carbon (10÷15 weight %)

Keywords Hydrogen, Electrolysis, Electrode, Gascondensate, Plasma

Introduction
In structure of internal manufacture primary fuel and energy resources (PFER) hydropower makes accordingly 82 and 96 %. However, in structure of cumulative fuel and energy balance of region a share of Hydropower now it is insignificant (about 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 now used only 10 %. The basic volume of hydropotential is concentrated in Tajikistan (69%) and Kyrgyzstan (22 %) [1-2]. Tajikistan is rich of water resources. The total account of rivers in Tajikistan contains more than 25000 by total length of about 90000 km. 6 per cent of all territory of country is occupied by more than 8492 glaciers. Total annual volume of hydropower production in Tajikistan contains 527 Bln. kWt·h from which not less than 40-50 % are technically possible for development of the hydropower. Hydroelectric power stations develop more than 95 % of all electric power in republic. Water resources focuses, basically, on the large rivers – Vakhsh, Pyanj, Obikhingou and others. The specific saturation of potential water resources makes up significant size – 3682.7 kWt·h on 1.0 км² territories (the first place in the world) and per capita 87800 kWt·h per year.

Among problems that the whole world faces, it is climate change that poses a serious threat for all natural and economic complexes, including water and land resources. It is obvious that in processes of Global climate change the key factor is concentration of greenhouse gases in the atmosphere. An emission of polluting substances in Central Asia Region in 2005 has made of the total value of emissions from polluting substances from stationary sources were brought by gaseous and liquid substances (70.0 %). The main pollutants of the atmosphere are the weighed particles (35%) and SO_2 (31%), CO_2 (14 %) and nitrogen oxides (10 %) [3]. 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 for filling of the energy sector with cheaper and clean fuel. In the present work, there are problems in the use of water resources from upstream countries of the Central Asian Trans boundary Rivers and the surplus of the electric power during the summer period for production of hydrogen by electrolysis and the possibility of storage and hydrogen transportation for long distances are considered.

Production of Hydrogen by Electrolysis of Water

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

Electrolysis can successfully be realized directly at the hydropower plants, thermal and nuclear power plants when excess capacity can be used for production and storage of hydrogen. For this purpose can be used a powerful electrolysis with the capacity of 1.0 Mln. m^3 of hydrogen per day. 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 in some situations power the electrolysis of water, even under modern conditions, can become a competitive method for hydrogen production. Electricity consumption for production of one 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:

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

where 26.8 – number of Faraday's number (A·h) on mole; 2 – number of Faradays spent for allocation 1 mole H_2; 0.0224 – volume 1 mol. hydrogen at normal conditions.

At thermo-neutral voltage 1.48 V for production of 1.0 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 production of 1.0 m^3 H_2 and 0.5 O_2 it is necessary 805 gallons of water.

Gaseous hydrogen is transportable and can be stored in huge quantities in natural underground storehouses. An identical section pressure passes through the pipelines in the form of hydrogen or methane with the same quantity of energy. Transportation through pipelines in the form of hydrogen is approximately 4 times more favorable, in comparison with transfer of the same energy in the form of electricity. Now in Tajikistan 15 Billion kWt/h hydropower is produced and used, which increases in the summer period. However, nowadays condition of hydropower use is not purposeful. With acceptance in reform of hydropower, raising effectiveness of hydropower decreased the demand up to 25%. We can own the valuable hydropower 6 billion kWt/h only for production of hydrogen gas. In the future, Tajikistan is building two large hydropower stations – Rogun (3600 MWt) and Sangtuda (670 MWt) are continued, the hydropower source can increase. Use of these two stations will bring an additional 20 billion kWt of hydropower annually. All these are the evidence that the republic of Tajikistan has already the conditions for growing of hydrogen power [4].

For us the hydrogen electrolyser concept was used, which shown in Fig.1. Electrolysis of water held at a voltage stamps from 2.4 to 4, 4 V.
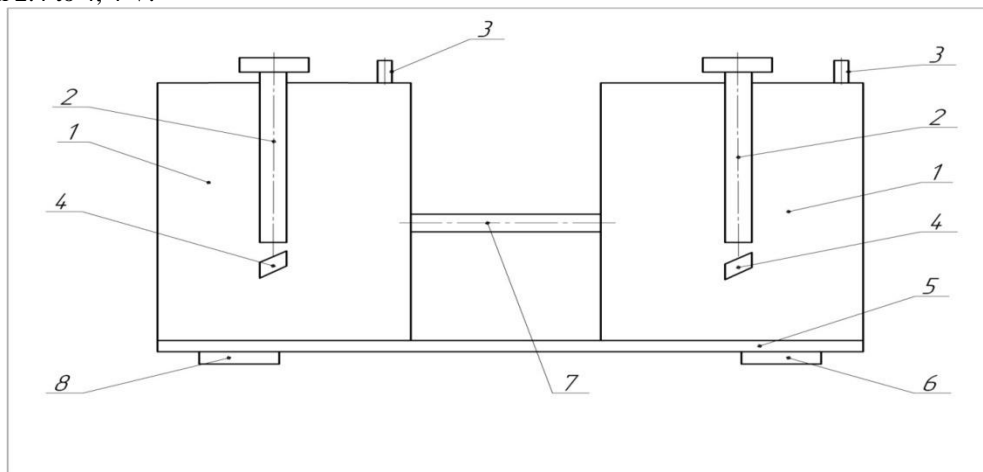

Figure 1: Schematic diagram of electrolysis cell. 1 - Cell, 2-electrode holder, 3 – pipe, 4- electrodes, 5 - cell basis, 6 - feet, 7-connecting tube

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 used river water and the water after the softening process.

It should be noted that when using river water without treatment were found deposition on the electrodes conglomerates of complex composition and process of the electrolysis of water was not almost observed. Monitoring the formation of hydrogen qualitatively determined by the formation of bubbles on the electrode surface and quantified by measuring manometer connected to the cell (Fig.1) It is known that formation of bubbles on a surface of electrodes influence an electrostatic field; reduce intensity of a field between plates and current in a chain. For elimination of this effect are usually used the external oscillatory device which causes vibration of plates. For 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 it electro-sedimentation.

The Fig.2 show that existence in composition of not conditioned river water of ions and cations of chemical elements becomes generation of processes of division at lower values of voltage. For the purpose of establishment of deposits of components of composition of water to shift of values of voltage at electrolysis the complex of physical and chemical analyses were carried (Fig. 3). The composite chemical composition of river water explains observed process of accumulation of conglomerates on a surface of electrodes and specifies about need of their preliminary cleaning for electrolysis implementation.
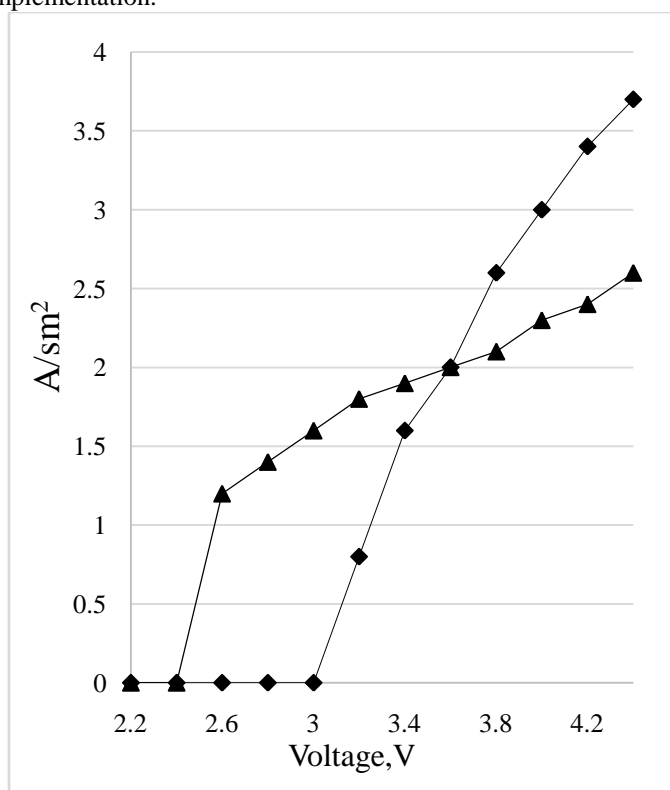

Figure 2: Volt -ampere characteristic of the electrolyze cell by electrodes from stainless steel at electrolysis of river water (▲) and after its electro-sedimentation (■)

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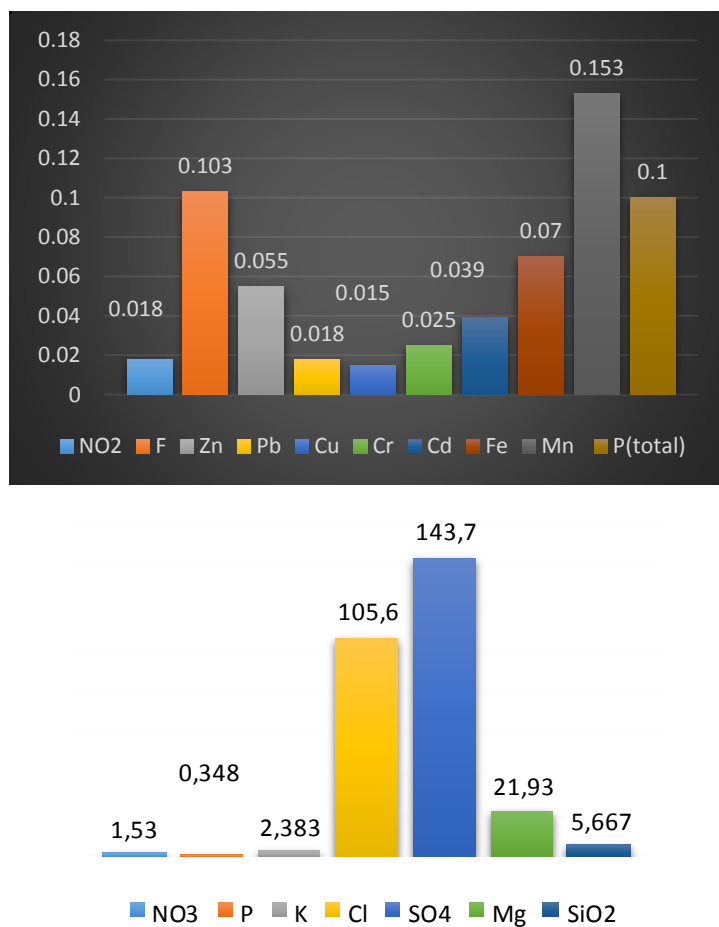
Figure 3: Water Chemical analysis of the Vakhsh River

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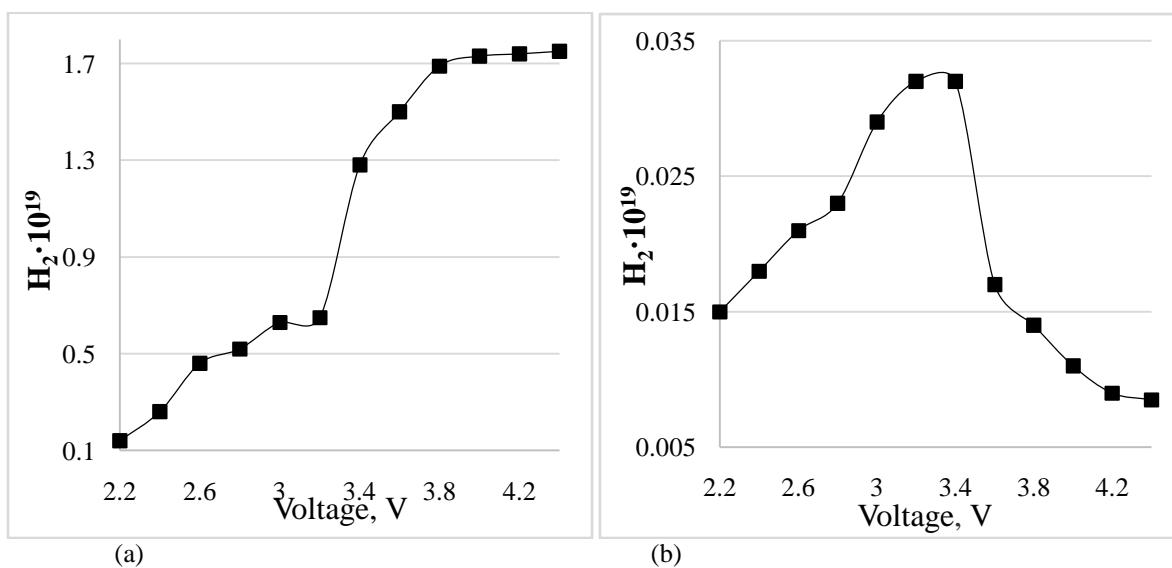

(a)   (b)

Figure 4: Amounts of hydrogen at electrolysis of water by use of (a) stainless steel electrodes and (b) coper electrodes

Plasmochemical Treatment of Gascondensate

The present work is devoted researches on research of possibility of the gascondensate treatment in low temperature plasma for production of no limiting hydrocarbons. The gas condensate meets 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. The gas condensates in depending containing of easy and heavy fractions are characterized by boiling temperature 60-350 ^{o}C. In our investigation have been used natural gas condensate deposits of "Kanibadam" of Republic Tajikistan with molecular weight 140 ($C_{10}H_{20}$) and average value of temperature of boiling about 55°C.

Plasmochemical pyrolysis of the gas condensate 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.

Result and discussion

For identification of components of the plasmochemical, pyrolysis of gas condensate in the plasma stream and their quantitative definition were used gasochroms analysis methods. The analyses of gases H_2, N_2, O_2, CH_4, CO, CO_2 spent by use of "Gazohrom". The helium as gas- vehicle with the expense of 55-60 sm^3 used. For the "Gazohrom" calibration has been used pure nitrogen, hydrogen, oxygen and methane. Calculation of the gaseous products concentration spent on calibrial curve method by comparison of the settlement areas of peaks of components. Definition of the ethane, ethylene, acetylene, propylene and homology impurity concentrations was spent on chromatograph UX-2. The dividing column by volume of 150 sm^3 that filled with a sorbent of 27 % dibutilphatalate deposited on INZ-600 was for this purpose applied. The temperature of an analyzed column supported at 50 ^{o}C and the expense of gas -vehicle (helium) near 35 sm^3/min.

The analysis of cyanic hydrogen were carried out on chromatograph PAXV-07 with filled by polethilenglikogole - 1500 on zeolite – 545 dividing column. As gas-vehicle used hydrogen, and the temperature of an analyzed column supported at 100°C. One of the basic problems of the plasmochemical technologies is creation of the conditions providing fast cooling and trainings of products of pyrolysis. If speed of cooling at a stage of end of reaction is insufficient, target products have time to decay. In the present work, cooling and training of products of the gas condensate pyrolysis carried out in housing-tube heat exchanger and by means of influence of steams of raw materials on a reactionary mix at an exit from the amalgamator reactor. It is necessary to notice that at cooling of products of reaction in the heat exchanger observed intensive deposition of the soot at which walls of tubes corked with them. It leads to undesirable effect of increase in pressure that breaks a steady operating mode of installation and involves a stop of process of pyrolysis.

Table 1: Results of the plasmochemical treatment of gas condensate in nitric plasma

No.	Parameters	Experiments				
		1	**2**	**3**	**4**	**5**
1	P, kWt	7.6	8.0	9.2	8.8	9.8
2	$G \cdot 10^{-3}$, m^3/sec	6.7	6.7	6.7	7.0	7.0
3	$M \cdot 10^{-1}$, g/sec	6.67	5.67	5.00	5.03	7.67
	T, K	1800	2000	2200	2100	2100
4	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
5	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 2: Results of the plasmochemical treatment of gascondensate in nitric plasma and training of products by stream of initial gas condensate

No.	Parameters	Experiments				
		1	**2**	**3**	**4**	**5**
1	P, кВт	6.9	7.2	8.4	9.2	9.8
2	$G \cdot 10^{-3}$, m^3/sec	7.0	7.0	7.0	6.7	6.7
3	$M \cdot 10^{-1}$, g/ sec	5.83	6.67	5.00	5.00	5.30
4	$m \cdot 10^{-1}$, g/ sec	2.50	1.70	1.70	2.00	2.00
	T, K	1900	2000	2200	2200	2300
5	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
6	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
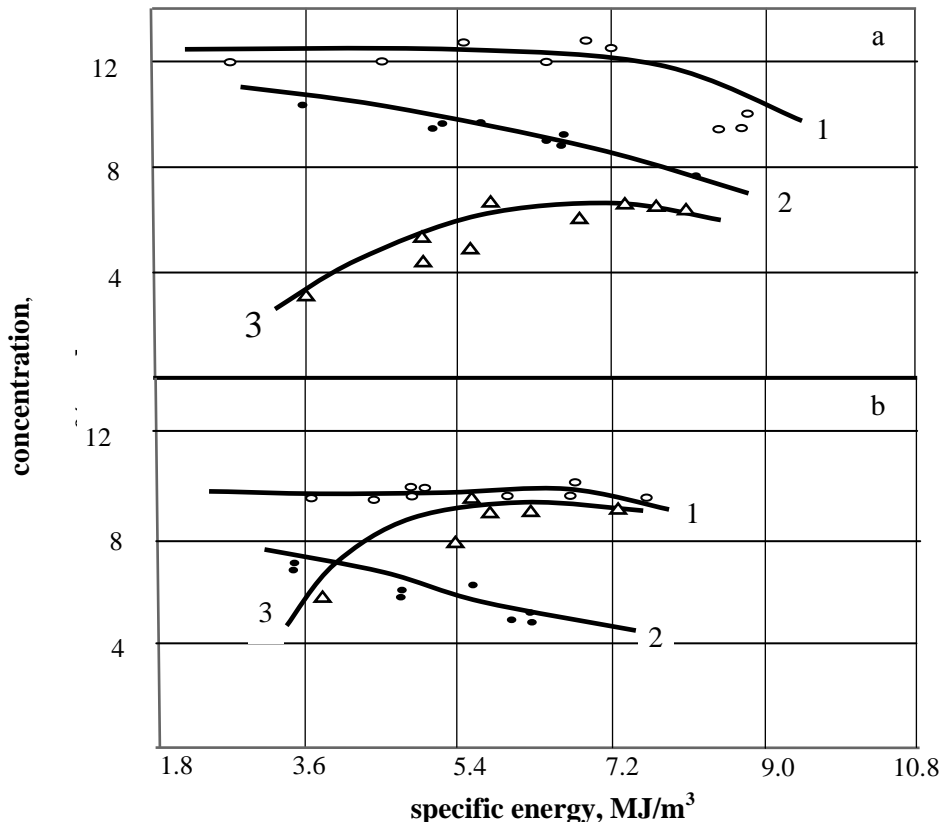

Figure 6: Influence of the plasma jet specific energy on output of the reaction products:
a - φ =0.5; b - φ =1.0; 1- C_2H_2 ; 2-C_2H_4 ;   3-HCN

On the Table 1 present the results of gas condensate treatment in nitric plasma at training of products of reaction in housing-tube heat exchanger. For prevention of the given effect, we used a method compulsory training of products

of reaction by influence on products of reaction by steams initial gas condensate at an exit from the reactor which results are presented in Table 2.

From the Table 2 can see that at compulsory system of cooling and training of products of reaction by raw material steams the increase in exits of no limiting hydrocarbons observed. It was revealed that the system works permanently and process submits to management on exits of products.

At change of the plasma stream specific energy from 1.8 to 10.8 MJ/m^3 and parities of plasma forming gas to raw materials ($\varphi = N_2$/raw materials) to equally 0.5 exit of cyanic hydrogen (7 % vol.) it is accompanied with no limiting 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. In products of pyrolysis, contain hydrogen (20-22 % vol.) and homological impurity in the sum (1.5-2.5 % vol.). The exit of the pyrolysis carbon has made 25-30 % of weights. At increase of φ to unit at the same values of specific energy the increase in values φ to unit leads to growth of exit HCN to 9 % vol. and to reduction of concentration of no limiting hydrocarbons C_2H_4 and C_2H_4 to 8 % vol. and 10 % vol accordingly. In case of use of not cooled reactors) decrease in an exit of no limiting hydrocarbons is observed, and concentration HCN increases to 10-12 %.On the Fig. 6 results of researches on influence of the plasma stream specific energy on the target products exit of the gas condensate pyrolysis are presented.

The 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).

Exits of pyrolysis carbon in recalculation on the transformed raw materials in not cooled reactors at specific energy 5.4 - 7.2 MJ/m^3 correspond to 23- 28 % weight. In reactors with compulsorily cooled walls at the same values of specific energy, the exit пироуглерода reaches 30 % weight. It is connected with hashing of reagents in a sphere of formation of target products and distribution of temperatures in a zone of reaction of chemical decomposition of raw materials.

The great influence of the raw materials (τ) stay time in the reactor on the target products exit observed. At increase in time of stay of raw materials in the reactor concentration HCN increases and the exit of the pyrolysis carbon grows but decreases of no limiting products at the same time is observed. On the contrary, at reduction of time of stay of raw materials in the reactor concentration of cyanic hydrogen decreases and the exit of ethylene and homologies impurity grow. Besides, if pyrolysis of gas condensate accompanied by compulsory training with hydrocarbon raw materials exits of acetylene and ethylene together with homologies of acetylene impurity increase. It concerns as to not cooled, and to cooled reactors in which training made by the gas condensate stream.

Due to intensive soot, deposition on the cooled reactor walls use of not cooled reactor is more preferably. In not cooled reactors, created the optimal conditions of distribution of temperature and high-speed fields.

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 not cooled reactors.

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.

Pyrolysis of gas condensate in nitric plasma has shown about basic possibility of production of no limiting hydrocarbons and cyanic hydrogen. Essential influence of cooling processes and training on the target products exit established. The dependence of a percentage parity of the no limiting hydrocarbons and cyanic hydrogen exits from the plasma stream specific power and time of stay of raw materials in a plasma stream specifies in possibilities of management of process of pyrolysis on maintenance of the maximum exit of separate components of products of reaction is shown.

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