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Electric arc plasma pyrolysis of natural gas by a high-voltage AC plasma torch

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Abstract. The article considers the plasma pyrolysis of hydrocarbons by the high-voltage AC plasma torch. Calculations are given for various hydrocarbons and their mixtures, as well as experimental data on plasma pyrolysis of natural gas. The methane conversion in the experiment was from 76 to 86%, and the energy consumption was 20.6–23.3 kWh/kg of hydrogen.
Keywords: hydrogen, plasma pyrolysis, argon, AC plasma torch, natural gas.

1. Introduction

The development trend of the global community is aimed at reducing carbon dioxide emissions and achieving carbon neutrality. The European Union and the US plan to achieve carbon neutrality by 2050, while some other countries, including China, have set the goal of achieving carbon neutrality by 2060 [1]. One of the ways to reduce carbon dioxide emissions is considered to be a significant increase in the use of hydrogen in various areas of industry and human life.

Hydrogen is an ideal and environmentally friendly energy carrier. The calorific value of its combustion is 141 MJ/kg (39.2 kWh/kg). When converting hydrogen into any form of energy (thermal or electrical), no harmful carbon dioxide emissions are produced.

Hydrogen is one of the most common elements in the universe, but unfortunately it is not found on Earth in its pure form, and modern technologies for its production cause the formation of a large number of pollutants.

As of 2020, more than 95% of the world's hydrogen is produced using the steam catalytic methane reforming (SMR) process [2]. This technology allows the production of the cheapest hydrogen in large volumes, but has a significant environmental disadvantage: more than 11 kg of carbon dioxide is produced per kilogram of produced hydrogen [3].

The technological process of hydrogen production by water electrolysis can be recognized as conditionally environmentally friendly. Currently, this method produces up to 4% of hydrogen in the world. Currently, there are three electrolysis technologies: alkaline, with a solid polymer electrolyte, with a solid oxide electrolyte [4] (Table 1).

Table 1. Water electrolysis methods

Electrolyzer type	Energy costs, kWh/Nm^3 H_2	Capacity, Nm^3/h H_2	Power, kWt	Pressure, MPa	Efficiency, %
Alkaline	4.3–7.5	up to 760	3534	0.1–8.5	47.2–82.3
PEM	5.4–7.2	10–30	7.2–20	0.8–7.6	48.2–61
Solid oxide electrolyzers	6.55	0.6 (experimental installation)	39.2	–	53.8

Currently, on an industrial scale, mainly alkaline type electrolyzers are used. The energy costs for obtaining 1 kg of hydrogen by the electrolytic method at industrial HySTAT plants from HYDROG(E)NICS are 55–60 kWh [5]. These values do not include the cost of expensive water treatment.

If we take into account that about 70% of the electrical energy produced in the world is generated by thermal power plants by burning fossil fuels, hydrogen produced by electrolysis will not be green at all.

According to the IEA, the emission of carbon dioxide per 1 kWh of electricity generated from fossil fuels is: for natural gas 400 g CO_2/kWh, for oil 600 g CO_2/kWh, for coal, depending on its type, – 845–1020 g CO_2/kWh.

Thus, for electrical energy produced from gas, CO_2 emissions from the production of one kilogram of hydrogen by electrolysis can reach 24 kg, which is twice as high as that of SMR. The situation may change for the better when the generation of electricity will be carried out mainly by "green sources", the transition to which is associated with certain difficulties and will not be quick. For example, according to the German Federal Environment Agency, electricity generation is more efficient: natural gas 201 g CO_2/kWh, oil 279 g CO_2/kWh, coal 354–364 g CO_2/kWh [6]. Nevertheless, there is already a way to significantly reduce carbon dioxide emissions in the production of hydrogen from natural gas and gas condensates.

As the technical characteristics of plasma devices develop, plasma pyrolysis of hydrocarbons becomes more and more attractive. This is due to the advantages of plasma chemical processes: high reaction rate, relatively low inertia of chemical plants, and simplification of technological process adjustments. For a long time, the main problem in the use of plasma torches was the low stability of the operation of such devices, as well as the standard service life of individual elements (for example, electrodes).

2. Pyrolysis of hydrocarbons

In order to achieve a sufficient degree of conversion of light hydrocarbons, it is necessary to heat the feedstock to the pyrolysis temperature, and it will decompose into hydrogen and carbon black. For example, methane must be heated to a temperature of 1000°C.

$CH_4 = 2H_2 + C(solid)$

Theoretically, 250 g of hydrogen and 750 g of carbon black can be obtained from 1 kg of methane. In fact, pyrolysis produces by-products such as acetylene and other unsaturated hydrocarbons. Their concentration can be reduced by maintaining the required temperature and residence time.

Table 2 presents theoretical estimates of energy consumption for the decomposition of hydrocarbons. As can be seen from the table, the process of thermal decomposition of hydrocarbons is energetically more favorable than the process of water electrolysis, in which hydrogen and oxygen are formed as products.

Table 2. Estimation of plasma pyrolysis of hydrocarbons

Hydrocarbon (mixture)	Pyrolysis temperature, °C	Energy consumption, kW·h/kg of raw materials	Energy consumption, kWh/kg H_2	Yield of H_2 g/kg of hydrocarbons	Carbon yield g/kg of hydrocarbons
CH_4	887	0.88	10.8	244	726
Natural gas (CH_4–98%)	887	0.87	10.9	239	710
Propane	837	0.57	9.8	176	795
Straight-run gasoline fraction	817	0.49	9.7	152	820

But in order to implement the technology for the production of hydrogen by the method of plasma pyrolysis of hydrocarbons, it is necessary to solve the problems of separating gas flows, separating solids from gas flows and heating hydrocarbons to high temperatures. The first and second tasks have already been solved by the world and Russian industry. And the task of heating hydrocarbons is complicated by the fact that classical methods of heating gases, for example, in tube furnaces, are not applicable to hydrocarbon gases and vapors, since during pyrolysis the surfaces of heating elements are covered with soot in a very short period of time. Plasma heating is the most promising for the pyrolysis of hydrocarbons. This is confirmed by a functioning installation created by Monolith [7].

The scientific team of the IEE RAS created a high-voltage AC electric arc plasma torch using a mixture of gaseous hydrocarbons (or their vapors) with a carrier gas, which can be argon, nitrogen, carbon dioxide, water vapor and other gases, as a plasma-forming medium (Fig.1).

The carrier gas is necessary to remove carbon material from the electric discharge chamber of the plasma torch, which prevents carbon sticking to the insulators of the plasma torch and ensures long-term and trouble-free operation of the plasma torch.

When operating on an argon-methane mixture, the plasma torch has the following characteristics: power 40–70 kW, thermal efficiency 95%, electrode life up to a change of 2000 hours [8]. Plasma-forming mixture argon 5 g/s, methane 1–2.5 g/s.

Fig.1. High-voltage AC plasma torch.

Argon was chosen as the carrier gas because it does not take part in chemical reactions with pyrolysis products. At the same time, the technologies for extracting argon from gas flows are known and well developed. The material and energy balance of the process of plasma pyrolysis of methane in a methane-argon mixture is presented in Table 3.

Experiments on plasma pyrolysis were carried out on the experimental setup described in [9]. The experiments were carried out on an unheated reactor (cold experiment) and on a reactor preheated to a temperature of 600°C (hot experiment). The installation diagram is shown in Fig.2.

The power of the plasma torch during the experiment was 40 kW, the consumption of the plasma-forming mixture: argon 5 g/s, natural gas 1 g/s. The results of the experiments are shown in Table 4.

The high concentration of carbon black made it impossible to determine its content in the gas flow. The analysis of the carbon material was carried out by a set of methods: X-ray phase analysis, X-ray fluorescence analysis, BET method, optical spectroscopy in the UV/visible region. The physicochemical analysis of the obtained carbon material showed that the obtained soot contained particles of graphite (from 5% in the hot zone to 70% in the cold zone) and amorphous carbon (up to 90%), as well as light C60/C70 fullerenes in amounts up to 5%; specific surface of carbon black according to the BET method – 60.4 m^2/g; the iodine number according to ISO 1304 is 87 g/kg. Fullerenes were separated from the extract by HPLC. The concentration of C60 fullerene is 3.67 wt %, C70 fullerene is 1.18 wt %.

Table 3. Material and heat balance for processing 1 kg of methane

Parameters	Process efficiency 100% (theoretical)	Process efficiency 80% (experimental)
Inlet		
Methane flow rate, kg	1	1
Argon flow rate, kg	2	2
Energy consumption, MJ/kg of plasma-forming mixture	3.13	3.91
Energy input, MJ/kg of methane / **kWh/kg of methane**	9.39/**2.60**	11.73/**3.26**
Outlet*		
Methane flow rate, kg	0.0099	0.0099
Hydrogen flow rate, kg	0.2475	0.2475
Carbon black flow rate, kg	0.7425	0.7425
Argon flow rate, kg	1.9800	1.9800
Gas Yield, kg	2.2374	2.2374
Energy consumption, MJ/kg of hydrogen / **kW·h/kg of hydrogen**	37.94/**10.54**	47.42/**13.17**
Energy consumption, MJ/kg of Carbon black / **kW·h/kg of Carbon black**	12.65/**3.51**	15.8/**4.39**

*Assumed losses 1%. Atmosphere pressure.

Table 4. Results of Plasma Pyrolysis of Natural Gas

Substance	Cold experiment	Hot experiment
	Concentration, % vol.	
Ar	49.97	46.21
H_2	37.5	42.5
CH_4	10.25	10.25
C_2H_2	2.25	1.01
C_2H_6	0.01	0.01
C_2H_4	0.02	0.02
Methane conversion,%	74	86
Energy consumption kWh/kg of H_2	23.3	20.6

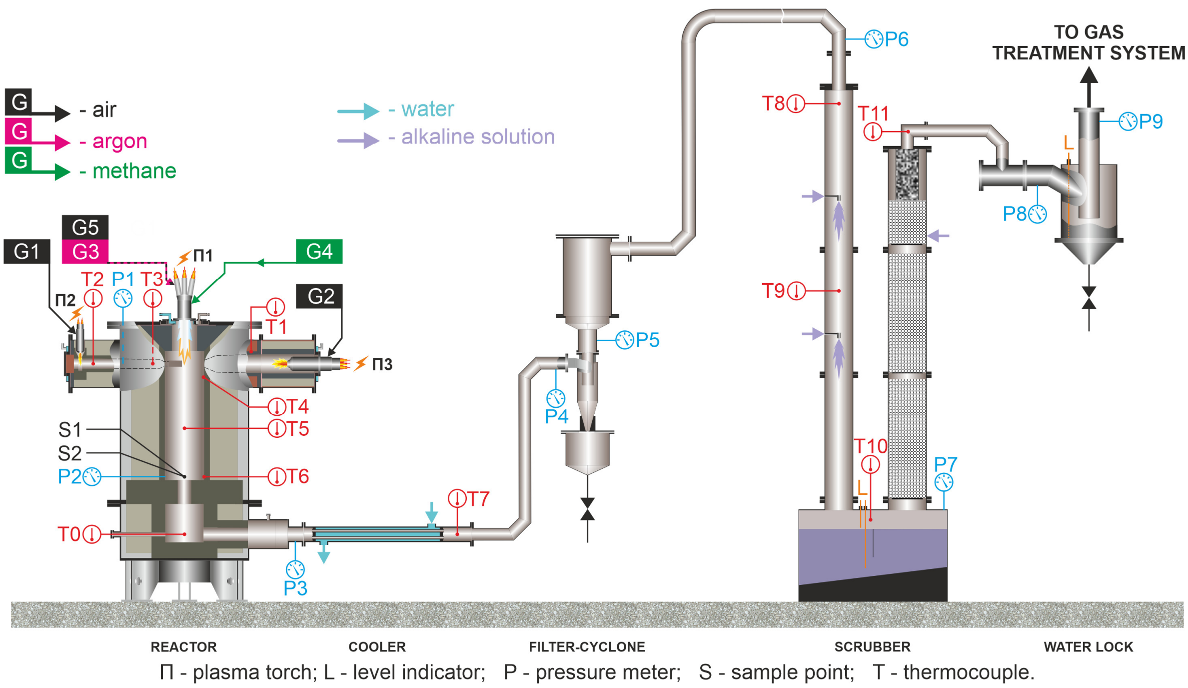

Fig.2. Scheme of the experimental installation.

3. Discussion

Based on the results obtained, it can be said that the difference between the theoretical estimates and the obtained experimental results is explained by the shortcomings of the plasma reactor used. At the same time, the energy consumption for hydrogen production using a non-optimized plasma reactor is significantly lower than for hydrogen production by electrolysis.

On the basis of the created plasma equipment, it is possible to create a plant for the production of hydrogen and carbon black by adding technological units for the separation of solid carbon and the separation of gas flows to the technological scheme. Such equipment is produced in many countries of the world, including the Russian Federation and China. The scheme of the proposed installation is shown in Fig.3.

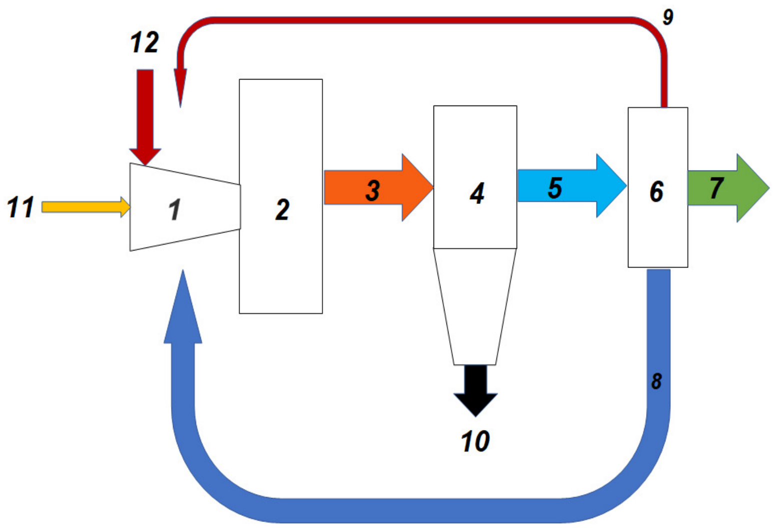

Fig.3. Scheme of the technological process of plasma production of hydrogen and carbon black from natural gas or gas condensates: 1 – plasma torch, 2 – plasma reactor, 3 – flow containing H_2, carbon black and argon, 4 – device for separating solid carbon. 5 – mixture of gases, 6 – installation for gas separation, 7 – hydrogen to the consumer, 8 – argon recycling, 9 – return of unreacted methane to the technological process, 10 – carbon black, 11 – electrical energy, 12 – natural gas.

According to our estimates, the additional energy required for the release of carbon black and the separation of gas flows for an industrial plant will not exceed 5 kWh/kg H_2. Accordingly, the total energy consumption per 1 kg of produced hydrogen and 3 kg of carbon black will not exceed 18 kWh.

Table 5 compares energy costs and carbon dioxide emissions per 1 kg of hydrogen produced.

Table 5. Comparison of hydrogen production methods

Parameters	Plasma production of hydrogen (this article)	Electrolysis	Steam reforming of natural gas
Energy consumption, kWh/kg of H_2	18.1	55–60	≈1
CO_2 emissions, kg/kg of H_2	7.24	22–24	≈11

4. Conclusion

The experimental data obtained indicate the feasibility of the technological process.

The proposed technology already makes it possible to significantly reduce carbon dioxide emissions in the production of hydrogen and carbon black. The proposed technology may be of interest for the creation of small, medium and large-scale production.

The raw material base for hydrogen production can be natural gas, gas condensate and other hydrocarbons and their mixtures.

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