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Research article

Hydrogen production by methane pyrolysis in the microwave discharge plasma

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Abstract: We present the preliminary results of experimental studies on hydrogen production through methane pyrolysis. Based on the analytical review, the technology of methane pyrolysis in the plasma of a microwave discharge was chosen. To implement this method, an installation for applied research PM-6 was developed, and experimental data on the possibility of producing hydrogen was obtained. The methods of mass spectrometry and optical emission spectrometry were used to analyze the products of the methane decomposition reaction. It has been established that at a microwave forward power of 0.6 kW, plasma pyrolysis of methane occurs with the formation of hydrogen, carbon, and hydrocarbons. Preliminary calculations of methane conversion, as a result of the conducted studies, showed a hydrogen selectivity of 4–5%. The developed installation and the applied method are under modernization at the present time.

Keywords: plasma; methane; microwave discharge; pyrolysis; hydrogen; carbon

1. Introduction

Currently, such a scientific direction as hydrogen energy is widely developed in energy industry around the world [1]. The major challenges of the energy industry are methods for both the production and storage of hydrogen. In this regard, it is required to create energy efficient and safe commercial systems.

When storing hydrogen, the most common methods are compressed, liquid, and solid storage [2]. However, it is important to take into account the volume of the transported product, the distance during transportation, and the operating modes of a hydrogen producer and consumer [3].

Storage of hydrogen in a liquid state provides an opportunity to obtain a high mass density of the substance. When storing hydrogen in a solid state, special materials are used for sorption and desorption of hydrogen based on physicochemical interaction [4]. Each of these methods has its own advantages and disadvantages and is developing in accordance with global scientific and technological progress.

The research presented in this paper relates to the hydrogen production. One of the major challenges in this industry is the complexity of a variety of production methods. Each method has strengths and weaknesses. Steam reforming of methane and natural gas, coal gasification, and methane pyrolysis methods are easier to implement and more common, although each of them has advantages associated with the availability of natural resources, technical support, geographical location, minerals, and regional infrastructure [5].

Economic and environmental aspects are important criteria when choosing a production method.

From an economic point of view, the steam methane reforming method holds a leading position. Thus, when decomposing methane by pyrolysis, the costs are 1.6–2.2 euros/kg of hydrogen, and for steam reforming 1.0–1.2 euros/kg. The most expensive method is electrolysis, the cost of which is 2.5–3.0 euros/kg [6].

From an environmental point of view, electrolysis has no competitors since this method does not produce CO_2 emissions, but there is an issue regarding energy sources for this reaction. Since the energy supply comes from non-renewable sources, the issue of environmental safety remains open. Methane pyrolysis also has environmental advantages over other methods. This is because the reaction does not produce gaseous emissions and solid carbon can be processed, stored, or used in other industries without harm to nature.

Along with the described criteria, the prevalence of use and simplicity of methods for producing hydrogen are of great concern. Electrolyzers lead in terms of popularity of method applications, since they are already commercially available in various designs from small installations to large ones. This is the simplest but most expensive method of producing hydrogen.

Thus, taking into account all the factors and criteria in the Republic of Kazakhstan, electrolysis, pyrolysis, and coal gasification are the most promising methods for producing hydrogen. Considering small water reserves for industrial hydrogen production and the environmental situation regarding CO_2 emissions, methane pyrolysis is the most profitable method. Moreover, the country has quite large reserves of natural gas and this method requires the least energy consumption compared to others [7]. Furthermore, by-product solid carbon resulting from pyrolysis can be used as an industrial raw material for the production of steel, batteries, carbon fibers, as well as in mechanical engineering, electronics, and space industries, thus making an additional contribution to the country's economy.

In this regard, the creation of new technologies for pyrolysis and methane, as well as the improvement of existing ones, becomes an urgent task. We present the major theoretical and practical methods for methane decomposition and reflects preliminary results of experiments on the production of hydrogen by plasma pyrolysis of methane in a microwave discharge at an applied research installation. The study of methane decomposition technology in a plasma-beam discharge was previously conducted by us on a plasma-beam installation [8,9].

Currently, there are many laboratory and industrial installations that allow the production of hydrogen and carbon based on the decomposition of natural gas. The diversity of these installations is due to the use of different pyrolysis methods. As is known, methane pyrolysis belongs to a number of processes that can be divided into 4 large classes-thermal, catalytic, plasma pyrolysis and pyrolysis in metal melts [10,11]. The main difference between them lies in the methods of heating the reaction mixture and cooling the reaction products, since the decomposition of methane requires a temperature of 1000 °C and above.

Figure 1 shows one of the known thermal pyrolysis reactors of methane using a moving bed of carbon pellet catalyst [12,13].

Operating parameters	
Process temperatures	1000 – 1400 °C
Natural gas feed	10 m^3 h^{-1}

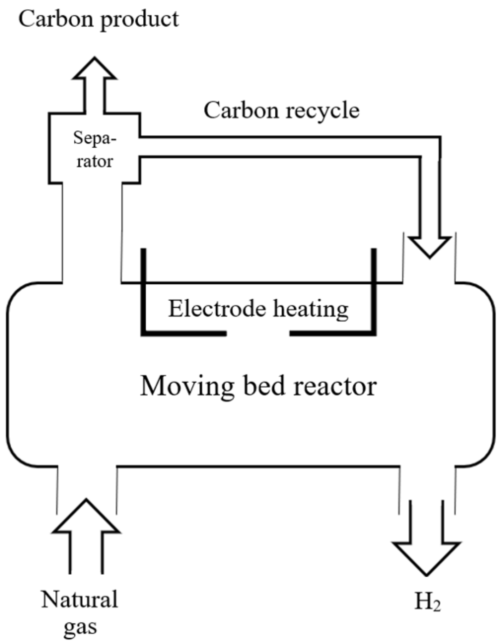

Figure 1. Parameters and scheme of the thermal pyrolysis reactor.

Gas is supplied to the lower section of the reactor, and carbon granules are transported in countercurrent to the upper section, heated by direct current to 1000–1400 °C. The heat is transferred to the natural gas, which then decomposes into solid carbon. This solid carbon deposits on carbon particles and settles to the bottom of the vessel, while gaseous hydrogen cools at the top and exits the reactor. In a small-scale hydrogen production scenario, this method is comparable in cost to electrolysis but inferior to plasma pyrolysis. On a small scale, this method compares in cost to electrolysis but lags behind plasma pyrolysis [14].

In the case of pyrolysis in a liquid atmosphere, methane decomposes when passing through a column of liquid metal with a temperature of >1000 °C. In such an installation [15], gas is supplied from below into a column filled with molten tin, bismuth or a mixture of metals. As methane rises in the melt, a cracking reaction occurs: Carbon is pushed out and deposited as a powder on the surface of the liquid metal, and hydrogen is pumped out from the top of the reactor. This method produces hydrogen with a conversion of up to 78 percent at about 1200 °C, as shown in Figure 2.

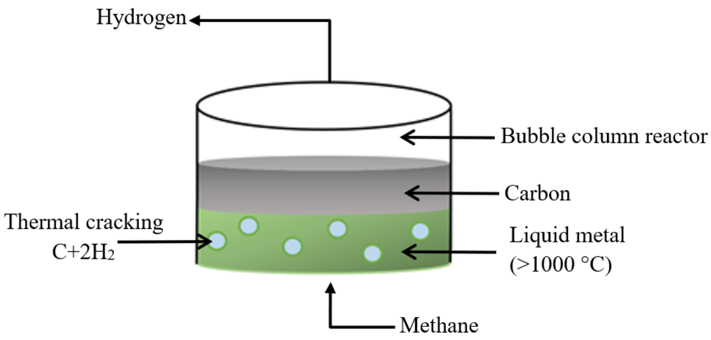

Figure 2. Scheme of methane pyrolysis in liquid metal.

This method can lead to 95% methane conversion in a bubble column containing Ni 0.27 and Bi 0.73 melts at a temperature of 1065 °C [16]. In a reactor with liquid tin at a temperature of 1080 °C, it was shown that addition of ethane to methane leads to an increase in hydrogen conversion [17].

Plasma pyrolysis is the most promising because it is considered cost-effective compared to the methods described above. There are currently many pilot installations and even small plants producing hydrogen and carbon using this method. For example, James Atwater et al. reported conversion rates close to 100% [18]. At the enterprise [19] for the production of hydrogen, solid carbon, ammonia, and methane are split at a temperature of 1500–2000 °C, at a cost seven times lower than with electrolysis. However, during the pyrolysis process, a small proportion of CO_2 is present.

Referring to the research [20,21], we present the choice of method and installation based on gas decomposition under the influence of microwave discharge. It is shown that with a power of the pilot installation of 5 kW, the hydrogen productivity was 400 g/kWh. Figure 3 shows the operating principle of the installation [21].

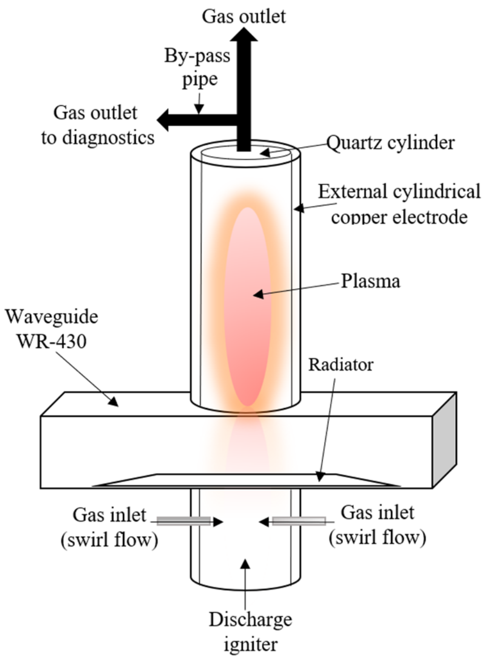

Figure 3. Scheme of methane pyrolysis in microwave plasma.

The key feature of such high productivity is the technology of eddying motion of methane in the reaction chamber due to the configuration of the nozzle. The degree of methane selectivity for hydrogen was 100%. One of the disadvantages is deposition of soot on the reactor's walls during pyrolysis as a result of exposure to eddy current.

Based on the analysis of scientific and technical literature and a patent search by scientists of the "Institute of Atomic Energy" Branch of the Republican State Enterprise "National Nuclear Center of the Republic of Kazakhstan", our own applied research installation PM-6 (installation PM-6) was designed and assembled for hydrogen production by plasma pyrolysis of methane [22].

2. Materials and methods

All hydrocarbon compounds are more or less unstable at high temperatures, and are destroyed by strong heating. Methane at temperatures above 1000 °C decomposes into carbon and hydrogen, as shown in the chemical reaction:

$$CH_4 \text{ (gas)} \rightarrow C \text{ (solid)} + 2H_2 \text{ (gas)} \; \Delta H = 74{,}85 \text{ kJ/mol} \quad (1)$$

However, the process of pyrolysis is also accompanied by other chemical processes, resulting in the formation of methane radicals and organic gaseous compounds. In microwave discharges, the energy of electromagnetic waves is transferred to plasma electrons. Under the action of an electric field, electrons acquire kinetic energy, which is then converted into the energy of thermal motion of electrons, as well as into excitation energy and thermal energy of molecules. The degree of conversion in this process can reach 95–98%. Carbon, hydrogen and acetylene are formed as the main primary products of pyrolysis. Figure 4 shows a general scheme of the designed installation for implementing the method we have chosen.

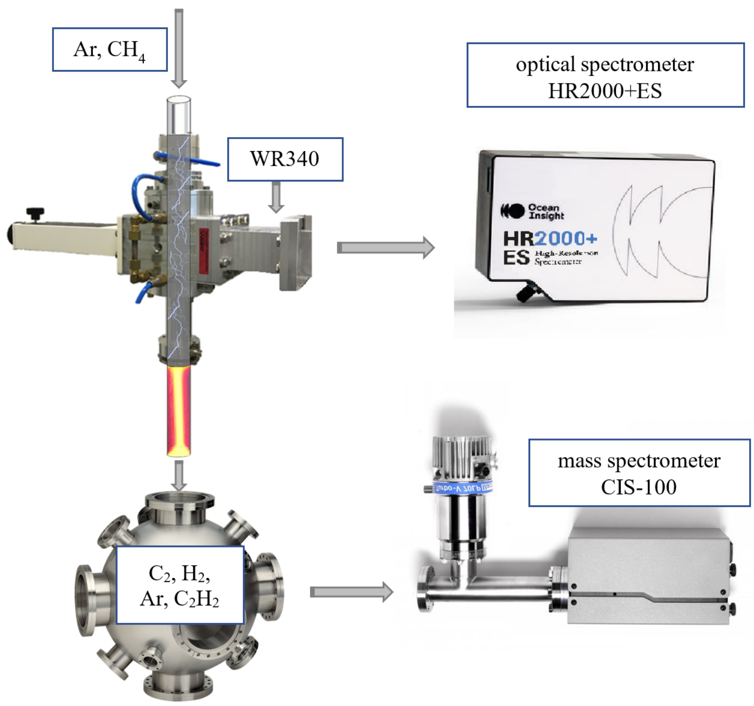

Figure 4. Scheme of the applied research installation.

The installation PM-6 consists of a spherical analytical chamber with a diameter of 450 mm, a microwave generator with a frequency of 2450 MHz with a maximum power of 6 kW. The analytical chamber has an independent pumping system based on vacuum pumps. The major technical characteristics of the GMP G4 microwave generator are presented in Table 1.

Table 1. Technical characteristics of the microwave generator.

Parameter	Value
Microwave output	6 kW (from 10% to 100%)
Frequency	2450 MHz ± 25 MHz
Waveguide output	WR340
Operating mode	pulse, constant
Working gas	Ar, N_2, O_2, H_2, CH_4, He, air

For the methane decomposition experiment in the analytical chamber, a rarefied medium was created using the IDP-7 vacuum pump, maintaining a pressure of 10^{-2}–10^{2} Torr. This ensured the flow of the working gas (methane + argon) through the reaction chamber (quartz tube ⌀30 mm) of the GMP G4 microwave generator. Subsequently, the magnetron was warmed for 180 seconds, and the required microwave radiation power was set. Microwaves propagated along rectangular waveguide WR340 (with section size of 138 × 95 mm) to a quartz tube (positioned perpendicular to the waveguide) where plasma-chemical reaction occurred. The resulting pyrolysis products entered the analytical chamber and were safely removed into the exhaust gas system from there.

The reflected power of microwave radiation is set by a tuner for adjusting and tuning the resonant frequency, as well as a tuner with three microwave chokes. To monitor microwave leaks during operation of installation PM-6, a microwave meter of 0–5 mW/cm^2 is used.

Various methods are used to diagnose and record the composition of the gas during the pyrolysis process and after the decomposition of methane on the installation. In particular, the emission spectrum in the quartz tube was determined by an HR2000+ high-resolution optical spectrometer with the OceanView licensed software. The reaction chamber has a special technological opening for real-time spectral analysis during plasma combustion. This system allows you to adjust the modes of the microwave generator as well as select the best ratio of the mixture of gases and set their optimal consumption.

In the analytical chamber, the reaction products are taken into a separate chamber to determine the composition of gases by mass spectrometry. The analyzer is a CIS100 quadrupole mass spectrometer with proprietary RGA software. The device allows you to determine the components contained in the gas mixture in the range of 1 amu-100 amu at a pressure in its chamber not higher than 10^{-3} Torr. Mass spectrometry is measured online, which allows you to change the parameters of the working gas and microwave power during the experiments.

Technological systems of the magnetron must meet high requirements. The following of them have been calculated, designed and installed for the safe and correct operation of the installation PM-6:

- A system for supplying plasma-forming gas(es) to the reaction chamber of the GMP G4 microwave generator. The main requirement for this system is tightness and provision of gas pressure in the duct no more than 760 Torr with a maximum flow rate of up to 150 l/min. The inlet of working gas is provided through a needle-type leak, and monitored with a gas flow regulator and a pressure sensor;
- Self-contained closed-loop liquid cooling system using a chiller to cool the microwave generator, microwave head power supply, reflected power tuner, and reaction chamber components. The

coolant parameters in the magnetron cooling paths are set to a flow rate of 4.0–4.5 l/min, a pressure of 1.0–1.2 kgf/cm^2 and a temperature of 23–27 °C;

- Paths for controlling the automatic ignition system of a microwave discharge using compressed air with a pressure of 4–6 kgf/cm^2;
- Information and control measuring system of the installation PM-6 is a personal computer with software and special modules. The modules provide control of the elements of the installation, as well as the collection and storage of information regarding the parameters of all systems.

3. Results and discussions

This section presents results of experiments on the decomposition of methane by plasma microwave pyrolysis. The operating modes of the magnetron and the ratio of CH_4:Ar were selected based on a literature analysis of similar research [23–25]. During the experimental work, the power of the microwave discharge was set to 1 kW using a control unit. In this case, the reflected power was reduced to 0.4 kW by adjusting the chokes of the microwave tuner. Figure 5 shows a microwave discharge during an experiment using a mixture of working gases of argon and methane.

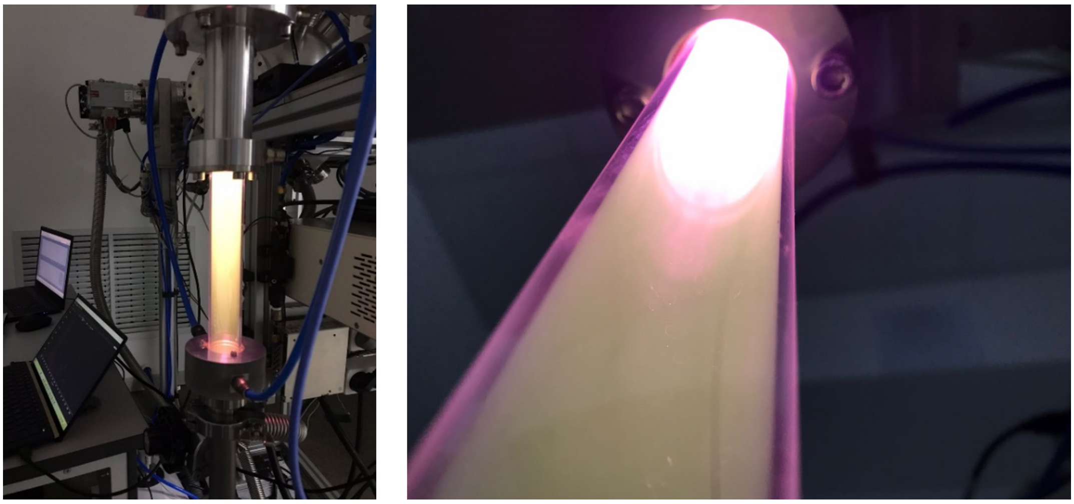

Figure 5. Microwave discharge using argon and methane mixtures.

Mass spectrometry of the gas mixture after the reaction chamber was performed using a capillary system that connects the analytical chamber and the working chamber of the device. Figure 6 presents the exhaust gas partial pressure diagram.

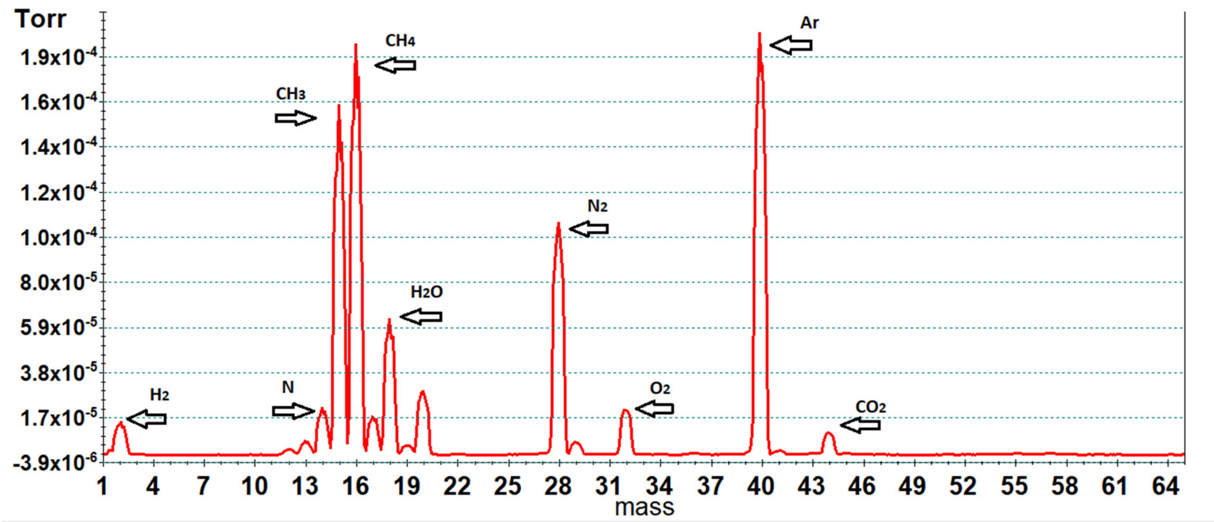

Figure 6. Diagram of partial pressures of residual gases during sampling.

Based on the results of mass spectrometric analysis, it was revealed that the ratio of the working gases of argon (40 amu) and methane (16 amu) is equal to 1:1 at a partial pressure of $(2.0 \pm 0.1) \times 10^{-4}$ Torr. The detection of the presence of hydrogen molecules (2 amu) with a partial pressure of $(1.7 \pm 0.1) \times 10^{-5}$ Torr is an important fact; this confirms the possibility of producing hydrogen by this method. The presence of peaks of nitrogen, oxygen and water vapor is due to the presence of a leak from atmospheric air in the automatic ignition system of the microwave discharge. There is no carbon peak because the element deposits as a solid after the reaction chamber and is not detected by the mass spectrometer. The presence of carbon in the discharge is indicated by the optical spectrum presented below.

Spectroscopic analysis in the reaction chamber of the installation was performed online throughout the experiment with an integration time of 10 ms. Figure 7 shows a graph of the intensities of spectral lines depending on the wavelength.

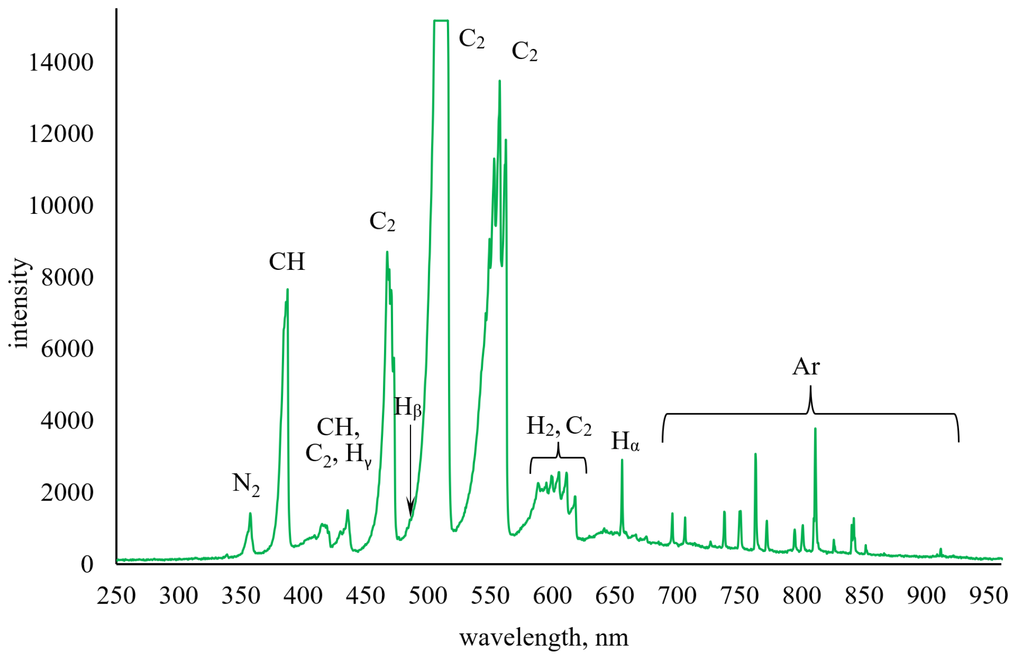

Figure 7. Graph of spectral line intensities depending on the wavelength.

Based on the results of optical spectroscopy of a plasma microwave discharge of a mixture of argon and methane, the major intensity peaks were identified. The graph clearly shows the region of spectral lines inherent in argon in the range from 696.543 to 922.450 nm [26]. The major high-intensity peaks belong to carbon, starting at 460 nm and ending with a series of small peaks at 610 nm [27]. Peaks of molecular hydrogen in the 590–610 nm region are also part of this series [28]. The Balmer series for hydrogen is evident in the graph, but H_β and H_γ merge with the spectral lines of C_2, CH, and O, while the H_α line distinctly stands out at a wavelength of 656.3 nm [29]. Wavelengths of 388 and 436 nm correspond to CH radicals [27,28] and atomic oxygen, and the line at 559.1 nm, merging with the carbon line, belongs to molecular oxygen O_2 [30]. In addition, the graph presents a nitrogen peak with a wavelength of 358.21 nm [31], which confirms the diffusion of air from the surrounding atmosphere into the reaction chamber through leaky seals.

Thus, the presence of hydrogen as a result of exposure to microwave radiation was detected using optical emission spectrometry and mass analysis of methane pyrolysis reaction products. Preliminary calculations of hydrogen selectivity were implemented using the formula [32,33]:

$$S_{H2} = 100\% \times \frac{P_{H2}(yield)}{P_{CH4}(\text{yield})} \quad (2)$$

Using Eq (2), where H_2(yield) and CH_4(yield) are the percentage of hydrogen and carbon after reaction (1), the selectivity of hydrogenwas determined, which was about 4–5%. Currently, these studies continue towards increasing methane conversion and reducing carbon formation on the walls of the reaction chamber.

Further increase in methane conversion and hydrogen selectivity is possible by increasing the temperature of the plasma-chemical reaction by 10–20%, but this may have a negative effect for a reaction chamber made of quartz glass. A significant increase in efficiency will be achieved through the use of catalysts. In particular, the use of metal alloys based catalysts (Fe-Ni, Fe-Mo, Ni-Cu, Ni-Zn, Fe-Pd and Ni-Cu-Al, etc.) will lead to an increase in the temperature of a gas introduced into the reaction chamber, an increase of methane conversion (up to 80–90%), hydrogen selectivity and the efficiency of this installation.

4. Conclusions

An analysis of global technologies and developments of hydrogen production has shown that currently the pyrolysis of methane in a microwave discharge has a high prospect for widespread development. This is due to key factors such as abundant raw materials, low energy costs, high productivity, zero CO_2 emissions and flexible technical specifications.

For pyrolysis, a modern installation with a microwave heating source of natural gas has been developed. Control of the chemical process and management of technological parameters is provided by modern analytical equipment. The configuration of the installation's components is aimed at achieving high hydrogen productivity with the prospect of obtaining carbon materials.

To implement the experiments, the magnetron power parameters, flow rate, pressure and working gas ratio were selected. A mixture of working gases of argon and methane was used in approximate ratio of 1:1. Argon was used as an initiator of the microwave discharge.

It was established that the plasma pyrolysis reaction was achieved in the installation PM-6 at an absorbed discharge power of 0.6 kW. Mass analysis detected 2 amu of hydrogen in the reaction products. Spectroscopic analysis also confirmed the presence of hydrogen, as evidenced by the spectral lines of the Balmer series.

As a result of the endothermic reaction, C_H and C_2 radicals were also observed in the reaction chamber of the installation, which confirm the efficiency of the applied method, as they are products of the pyrolysis process. Elements such as nitrogen, oxygen, and water were identified, which originated from the atmosphere and were discharged during the process.

Based on the applied research on hydrogen production by pyrolysis, primary quantitative and qualitative characteristics of the reaction product were obtained. According to diagnostic and measuring systems, the hydrogen selectivity in the implemented concept at the designed installation was about 4–5%. At the next stage, technical solutions will be introduced to increase the methane conversion, hydrogen selectivity, and eliminate impurities in the reaction chamber of the installation PM-6.

Use of AI tools declaration

The authors declare that they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work presented in this paper.

Author contributions

The list of Authors should accurately reflect who carried out the research and who wrote the article. All multi-authored papers should include an Authors' Contributions' section at the end of the paper. When the corresponding author submits an article, this implies that all authors and responsible authorities where the work was carried out have approved its publication. The corresponding author has to declare the contributions of individual authors when submitting the article. Please follow the ICMJE definitions when defining authorship.

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