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Plasmolysis of methane using a high-frequency plasma torch

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The possibility of converting methane into hydrogen using a high-frequency induction plasma torch at the atmospheric pressure has been experimentally studied. The dependencies of the degree of methane conversion and the rate of hydrogen production were studied depending on the process conditions. It has been demonstrated that the degree of the methane–to–hydrogen conversion can reach values close to 100%.

Keywords: methane plasmolysis, HF plasma torch, hydrogen.

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Nowadays, hydrogen is recognized as one of the purest next-generation energy resources which will be applicable as raw materials for producing chemicals or as power-plant fuel. In this connection, of great interest are hydrogen production techniques free of greenhouse gas emissions. One of such techniques might be methane plasma pyrolysis (plasmolysis) [1–4]. The methane plasmolysis with an arc plasma torch was previously regarded as an acetylene production method exhibiting a high degree of conversion [5,6]. In addition, the methane plasmolysis was considered as a method for obtaining carbon nanopowders and carbon nanotubes [7,8].

Among all the atmospheric-pressure discharges, arc discharges possess the maximum efficiency of the electric energy to gas enthalpy conversion [9,10]. However, spatial confinement of current channels precludes from relying on achieving the methane conversion degree of 100%, a part of the gas can pass through colder sections. A sliding arc [11] or barrier discharge [12] also do not exhibit uniformity of the gas flow parameters. This paper proposes to use for the methane conversion a high-frequency (HF) plasma torch in which it is possible to create a uniform hot gas flow with the parameters necessary for the complete methane conversion. Equilibrium methane dissociation begins at about 500°C and becomes total when approaching 1000°C. Equilibrium products between 1000 and 2500°C are solid carbon and molecular hydrogen. Fig. 1 presents the temperature dependence of the equilibrium composition. Calculations were carried out by using program code TERRA [13]. As the plasma-torch plasma-forming gas, argon is used most often. Taking into account that the plasma-center argon temperature typical of the HF plasma torch is 8000 K and bulk temperature of the entire argon flow is 4000–5000 K, obtain that heating the methane to 1300–2500 K needs an argon flow exceeding the methane flow by 3–12 times.

Experiments on the methane plasmolysis with the HF plasma torch were performed at a plant schematically illustrated in Fig. 2. The HF–emission source was a generator based on lamp GU23-A up to 60 kW in power and 5.28 MHz in frequency. The HF emission excited and maintained in the plasma torch a discharge with the gas-flow vortex stabilization. Diameter of the plasma torch quartz tube was 90 mm; a four-turn copper water-cooled inductor was used. As the plasma-forming gas, high-purity (99.99%) argon was taken. Stable operation of the HF plasma torch was possible in a wide range of parameters: the plasma-forming gas feeding rate of 2–20 m^3/h, power of 2–40 kW. Methane was supplied to the plasma torch lower part through three symmetrically arranged nozzles. The gas feeding rate was controlled by using float-type rotameters. The methane decomposition and mixture cooling took place in the reactor. After that, the substantially cooled gas is fed to the filter. The reactor and filter are airtight cylindrical chambers with water-cooled walls, cone-shaped bottoms and tightly closed collectors for solid-phase products. In the filter, high-temperature cloth FNI-3 was used. After leaving the filter, gas fully cleaned from solid fractions is removed from the system. During the experiments, volume fractions

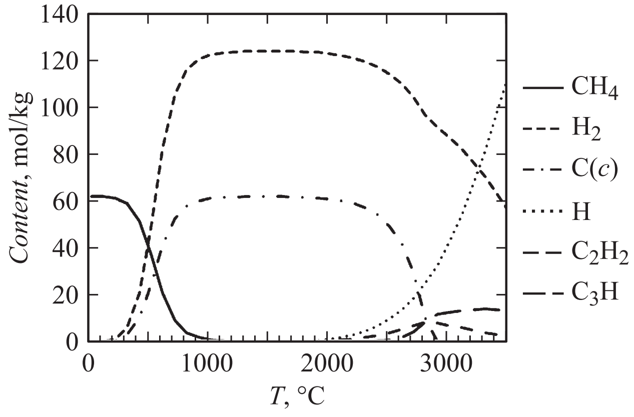

Figure 1. Equilibrium methane composition chart.

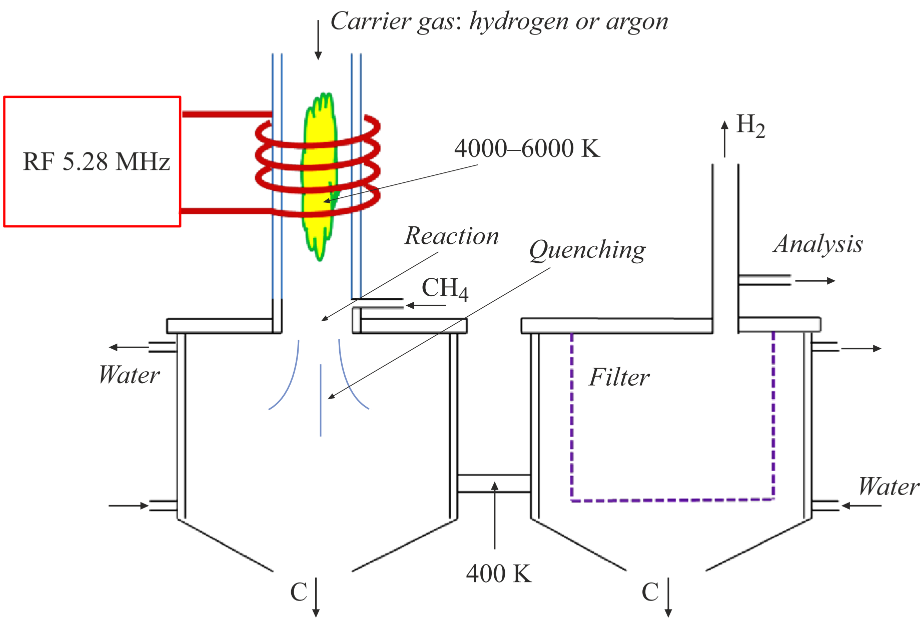

Figure 2. Layout of the methane pyrolysis plant.

of methane, hydrogen, oxygen, gaseous carbon-dioxide and carbon-monoxide were continuously measured with gas analyzer TEST-1. In addition, samples were taken for the purpose of detailed examination and extra control by means of the chromatography-mass spectrometry analysis [14]. The plant operation was monitored by continuously measuring the power absorbed in the cooled loops of the plasma torch, reactor and filter.

In the process of measuring the extent of decomposition in each operating mode of the plant, the gas composition was analyzed uninterruptedly; the experimental procedure was as follows. After purging the plant with argon, the HF discharge was ignited. After that, methane with the preset flowrate was supplied into the system; the gas composition at the system output was measured at a certain plasma torch power. The time of establishment of the stationary distribution of the output flow components was about 3 min. Then the heating power was changed; the measurements were performed at several power levels. Then heating was switched off, and the gas composition in the absence of heating was analyzed. After that, the methane supply was stopped, and the system as a whole was again purged with argon. Thus, the measurements were performed at a fixed gas feeding rate at several heating powers. Then the entire measurement cycle was repeated at another argon/methane ratio.

The measurement result was the volume percentage of each output-flow gas (methane and hydrogen) versus the heating power. In the absence of HF heating (free of plasma), the measured methane percentage $I^0_{CH_4}$ is determined by the supplied gases: $I^0_{CH_4} = Q_{CH_4}/(Q_{CH_4} + Q_{Ar})$, where Q_{CH_4} and Q_{Ar} are the volumetric flowrates of methane and argon fed to the plasma torch, respectively. In the absence of plasma there is no hydrogen at the output of the system ($I^0_{H_2} = 0$).

In the presence of HF heating (with plasma), a part of methane gets converted into hydrogen and soot, and the total output gas flowrate increases. At the system output, methane percentage $I^1_{CH_4}$ and hydrogen percentage $I^1_{H_2}$ are detected. To calculate the total output gas flowrate, assume that all the reacted methane has been converted into hydrogen. The total gas flowrate is $Q_{out} = Q_{Ar}/(1 - I^1_{CH_4} - I^1_{H_2})$. The extent of methane decomposition was calculated via formula $\eta_{CH_4} = 1 - I^1_{CH_4} Q_{out}/Q_{CH_4}$. The maximum thermal efficiency (about 50%) gets achieved at the power of 10–20 kW and plasma-forming gas flowrate above $5\,m^3/h$. Further increase in power leads to a gradual decrease in thermal efficiency of the plasma torch of the given design. Optimal flowrates of the plasma-forming gas and ratios Q_{CH_4}/Q_{Ar} were found for different preset values of the plasma torch power. Fig. 3 presents the dependences of the methane conversion degree (a) and hydrogen flowrate at the reactor output (b) on the methane flowrate at the system input in the plasma torch operating modes with the power and plasma-forming gas flowrate values close to the optimal ones. The power increase results in an increase in the bulk mean enthalpy of the plasma-forming gas, which makes higher the methane conversion degree. At the same time, variation in the plasma-forming gas flowrate within the range of $5-10\,m^3/h$ does not cause significant variations in the methane conversion degree. By reducing the methane flowrate, it is possible to find the $\frac{Q_{CH_4}}{Q_{Ar}}$ ratio at which $\eta_{CH_4} = 1$; by increasing the supplied methane flowrate, it is possible to achieve higher output hydrogen flowrates but at a lower conversion degree. Thereat, energy consumption for the hydrogen production appears to be considerably

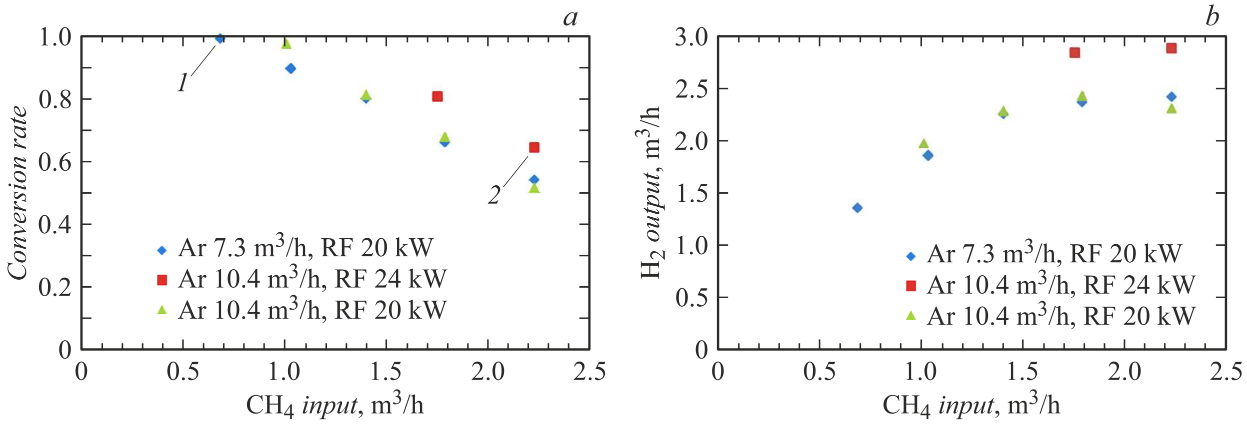

Figure 3. The conversion degree (*a*) and hydrogen flowrate at the system output (*b*) versus the methane flowrate.

(1.8 times) lower than in the case of the 100% conversion. The error in the methane conversion degree and hydrogen flowrate measurements is about 5% and is defined mainly by the measurement accuracy characteristics of optical cells of the TEST-1 gas analyzer, including the „zero drift" during a series of measurements.

To verify the obtained data, samples were taken in the most interesting operating modes, and gas composition was analyzed by chromatography-mass spectrometry. For instance, the gas composition in the mode providing 100% methane conversion (marked as *1* in Fig. 3, *a*) was as follows: H_2 — 15.6%, CH_4 — 0.3%, C_2H_2 — 1.1%, Ar — 83%. In the mode corresponding to the maximum hydrogen flowrate (marked as *2* in Fig. 3, *a*), the gas composition was as follows: H_2 — 20.1%, CH_4 — 3.2%, C_2H_2 — 1.5%, Ar —75.2%. The chromatography-mass spectrometry data confirm the measurements made with a gas analyzer based on optical cells.

As a result, the experimental investigation has demonstrated the possibility of direct methane–to–hydrogen conversion using the HF discharge plasma. It has been shown that the degree of the methane–to–hydrogen conversion can reach values close to 100%. By increasing the methane flowrate, it is possible to achieve significantly (1.8 times) higher hydrogen output at the same energy consumption.

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Conflict of interests

The authors declare that they have no conflict of interests.

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