Study of steam methane reforming in plasma generated by nanosecond surface gas discharge

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Abstract. The paper represents the results of the experimental study of steam methane reforming under the action of spark discharge on water surface. Values of conversion rate and output of reaction products at methane pressures of 1 to 5 atm were obtained, and specific energy consumption of reforming process was determined. Pulse generator with a voltage amplitude up to 200 kV and a pulse duration of 15 ns was used to power the discharge. Although an increase in pressure decreases both the methane conversion rate and the energy deposition into the gas mixture, the conversion efficiency and specific energy consumption remain the same. The obtained minimum value of specific energy consumption for steam methane reforming amounted to 10 eV/molecule.

1. Introduction

Natural gas, composed primarily of methane, is an important source of energy and feedstock for chemical production. Currently, the main method of processing methane is its reforming into the so-called "synthesis gas" (a mixture of hydrogen and carbon monoxide), from which, in its turn, the end chemical products are produced. Additional interest in methane processing is associated with the possibility of relatively cheap production of hydrogen for fuel cells in hydrogen power engineering. Existing chemical technologies for synthesis gas production require heavy capital expenses, as well as complex and expensive equipment. Therefore, the world continues to work on the development of simpler alternative methods for methane reforming at lower costs; an example of such developments is plasma technologies for natural gas processing [1].

The main methane reforming reactions are steam reforming \((\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2)\), dry reforming \((\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2)\) and partial oxidation of methane with oxygen. Steam methane reforming is mainly used in the chemical industry, in existing process units it is implemented at high temperatures (up to 1000°C) and high pressures (up to 40 atm) of the medium. Dry methane reforming, along with the production of synthesis gas, is also interesting due to the possibility of utilizing carbon dioxide, which is one of the main greenhouse gases [2]. Dry reforming and partial oxidation of methane are currently implemented only in experimental process units.

In plasma chemistry, gas-discharge plasma is mainly used for methane reforming reactions [3]. Various types of discharges are used (arc, spark, microwave discharges, DBD, etc.), pulsed and continuous, low- and high-pressure, with different discharge voltages. In our experiments, to generate plasma, we used high-voltage pulsed gas discharges with a duration of several nanoseconds and a voltage up to 200 kV. High voltage ensures gas mixture excitation at pressures up to several atmospheres, and short duration gives a high specific power of the action.
The study of steam methane reforming in the discharge plasma is technically difficult as compared to dry reforming, since it is related to a change in the aggregate state of water in the installation during experiments. But steam reforming, in our opinion, has great opportunities due to the larger availability of reagents. In this paper, to create a plasma medium, we used a discharge on the surface of water, as one of the reacting substances, inside a gas-discharge chamber filled with methane at various pressures. This approach, despite the uncertainty in water vapor concentration in the discharge plasma, nevertheless allows assessing the efficiency of steam methane reforming under the action of a pulsed gas discharge and determining some gas-kinetic regularities.

Earlier in paper [4, 5], when studying dry reforming under the action of pulsed gas discharges of various types, we showed the spark discharge to be the most efficient. Therefore, this paper also focuses on methane reforming in a spark discharge.

Thus, this paper represents the results of experiments on steam methane reforming under the action of a spark discharge at pressures of 1 to 5 atm. The main reforming parameters to be determined were the methane conversion rate and the specific energy consumption per methane molecule, as well as the regularities in the output of reforming products.

2. Experimental setup
The study of steam methane reforming was carried out in the installation, which was previously used in the experiments with dry reforming [6]. The main parts of the installation are the SM-4N high-voltage nanosecond pulse generator and the gas-discharge chamber connected to the output flange of the generator. The diagram of the experimental installation is shown in figure 1(a).

![Diagram of the installation and cross-section of the discharge chamber](image)

**Figure 1.** Diagram of the installation (a) and cross-section of the discharge chamber (b). A – anode, C – cathode, W – window, Rsh – shunt, R1, R2 – voltage divider.

The SM-4N generator has an output inductive energy storage unit with a semiconductor current interrupter based on SOS diodes [7]. The use of an all-solid-state switching system ensures high stability of the generator output pulses and long service life of the device. The specifications of the
SM-4N generator are as follows: the voltage pulse amplitude is up to 200 kV, the current pulse amplitude is up to 3.5 kA, the half-amplitude pulse duration when powering the spark discharge is 15 ns, and the pulse repetition frequency is up to 50 Hz.

The discharge chamber is a stainless steel cylinder with an inner diameter of 8 cm, a length of 20 cm, and a volume of 1000 cm$^3$. The inner surface of the chamber is used as an anode and the central electrode connected to the generator output – as a cathode. The chamber, partially filled with water, is evacuated to a residual pressure of water vapor, and methane is pumped in to the required pressure. The central electrode ends with an asymmetric plate 0.5 mm thick, partially submerged in water (figure 1(b)). A spark discharge occurs on the water surface between the edge of the plate and the side surface of the chamber. The length of the discharge gap is determined by the size of the plate and lies in the range of 10 to 30 mm.

The discharge current was measured with a coaxial shunt located between the generator housing and the discharge chamber. The discharge voltage was determined using the internal divider of the SM-4N generator. The pulses from the shunt and the divider were recorded with a Tektronix TDS 5054 oscilloscope.

The main significant characteristic of the discharge action on the gas mixture is the energy deposition into the gas. To determine the energy deposition, we integrated the product of the discharge voltage and current. Integration, similar to paper [8], was carried out with an oscilloscope simultaneously with recording of current and voltage pulses. For high-voltage nanosecond gas discharges, the energy deposition into the gas is a more consistent parameter than the discharge current or voltage.

The composition of the gas mixture before and after processing was determined using a gas chromatograph. The concentrations of methane, hydrogen and carbon monoxide were measured. Specific energy consumption for reforming a methane molecule was determined as the ratio of the energy deposited in the gas to the decrease in the methane concentration.

The maximum pressure in the discharge chamber was determined by the mechanical strength of the unit structure and gas lines and was equal to 5 atm. The experiments were carried out at room temperature (~25°C).

3. Results
As a result of the experiments, the concentrations of methane and steam reforming reaction products were determined as a function of the deposited energy at various methane pressures. Figure 2 shows the dependences of the methane conversion on the initial gas pressure in absolute and relative units. Although an increase in pressure decreases the relative value of conversion, the absolute value of conversion remains approximately the same. The maximum relative conversion rate is 5.5%, which corresponds to an absolute value of $1 \times 10^{21}$ molecules. With an increase in the pressure of the medium, the energy input to the gas decreases insignificantly. Therefore, the values of specific energy consumption also changes insignificantly and lie in the range of 20–30 eV/molecule (figure 3).

These values approximately correspond to the energy consumption of dry methane reforming under the action of a spark gas discharge, obtained earlier in paper [6]. At the same time, the obtained absolute values of conversion rate are much lower than those of dry reforming. It is explained by the lower energy input for steam reforming.

The main products of steam methane reforming are hydrogen and carbon monoxide. If the formation of hydrogen approximately corresponds to the methane decomposition data, then the output of carbon monoxide is lower than expected. Apparently, it occurs due to the reaction between carbon monoxide and water with the formation of carbon dioxide and hydrogen, wherein carbon dioxide can dissolve in water. The production of hydrogen increases with an increase in the methane pressure, probably due to the more efficient conversion of CO to CO$_2$ at high pressures of the medium.

The methane conversion rate and the output of hydrogen for various interelectrode gaps at a certain initial pressure of the mixture are shown in figure 4 and figure 5. As we can see from figures, a decrease in the interelectrode gap increases the methane conversion rate and hydrogen production.
Figure 2. Dependences of the steam methane reforming on the initial gas pressure, $6 \times 10^3$ pulses.

Figure 3. Specific energy consumption at different pressures, $6 \times 10^3$ pulses.

Figure 4. Methane conversion as a function of the energy input at different discharge gaps. Initial methane pressure – 1.1 atm.

Figure 5. Hydrogen production as a function of the energy input at different discharge gaps. Initial methane pressure – 1.1 atm.

At approximately equal total energy input, the specific excitation power is much higher for a short spark. An increase in the active plasma volume cannot compensate for a decrease in the conversion rate with a decrease in the specific excitation power. Parameters of steam conversion of methane for interelectrode gaps of 9 and 19 mm are given in table 1. When using a spark discharge on the water surface with an interelectrode gap of 9 mm, the minimum value of the specific energy consumption for the steam conversion of methane was obtained. This value is equal to 10 eV/molecule, the initial pressure of methane was 1.1 atm. The obtained value of the energy consumption for the conversion of a methane molecule is approximately two times less than the energy consumption for the dry reforming of methane given earlier in paper [6].

Table 1. Characteristics of steam methane conversion. Methane pressure – 1.1 atm, $7.5 \times 10^3$ pulses.

| Gap (mm) | Pulse energy (J) | Conversion (%) | Conversion (abs, $\times 10^{21}$) | Energy consumption (eV/molecule) |
|----------|------------------|----------------|-----------------------------------|----------------------------------|
| 9        | 0.54             | 13.6           | 2.7                               | 10                               |
| 19       | 0.56             | 6.6            | 1.3                               | 21                               |
4. Conclusion

As a result of the experimental study of the steam methane reforming under the action of a spark discharge on the water surface, it was shown that an increase in the initial pressure of methane from 1 to 5 atm leads to a decrease in the relative degree of conversion. In this case, due to an increase in the concentration of methane molecules, the absolute value of conversion remains the same with increasing pressure. Correspondingly, the specific energy consumption for the conversion of the methane molecule changes insignificantly when the initial pressure changes within these limits.

A decrease in the interelectrode gap while maintaining the pulse energy leads to an intensification of the methane conversion processes due to an increase in the specific power of gas excitation. The lowest energy consumption for the methane conversion was approximately 10 eV per molecule at a pressure of 1.1 atm and at a spark gap of 9 mm.

The products of the reaction are hydrogen and carbon monoxide, and the ratio of the products is shifted towards hydrogen, which can be explained by the reaction between carbon monoxide and water.

Thus, the surface discharge is considered to be a promising source for steam methane reforming. Possible methods to increase the reforming efficiency are to increase the temperature of the mixture, use short spark gaps, and introduce the catalyst into the discharge area.

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