Effect of gas pressure and pulse duration on dry reforming of methane in nanosecond spark discharge

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Abstract. This paper presents the results of experiments on dry reforming of methane under the action of a nanosecond spark discharge at medium pressures up to 5 atm. High-voltage pulse generators with pulse length of 1 to 15 ns and voltage pulse amplitude of 50 to 200 kV were used to power the discharge. It was demonstrated that the spark discharge efficiency significantly exceeds the corona and diffuse discharge efficiency. With increasing pressure, the methane conversion value decreases, and the specific energy consumption increases. As the pulse length increases, the conversion value increases due to the increase in the energy deposition in the gas. The lowest energy consumption for the conversion of a methane molecule was 20 eV per molecule at pressure of 1 atm and discharge pulse length of 15 ns.

1. Introduction
Currently, studies of plasma technologies for processing natural gas are on-going in many countries [1]. The aim of these studies is to develop relatively inexpensive and small-size installations for producing liquid products from methane (the so-called GTL (gas to liquid) installations). Such equipment can be used in small natural gas fields where conventional methods of gas processing and transportation are unprofitable.

One of the promising conversion reactions in plasma chemistry of methane is the reaction of carbon dioxide conversion (dry reforming) between methane and carbon dioxide (\( \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \)). It produces the so-called synthesis gas (the mixture of carbon monoxide and hydrogen), which is then used to synthesize various final products. Reagents of this reaction are gases under normal conditions; they do not generate explosive mixtures – all that simplifies experimentation. Additional interest in this reaction is associated with the possible recover of carbon dioxide in order to reduce the greenhouse effect [2].

Various types of discharges are used to generate plasma medium and perform the methane conversion reaction: corona, high-frequency discharge, dielectric barrier discharge, spark, arc discharge, etc. In recent years, interest in nanosecond discharges has increased again, which provide high excitation power of the medium while retaining the bulk nature of the effect. Moreover, even at a millisecond voltage applied in the barrier discharge, the medium is excited by microdischarges with the pulse length of several nanoseconds.

Earlier in [3] we have demonstrated that the spark discharge is the most efficient when a medium is excited with a short pulse of 1 ns. However, the volume of the gas-discharge chamber during these experiments did not exceed 20 cm\(^3\), and the mixture pressure was 1 atm. For the practical application
of the gas-discharge technology to methane processing, it is required to conduct experiments on larger-scale installations with increased length of discharge pulses. In addition, the natural way to improve the efficiency of the chemical reactions in the gas phase is to increase the mixture pressure. In [4], it was established that for a diffuse discharge of 15 ns, the degree of methane conversion depends heavily on the medium pressure and the ratio of reacting gases. This paper presents the results of experiments on the carbon dioxide conversion of methane under the action of the spark discharge at pressures up to 6 atm. The main definable parameters were the degree of methane conversion and the specific energy consumption for the methane molecule conversion. The paper also contains a comparison of the carbon dioxide conversion efficiency for spark discharges of 1, 5 and 15 ns.

2. Experimental setup
When performing the studies on dry reforming under the action of the nanosecond gas discharge, we used two experimental installations.

![Figure 1. Layout of the installation (a), exterior of the SM-4N pulse generator and the discharge chamber (b). A – anode, C – cathode, W – window, R_{sh} – shunt, R_1, R_2 – voltage divider.](image)

In the first installation, a Proto-1m generator [5] is used as a high-voltage pulse source. The characteristics of the generator are as follows: voltage pulse length – 1 ns, high voltage pulse amplitude – 50 kV, and pulse repetition frequency – up to 100 Hz. The layout of this installation is shown in figure 1a. The pulse from the generator is fed to the discharge cell via a high-voltage cable 1 m long. The discharge cell is made of a quartz tube 20 mm in diameter. The cathode consisted of 4 copper tips 0.3 mm in diameter secured on the high-voltage cable end. A stainless steel disc 15 mm in diameter served as an anode. The spark discharge was generated when the distance between the electrodes was less than 3 mm. The initial pressure of the gas mixture in this installation was 1 atm.

The second installation is equipped with a discharge chamber with a volume of $10^3$ cm$^3$. Earlier we studied the characteristics of corona and diffuse discharges in methane-containing mixtures using this installation [6]. The layout of the installation is shown in figure 1a.

The discharge was generated in a cylindrical stainless steel chamber with a diameter of 80 mm and length of 200 mm. The inner surface of the chamber served as an anode; a single titanium tip was used as a cathode for the spark discharge, and the interelectrode gap was 10 mm. When studying the pulse corona, a central stainless-steel wire electrode 0.3 or 1.6 mm in diameter was used as a cathode. To generate the diffuse discharge, we used star-shaped electrodes made of titanium foil 0.1 mm thick secured on the chamber axis. The interelectrode gap for the pulse corona was 40 mm; for the diffuse discharge, it was determined by the size of the cathode and was within the range from 30 to 15 mm.

To power the discharge in the second installation, we used high-voltage pulse generator SM-4N or generator SM-2S. The SM-4N generator has the following parameters: voltage pulse amplitude – 200 kV, current pulse amplitude – up to 3.5 kA, pulse length when powering the spark discharge – 15 ns, and pulse recurrence frequency – up to 50 Hz. The SM-2S generator has the voltage pulse amplitude of 100 kV and the pulse length of 5 ns. These generators have an output inductive storage with all-solid-state high-voltage circuit switching system [7], which ensures high stability of output.
pulses, long service life, and small dimensions of the devices. Figure 1b shows the exterior of the discharge chamber and the SM-4N pulse generator [6].

To measure the discharge current pulse, a shunt was used between the discharge chamber and generator frame. The voltage pulse from the internal generator divider and the current pulse from the shunt were recorded with an oscilloscope. Since the current and voltage pulses for gas discharges often have an oscillatory component, it was found to be convenient to measure the pulse energy being a more stable characteristic of the discharge [8]. In our experiments, the energy deposition in the gas was determined by integrating the product of the discharge voltage and current. The integrating was performed by the oscilloscope simultaneously with recording of current and voltage pulses.

During the experiments, we measured the methane concentration in mixtures of CH₄ and CO₂ of various content before and after the spark discharge treatment. To measure the methane concentration, we used a gas chromatograph. The specific energy consumption per methane molecule conversion was determined as the ratio of the energy deposition in the gas and the magnitude of the methane concentration change.

The maximum pressure in the chamber was 6 atm, which was determined by strength of the structure and the gas control valves used. The experiments were carried out at room temperature (25°C).

3. Results
When conducting experiments on dry reforming of methane in the nanosecond gas discharge plasma, we determined the dependences of the methane concentration on the pressure for various types of discharges and lengths of the medium excitation pulses. Figure 2 shows the dependences of the methane conversion on the initial gas pressure for the pulse corona, diffuse and spark discharges with a length of 15 ns. As can be seen from the figure, the conversion value for the spark exceeds several times the conversion value in the diffuse and corona discharges. Therefore, further experiments were conducted with the use of the spark discharge. As the gas pressure increases from 1 to 5 atm, the methane conversion decreases from 50 to 10% under identical conditions of the medium excitation.

![Figure 2](image1.png)

**Figure 2.** Dependencies of the methane conversion on the initial gas pressure. CH₄/CO₂ in proportion of 1:1, 1.8×10⁴ pulses.

![Figure 3](image2.png)

**Figure 3.** Dependencies of the conversion value on the pressure for discharges with a length of 5 and 15 ns. CH₄/CO₂ in proportion of 1:1, 1.8×10⁴ pulses.

Figure 3 shows the dependences of the conversion value on the pressure for discharges with a length of 5 and 15 ns. A lower conversion value for the discharge with a length of 5 ns is explained by a lower energy deposition in the gas.

Figure 4 presents the experimental results at different ratios of methane and carbon dioxide in the mixture. As can be seen from the figure, the relative conversion value in percent decreases with the
increase in methane concentration, while the absolute value of the conversion increases due to a higher initial methane concentration.

Figure 4. Methane conversion as a function of the methane concentration. $1.8 \times 10^4$ pulses with a duration of 15 ns.

Figure 5. Dependencies of methane concentration on the energy input to the gas for discharges with a duration of 1 and 15 ns. CH$_4$/CO$_2$ in proportion of 1:1 at a pressure of 1 atmosphere.

To determine the effect of the duration and excitation power of the medium on the processes of carbon dioxide conversion, the high-voltage pulse generators with pulse length of 1, 5 and 15 ns were used to power the discharge. Figure 5 shows the dependencies of the methane conversion value on the energy deposition in the gas for the spark discharge of 1 and 15 ns. It can be assumed that the increase in the length of the excitation pulse significantly increases the methane conversion efficiency.

Figure 6 shows the change in the methane concentration as a function of the number of pulses for the spark discharge of 5 and 15 ns. A large conversion value for the discharge of 15 ns is related to a higher energy of a single pulse. If we look at the dependences of the methane concentration on the energy deposition in the gas for discharges with a length of 5 and 15 ns, they are very close (figure 7).

Figure 6. Methane concentration as a function of the number of pulses for the spark discharge of 5 and 15 ns. CH$_4$/CO$_2$ in proportion of 1:1 at a pressure of 1 atmosphere.

Figure 7. Methane concentration as a function of the energy deposition in the gas for discharges with a length of 5 and 15 ns. CH$_4$/CO$_2$ in proportion of 1:1 at a pressure of 1 atmosphere.
Table 1 shows some characteristics of the pulse generators used and experimental findings when using them. As can be seen from the table, the power of discharges with a length of 5 and 15 ns is approximately the same, which can explain similarity of dependencies in figure 7. At the same time, the power of discharges with a length of 5 and 15 ns is significantly higher than the discharge power with a length of 1 ns. It is apparently for this reason the conversion efficiency for the discharge of 15 ns is higher than for the discharge of 1 ns (figure 5).

**Table 1.** Characteristics of the pulse generators used and the corresponding energy consumption.

| Pulse generator | Pulse energy (J) | Pulse duration (ns) | Pulse power (W) | Energy consumption (eV/molecule) |
|-----------------|------------------|---------------------|-----------------|----------------------------------|
| Proto-1m        | 0.05             | 1                   | $0.5\times10^8$ | 30                               |
| SM-2N           | 0.5              | 5                   | $1\times10^8$   | 19                               |
| SM-4N           | 1.3              | 15                  | $0.87\times10^8$| 20                               |

The estimates of the energy consumption for the conversion of one methane molecule shown in the table also demonstrate that for discharges of 5 and 15 ns the energy consumption is approximately the same and amounts to 20 eV per molecule. For the discharge of 1 ns the specific energy consumption is much higher – about 30 eV per molecule.

**4. Conclusion**

Having studied dry reforming of methane in the nanosecond gas discharge, it was determined that the spark discharge has the highest efficiency among the corona, diffuse and spark discharges. Notwithstanding that it is not a bulk discharge, the conversion value for this type of discharge is several times higher, and the specific energy consumption is several times less than for other types of discharge.

The data obtained showed that as the pressure increases to 5 atm, the conversion value decreases for the spark discharge. Despite the decrease in the specific energy deposition in the gas with pressure increase, the specific energy consumption for the methane molecule conversion increases. The lowest energy consumption for the methane molecule conversion was approximately 20 eV per molecule at a pressure of 1 atm.

As the pulse length of the nanosecond discharge increases, the conversion value increases due to the increase in the energy deposition in the gas in a single longer pulse. The conversion efficiency is influenced by the pulse power; with the same energy deposition in the gas, the conversion efficiency is higher for higher power in the discharge pulse.

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