Characteristics of high pressure nanosecond discharge in methane-containing gas mixtures

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Abstract. A nanosecond discharge of voltage up to 240 kV and pulse length of 10÷25 ns in mixtures of CH₄ and CO₂ at gas pressures up to 6 bar was investigated. For a pulse corona discharge and diffuse discharge from pointed cathodes, the dependences of the energy input in the gas on pressure, gas composition, and electrode geometry were obtained. It is demonstrated that the pulse energy of the diffuse discharge far exceeds the pulse energy of the corona discharge. The maximum specific energy input per pulse for the diffuse discharge was 0.5 J/cm³. The data obtained are necessary to determine the specific energy consumption for methane reforming and correct assessment of the efficiency of discharge technologies for processing natural gas.

1. Introduction

Gas discharges of various types are widely used in plasma chemistry to create an active medium and to perform chemical reactions [1]. With the help of the gas-discharge plasma, the challenges of environment decontamination from industrial pollution, organic substance synthesis, and processing of toxic waste are being met. An important mission of plasma chemistry is to develop an efficient technology for producing valuable liquid products from natural gas (the so-called GTL (gas to liquid) technology). In recent years, interest has risen in plasma techniques for processing greenhouse gases, primarily carbon dioxide [2].

The listed technologies presuppose the processing of large volumes of gases, which makes it necessary to use gas discharges of high (atmospheric and higher) pressure. In addition, application of short nanosecond excitation of the medium makes it possible to realize high specific energy input to the plasma medium and to retain the bulk nature of the effect.

In plasma chemistry, such types of pulse discharges as corona, pulse gliding discharge, spark, and diffuse discharge from pointed electrodes are typically used [3]. And often the change in gas conditions, excitation power, pulse repetition frequency while maintaining the geometry of the electrodes leads to the change in the type of the discharge. Corona and diffuse discharges are more suitable for bulk excitation of the medium; therefore one of the aims of this paper was to determine the conditions for formation of these particular discharges.

Earlier in [4], we have studied the processes of methane reforming in plasma of diffuse and spark discharges at atmospheric pressure. We studied the carbon dioxide conversion of methane (dry reforming): the reaction between methane and carbon dioxide (CH₄+CO₂=2CO+2H₂). This is one of the basic industrial reactions, which solves both the problem of methane processing and reducing...
greenhouse gas emissions. To increase the efficiency of dry reforming, it is planned to increase the pressure of the gas medium to several atmospheres, which involves studying the used discharges at these pressures. In this paper we introduce the discharge characteristics in methane-containing mixtures at pressures up to 6 bar. We primarily focus on a mixture of methane and carbon dioxide in a proportion of 1:1, which is typical for the reaction of dry methane reforming. The discharge efficiency substantially depends on the energy input in the gas. Therefore the main measured parameter of the experiments was the energy input in the discharge. The effect of the mixture proportion, pressure, discharge type, and electrode geometry on the energy input was studied. Considering the estimate of the volume of the excited plasma, data on specific energy input have been obtained, which will allow planning experiments on dry reforming of methane.

2. Experimental setup

The layout of the installation for carrying out studies is shown in figure 1a. The equipment included a discharge chamber, high-voltage pulse generator, recording system and gas system. Figure 1b shows the exterior of the generator and discharge chamber.

![Figure 1. Layout of the installation (a) and exterior of the generator and discharge chamber (b). A – anode, C – cathode, W – window, Rsh – shunt, R1, R2 – voltage divider.](image)

The discharge was generated in a cylindrical stainless steel chamber with a diameter of 80 mm and a volume of \(10^3\) cm\(^3\). The inner surface of the chamber served as an anode, and a central stainless-steel wire electrode of 0.3 or 1.6 mm in diameter was used as a cathode in the study of the pulse corona. To generate the diffuse discharge, we used star-shaped electrodes made of titanium foil of 0.1 mm thick secured on the chamber axis. In this case, the number of electrodes and their shape (the number of beams) could vary and were determined by the purposes of the experiment. The usual number of the electrodes used was from 1 to 3 with 10 beams each. The interelectrode gap for the pulse corona was 40 mm; for the diffuse discharge, it was regulated by the size of the cathode and was within the range from 30 to 15 mm. The end of the discharge chamber was covered with a transparent window made of plexiglas. The maximum pressure in the chamber was 6 bar, which was determined by the structural strength and the gas valves used. The experiments were carried out at room temperature (~25°C).

A high-voltage pulse generator SM-4N [5] was used as a source of discharge power, with the following parameters: voltage pulse amplitude – 180 to 240 kV, current pulse amplitude – up to 3.5 kA, pulse duration – 10 to 25 ns, pulse repetition frequency – up to 50 Hz. This generator has an output inductive storage with all-solid-state high-voltage circuit switching system [6]. The use of semiconductor opening switches (SOS-diodes) in the generator output stage provides high stability of output pulses, long service life, and small dimensions of the device.

To measure the discharge current pulse, a shunt was used between the discharge chamber and generator frame. The voltage pulse from the internal divider of generator SM-4N and the current pulse from the shunt were recorded by Tektronix TDS 5054 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 [7]. In our experiments, the pulse energy was determined by integrating the product of the voltage and discharge current. The integrating was performed by the oscilloscope simultaneously with the recording of current and voltage pulses. The key data were obtained at pulse repetition frequency of 2 Hz.

Figure 2 shows the photographs and corresponding electrode arrangement for the pulse corona and diffuse discharge taken at a frequency of 10 Hz. To reduce the probability of creeping discharges, 5-cm-length dielectric inserts were placed at the edges of the chamber at the electrode attachment points, which covered the inner surface of the chamber. Therefore, for the corona discharge, we estimate the excited volume on the part of the chamber open for the discharge; it makes ~5×10^2 cm^3. For the diffuse discharge, the estimate of the excited volume was performed by the discharge glow. For the electrode with 10 beams and interelectrode gap of 30 mm, we estimate the excited volume as 10 cm^3.

![Figure 2. The pulse corona (a) and diffuse discharge (b). A – anode, C – cathode. Mixture of CH₄/CO₂ in proportion of 1:1 at a pressure of 1 bar.](image)

3. Results

While studying the pulse corona using a central wire electrode, we determined the dependence of the gas discharge pulse energy on the pressure of the medium at different proportions of the mixture. Figure 3 shows these dependences for methane, carbon dioxide and mixture of CH₄/CO₂. As can be seen, the discharge energy rapidly drops with increasing pressure, and the type of the dependence does not change for different proportions of the mixture. Figure 4 shows the effect of the relative fraction of methane in the mixture of CH₄ and CO₂ on the pulse energy. The maximum value of the discharge energy is achieved with a methane content of about 70%. For a methane content of 50%, which is optimum for the reaction of dry reforming, the maximum energy was 2.4 J in the pulse at a pressure of 1 bar. This corresponds to the specific energy input of 5 mJ/cm³. With an increase in pressure to 6 bar, the pulse energy drops down to 0.25 J per pulse. With an increase in the diameter of the central electrode from 0.4 to 1.6 mm the discharge energy decreased from 2.4 to 2.0 J per pulse.

In a number of research, for example in [8], to increase the energy characteristics of the discharge and improve its stability, inert gases, usually argon, were added to the mixture of methane and carbon dioxide. Figure 5 shows the dependence of the corona pulse energy on the pressure for a two-component mixture of CH₄/CO₂ in proportion of 1:1, three-component mixture of CH₄/CO₂/Ar in proportion of 1:1:1, and nitrogen. As can be seen, the addition of argon does not lead to a significant increase in the energy input in the gas as compared to the two-component mixture.

The dependence of the pulse energy in the corona discharge on the pulse repetition frequency for several pressures is shown in figure 6. There is no significant increase in energy input when exceeding the frequency of 5 Hz.

For the diffuse discharge from the pointed cathode, the energy input in the gas far exceeds the energy input of the corona discharge with the wire cathode located on the chamber axis. Figure 7 shows the dependence of pulse energy on pressure for methane, carbon dioxide and mixture of CH₄/CO₂ in proportion of 1:1 when using the diffuse discharge. The dependence for the corona
discharge is given for comparison. In the case of 10-beam cathodes with a gap of 30 mm, the discharge energy is 5 J per pulse at a pressure of 2 bar and mixture of CH$_4$/CO$_2$ in proportion of 1:1. Specific energy input reaches 0.5 J/cm$^3$. The energy input in the corona discharge equals to 1.4 J under the same conditions.

Figure 3. Dependences of corona pulse energy on gas pressure.  

Figure 4. Dependences of corona pulse energy on methane concentration.  

Figure 5. Dependences of corona pulse energy on gas pressure. The effect of adding argon to the mixture.  

Figure 6. Energy input in corona discharge as a function of pulse repetition frequency. CH$_4$/CO$_2$ in proportion of 1:1.

However, as is clear from the figure, at pressures above 3 bar, the energy input for the diffuse discharge is rather small. A natural way to increase the current and thus the pulse energy at high pressures is to reduce the discharge gap. Figure 8 shows the pulse energy as a function of the pressure at different discharge gaps. Reducing the gap between the cathode and the chamber from 30 to 20 mm increases the discharge energy by several times. For example, for a pressure of 4 bar, the pulse energy increases from 0.4 to 3.6 J, and at a pressure of 3 bar from 1.8 to 7.7 J per pulse. The discharge is steadily generated at pulse repetition frequencies up to 25 Hz. At higher frequencies, periodic sparkovers in the interelectrode gap appear. Closing the anode with a dielectric to prevent sparkovers significantly reduces the current and, accordingly, the energy input in the gas (see, figure 8).

Since the excited volume for the diffuse discharge is localized near the tips, it is possible to increase the total energy of the discharge by using a large number of pointed cathodes. For example, the increase in the number of tips from 4 to 20 increases the discharge energy by a factor of 2 from
1.35 to 2.7 J (with the gap width of 30 mm, pressure of 3 bar and mixture of CH₄/CO₂ in proportion of 1:1).

Figure 7. Dependences of pulse energy on pressure for diffuse discharge.

Figure 8. Discharge energy as a function of pressure at different gaps (diffuse discharge, CH₄/CO₂ in proportion of 1:1).

4. Conclusion
In the study of the pulse corona discharge from the cylindrical wire cathode and the diffuse discharge from the pointed cathodes in methane-containing mixtures, it was demonstrated that the pulse energy of the diffuse discharge far exceeds the pulse energy of the corona discharge. The maximum specific energy input for the diffuse discharge was 0.5 J/cm³. To maintain high specific energy inputs when passing to high pressures of the medium, it is necessary to drastically reduce the discharge gaps. The increase in the total energy of the discharge can be achieved by increasing the number of the pointed electrodes.

Thus, we believe that the use of the nanosecond diffuse discharge is more promising for studying the dry reforming of methane under the action of the gas discharge at pressures of several atmospheres.

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