Studies of electric and spectral characteristics of surface spark discharge in atmosphere of carbon dioxide. Conversion of CO$_2$ and CO$_2$:H$_2$ to CO

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Abstract. The results are presented from studies of the high-voltage pulse-periodic surface spark discharge propagating along the water-gas interface. In the case of CO$_2$ or CO$_2$:H$_2$ mixture used as gaseous medium, the plasma-chemical conversion of CO$_2$ to carbon monoxide CO was also studied. In the experiments, we used the generator with reservoir capacitor energy of 1.6 J, a voltage of 20 kV, and pulse duration of 2–3 μs. The average velocity was determined of the discharge propagation along the water surface in the CO$_2$, CH$_4$ and Ar atmospheres. It was shown that the leader velocities in the CO$_2$ and CH$_4$ atmospheres coincide, and they turned out to be 3–4 times lower than that in the Ar atmosphere. The integrated emission spectra are presented of the discharge in the CO$_2$ atmosphere, in which the lines corresponding to CO$_2$, CO, H$_\alpha$, H$_\beta$, and OI are distinguished. The electron concentration in the discharge channel was $N_e = 10^{17}$ cm$^{-3}$. The dynamics of conversion of CO$_2$ to CO was traced at different energies inputted into the discharge. For the discharges in the atmospheres of CO$_2$ and CO$_2$:3H$_2$ mixture, the degrees of conversion were 24 and 61%, respectively. And in the quasi-linear stage, the energy efficiencies of conversion were $\sim$13 and $\sim$6 eV per molecule for the CO$_2$ and CO$_2$:3H$_2$ atmospheres, respectively.

1. Introduction
The goal of the studies performed was to solve one of the most pressing environmental problems: the problem of reducing the carbon dioxide content in the atmosphere and utilizing carbon dioxide recovered from the air or localized industrial or natural CO$_2$ outbursts. At present, the problem of developing the technology for “recovering”, collecting and burying the excess carbon dioxide seems to be fundamentally solvable, while the acceptable solutions to the problem of converting CO$_2$ to the
products demanded by the technology and power industries have not been adequately developed (especially, if we take into account the required productivity and the acceptable energy cost of conversion) [1–3].

Previously, the CO$_2$-to-CO conversion occurring in the plasma-chemical processes was considered involving different methods for discharge excitation: the glow [4–6], RF [7–9], and microwave [10–21] discharges were used. In this work, we used the surface high-voltage pulse-periodic spark discharge [22] developing at the liquid-gas interface. This type of discharge is of great interest due to its natural manifestations (lightning “striking” into water or wetted earth), as well as its applications in modern technologies [22–29] (water purification, plasma chemistry, etc.). In particular, the plasma formation in the presence of the liquid phase breaks new grounds in plasma-chemical synthesis or the formation of nanoparticles directly in liquids.

Dissociation of gas molecules and water vapors, as well as generation of UV radiation and active particles, occurs in the high-temperature discharge channel. The advantages of the proposed discharge system design are the possibilities of obtaining considerably long discharge channels and changing the discharge parameters by means of varying the conductivity of water at considerably high energy loads. In [28, 29], under conditions close to those of the experiments presented in this work, the characteristics of the surface discharge at atmospheric pressure in the air and argon were studied. The discharge system design with the extended underwater electrode and the generator with a storage capacitor energy of 1.6 J, a voltage of 20 kV, and pulse duration of 2–3 μs were used. The concentration and temperature of electrons and heavy particles were determined.

The plasma-chemical method, the conditions for which can be realized in a pulsed high-voltage discharge, was adopted as a possible method for the CO$_2$ conversion. The following gases were tried to be the initial gas medium: CO$_2$ and CO$_2$:3H$_2$ mixture. We chose such gas mixtures because it is well-known from the conventional chemistry that it is fundamentally possible to obtain high coefficient of conversion (90% or even more) of carbon dioxide to synthesis gas in the following reaction:

$$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + 2\text{H}_2 \quad (1)$$

However, it is difficult to realize the resource of this method within the framework of thermo-equilibrium chemistry, since high coefficients of conversion can be obtained at gas temperatures exceeding 1000 °C.

The use of the plasma-chemical methods makes it fundamentally possible to avoid difficulties that in some cases are irresistible within the framework of the conventional chemistry. In particular, it is possible to get over the difficulties occurring due to high temperature thresholds of reactions.

The paper presents the results of the experiments on the plasma-chemical conversion of CO$_2$ and CO$_2$:3H$_2$ to carbon monooxide CO. The experimental conditions are similar to those described in [25].

2. Experimental setup

The reactor schematic is shown in figure 1. Its design allows operating both in the closed volume, and under conditions of gas circulation.

Rectangular plexiglass cell (1) was completely filled with water (2) with the help of water valve (3), and then some part of water was forced out by gas mixture (4) prepared in advance (gas valve (5) was used for puffing gas mixture). The volume of reactor working chamber (1) was 200 cm$^3$; in the course of experiments, the volume of gas above the water surface varied from 30 to 100 cm$^3$. The electrodes were made of 1.5-mm-diameter copper wire. Negative electrode (6) consisted of the above-water and underwater parts (the underwater part was 10 cm in length, and its depth of submergence was 0.5–1 cm). Positive electrode (7) was sharpened, and it was located above the water at a distance of 1–3 mm from its surface. Power was supplied from the pulsed generator (U ≤ 20 kV) with the storage capacity C = 10$^{-8}$ F and the thyratron-based trigger circuit (energy of the storage capacitor was E ≤ 1.6 J). The pulse repetition rate was ≤100 Hz.
For recording the current and voltage, we used the 1:10 current transformer of the Rogowski coil-type (Stangenes Industries) and the 1:1000 voltage divider (Tektronix P6015A), respectively. The signals were fed to the input of the double-beam oscilloscope (Tektronix TDS 1002B). The discharge emission spectra were recorded using the Ava Spec 2048FT spectrograph. When measuring the conductivity of water, the HANNA DIST-5 HI 98312 conductometer was used.

The discharge photos in the uncompleted and completed stages are shown in figure 2. The underwater part of the electrode helped to stabilize the direction of the leader propagation from pulse to pulse. The current and voltage waveforms shown in figure 3 correspond to the surface discharge propagating in the CO$_2$ atmosphere. From the waveforms, it follows that the discharge proceeds in two stages: (a) the low-current stage (currents are $I \sim 15$ A, $\tau = 1$ μs); and (b) the high-current stage (the maximum current is $I = 250$ A, $\tau = 2$ μs, the gases are CO$_2$ and CH$_4$). In this case, the (a) and (b) stages are the leader and spark stages of the discharge. The waveforms almost coincide for the atmospheres of CO$_2$, CH$_4$ and the CO$_2$:3H$_2$ mixture. The mean leader propagation velocity can be estimated based on the duration of the first discharge stage. Taking into account that the spark channel length is 7 cm, we obtain $V=7 \cdot 10^6$ and $3 \cdot 10^7$ cm/s for the CO$_2$ and CH$_4$ gases and for Ar, respectively. In the (a) stage, the current circuit becomes closed through the water, so the considerable part of energy is released in the water. In the (b) stage, the most of energy is released in the highly conductive spark channel.

The time-integrated emission spectra (350–800 nm) of the discharge in CO$_2$ atmosphere are shown in figure 4. These spectra are characterized by the presence of hydrogen lines of the Balmer series (H$_\alpha$, H$_\beta$), the line of neutral oxygen atom OI and the dicarbon band (the Swann band). Assuming the Stark collisional mechanism for broadening of hydrogen lines [23], we determined the electron concentration in the spark discharge stage to be $n_e=10^{17}$ cm$^{-3}$, which coincides with the result obtained in [24] for air. The most informative is the spectral range (400–520 nm) shown in figure 4b for the
As can be seen from the figure, the presence of bands corresponding to CO$_2$, CO, and C$_2$ is typical. We note that the shape of the spectrum does not change with discharge duration increasing within a certain range.

3. Conversion

Two series of experiments were performed on the conversion of carbon dioxide. In the first and second series of experiments, the discharge proceeded in the atmospheres of CO$_2$ and CO$_2$:3H$_2$ mixture, respectively.

We consider the first case. The reactor was filled with water, and then carbon dioxide was injected into it, which displaced part of the liquid and filled a volume of up to 100 cm$^3$. The experiment was carried out under the following conditions: the pulse repetition rate was 50 Hz, the fluid conductivity was 100 μS/cm, and the voltage was 20 kV. The experiment was performed both under stationary conditions and under conditions of gas circulation. In both cases, the results on carbon dioxide transformation almost coincide. The degrees of CO$_2$-to-CO conversion as functions of the specific energy input (which is defined as the ratio of the energy inputted into the discharge to the volume of the processed gas) are shown in figure 5. The Specord M-80 IR absorption spectrometer was used to determine the degree of conversion.

It can be seen from the results presented that, at specific energies higher than 20 J/cm$^3$, the conversion curve reaches its saturation. And in these experiments, the maximum degree of conversion was 23%. The experiments on conversion were also performed in the regime of gas circulation. The gas flow rate was 0.5 l/minute. The gas sample taken at the outlet of the cell was analyzed using the IR spectroscopy technique. The results obtained on the conversion coincide with those of the closed-volume experiments: at equal inputted energies, the degrees of conversion are the same.

The next experiment on conversion in the atmosphere of carbon-hydrogen mixture was performed as follows. The chamber was filled with the working mixture: the CO$_2$ to H$_2$ ratio was 1:3, respectively.

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The change in gas pressure in the chamber was recorded using the combined pressure-and-vacuum gage.

Since reaction (1) proceeds with a decrease in pressure (due to the fast condensation of water formed in the course of this reaction), the combined pressure-and-vacuum gage was also used to determine the degree of conversion of the initial mixture to synthesis gas along with the IR spectroscopy analysis of the reaction products (CO and CO₂). During the experiment, the temperature was controlled, which remained almost unchanged. During this reaction, the release of the carbon solid phase was not observed.

The degree of conversion of the CO₂+3H₂ mixture to the synthesis gas CO+2H₂ as a function of the specific energy input is shown in Fig. 5b. The results were obtained by means of measuring a change in the pressure in the closed volume with allowance for the fact that, as a result of the reaction, three gas molecules and one H₂O molecule (in the liquid phase) form from the initial four gas molecules.

4. Discussion

During the process of gas treatment, an increase in the water conductivity is observed. Apparently, this happens due to the dissolution of CO₂ in water and its acidulation in accordance with the following reaction:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+ \]

The acidulation of the solution, which occurs in a considerably large number of discharge pulses, changes the discharge conditions. At the beginning of a series of discharges, the discharges are completed, and then the discharges become transformed into the uncompleted ones. We note that all results on the conversion of CO₂ to CO were obtained under conditions, in which the acidulation had almost no effect on the discharge characteristics.

The main product of the CO₂ treatment is carbon monoxide CO. The mechanism for its formation can be represented by a sequence of the following reactions:

\[ \text{CO}_2 \xrightarrow{\text{discharge}} \text{CO} + \text{O} \]
\[ \text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} \]
\[ \text{O}_2 \xrightarrow{\text{discharge}} 2\text{O} \]
\[ \text{CO} + \text{O} \rightarrow \text{CO}_2^* \]
\[ \text{CO}_2^* + \text{M} \rightarrow \text{CO}_2 + \text{M} \]
\[ \text{CO}_2^* + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{O} \]
The presence of the lines corresponding to in the discharge emission spectrum indicates that in the course of discharge, further conversion of CO takes place:

\[ CO_{\text{discharge}} \rightarrow C + O \]

As noted above, during the gas treatment, the rate of CO release considerably decreases (figure 5). The dependence of the CO concentration on the number of discharge pulses becomes almost saturated. This may be due to reaching the quasi-equilibrium CO concentration in the course of accumulation of the CO and O\(_2\) reaction products. This hypothesis is supported by the fact that the CO yield increases when hydrogen is present in the gas mixture and efficiently binds the produced oxygen (2H\(_2\) + O\(_2\) = 2H\(_2\)O). Another possible reason for slowing down the process of CO release is the subsequent decomposition of CO molecule. However, in this case, we should believe that the efficiency of CO decomposition is sufficiently high and, therefore, a considerable amount of graphite should be produced. In our experiments, the formation of graphite was not observed.

The energy yield of CO can be estimated from the available data corresponding to the initial stage of CO\(_2\) decomposition when the reverse reactions, as well as the reactions of further CO conversion, are inessential. For example, when 100 cm\(^3\) of CO\(_2\) are exposed to 100 discharge pulses, the concentration of CO produced in the closed volume will be 19.6 g/m\(^3\) or 0.7 mol/m\(^3\). Therefore, 7\(_{-10}^{-5}\) mol of CO is produced in 100 cm\(^3\). If we assume that 1 J is inputted into the discharge per one pulse, then energy of 100 J is spent on the formation of 7\(_{-10}^{-5}\) mol of CO. Thus, for CO\(_2\) and CO\(_2\):3H\(_2\) mixture, the energy yields of CO are \(\approx 13\) and \(~6\) eV/molecule, respectively.

5. Conclusions
The first experiments performed have demonstrated the high efficiency (up to 65%) of carbon dioxide conversion to synthesis gas under the effect of surface discharge. These results indicate that it is reasonable to continue the theoretical and experimental studies in this field of research, primarily in the field of determining the optimal conditions for the plasma-chemical utilization of CO\(_2\) and formulating requirements for the structure and characteristics of the device intended to operate with high output.

The work was supported by the Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences under the State Assignment (program No. 47.16 “Chemical aspects of power engineering; modeling of oxidation and combustion processes”, state registration number AAAA-A20-120020590084-9).

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