Suppression of reverse reactions during carbon dioxide decomposition in microwave discharge plasma

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The paper investigates the decomposition of carbon dioxide (CO_2) in a plasma maintained by microwave radiation from a gyrotron at a frequency of 24 GHz in a waveguide plasmatron in a flow of argon and CO_2. An increase in the degree of CO_2 conversion and energy efficiency up to 2.5 times was demonstrated due to cooling (quenching) of the post-discharge region by a counterflow gas. It is shown that the cooling efficiency depends on the density and heat capacity of the quenching gas, and the maximum degree of conversion is achieved when nitrogen and argon are used as quenching gases.

Keywords: CO_2 conversion, atmospheric pressure discharge, gyrotron, qenching.

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One step in reducing greenhouse gas emissions is to convert them into marginal chemical products using energy from renewable sources. In particular, the decomposition of carbon dioxide produces carbon monoxide, which can serve as a feedstock for the production of hydrocarbons, including methanol, dimethyl ether, and the Fischer–Tropsch process. Promising are plasma-chemical methods of carbon dioxide conversion in the plasma of various microwave-discharges, where due to stepwise excitation by electrons ($\sim 0.2-0.3$ eV) of vibrational degrees of freedom of CO molecules $_2$ their dissociation [1] takes place. In the present work, the discharge in a previously developed waveguide plasmatron [2] is supported by microwave-radiation from a gyrotron with frequency 24 GHz and power 20−5000 W. The use of shorter-wavelength radiation in comparison with traditionally used microwave-discharges with frequency 2.45 GHz allows to significantly increase the specific energy input and plasma density, which in turn increases the rate of plasma chemical reactions [3]. One of the factors reducing the efficiency of plasma chemical methods for CO_2 decomposition is the occurrence of reverse reactions in the plasma. Therefore, more and more attention is being paid to rapid cooling (quenching) of the gas mixture in order to suppress reverse reactions [4]. In the present work, a cold gas stream fed into the plasma torch region at the outlet of a microwave-plasmatron is proposed to be used for quenching.

The plasmatron (the scheme is shown in Fig. 1) is an extension of the supersized waveguide path of the gyrotron with an inner diameter of 32.6 mm, to which it is connected through a vacuum window made of boron nitride. In order to raise the radiation power density, the waveguide is made gradually tapering with a conical horn with a length of 60 mm and an outlet aperture of 10 mm at the end. The volume of the conical section is 23 cm ^{3}. The plasmatron is connected via a standard CF160 vacuum connection to a 10 l volume expansion chamber in the shape of a standard six-way cross. The plasma-forming gas (argon) enters the plasmatron through three symmetrically arranged tubes that make an angle 30° with the plasmatron cylinder. This tangential gas influx allows one to form swirling gas flows, thus limiting the area of contact of hot plasma with the waveguide walls. Carbon dioxide is supplied through a waveguide tee on the input side of the microwave-window. The quenching gas is supplied to the base of the plasma torch through a copper tube with four holes of 1 mm diameter. All gases are supplied to the plasmatron at atmospheric pressure using Bronkhorst gas mass flow controllers. The discharge is initiated by briefly inserting a thin metal wire into the horn. To determine the qualitative and quantitative composition, some of the reaction products from the chamber are directed to a gas analyzer „TEST-1“ measuring the volume fractions of gases: CO_2, CO, O_2.

The main parameters investigated are as follows:

1) Conversion rate (fraction of decomposed carbon dioxide molecules)

$$K_{CO_2} = \frac{CO_2(off) - CO_2(on)}{CO_2(off)} \cdot 100\%,$$

where CO_2 (*off*) — carbon dioxide concentration in the absence of microwave-radiation, CO_2 (*on*) — carbon dioxide concentration in the presence of microwave-radiation and plasma;

2) SEI (specific energy input) — microwave-radiation energy in terms of one molecule of CO_2,

$$\mathrm{SEI}\left[\frac{\mathrm{eV}}{\mathrm{molec}}\right] = \frac{P_{input}[\mathrm{W}]}{F(CO_2)[\mathrm{l/s}]} \cdot 2.54 \cdot 10^{-4}\,\frac{\mathrm{eV}\cdot 1}{\mathrm{J}\cdot\mathrm{molec}},$$

Where P_{input} — input microwave power, $F(CO_2)$ — flux CO_2;

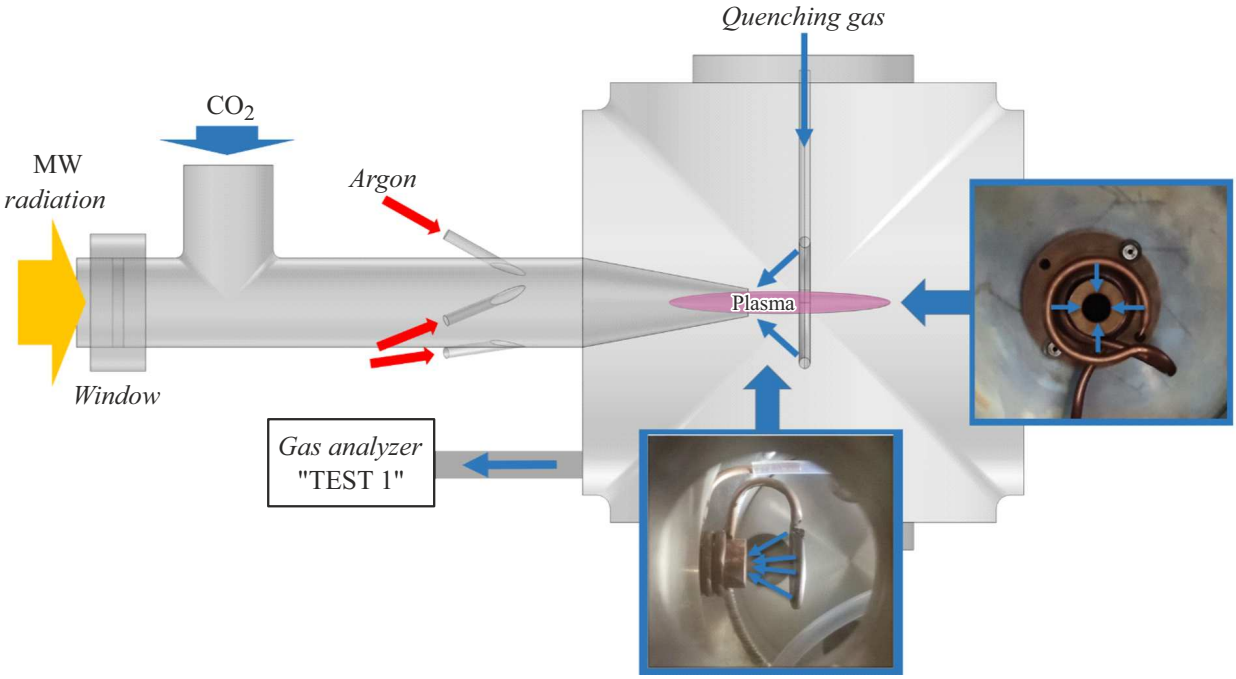

Figure 1. Schematic diagram of a waveguide plasmatron with combined gas supply.

3) energy efficiency (fraction of microwave-radiation energy spent on CO decomposition $_2$)

$$\eta = K_{CO_2} \cdot \Delta H / \mathrm{SEI}\,[\%],$$

where $\Delta H = 2.93$ eV/molec — specific enthalpy.

The discharge supported by microwave-radiation in a plasmatron at atmospheric pressure consists of two qualitatively different regions. The direct reaction region is located in the conical constriction zone of the plasmatron, where, according to estimates of the rotational temperature of CO_2 molecules from optical measurements, the highest temperature 4000–5000 K is reached. In this zone, the chemical equilibrium is strongly shifted towards the reaction products, and almost complete decomposition of carbon dioxide occurs: $2CO_2 \rightarrow 2CO + O_2$. After the region of strong field at the plasmatron outlet, a region of reverse reactions is formed, which is a plasma torch with a length of 6–10 cm at the plasmatron outlet. In it, cooling of the reaction mixture occurs mainly due to convective heat exchange with the atmosphere formed in the chamber, this leads to a shift in chemical equilibrium. Cooling from 3000 to 2000 K plays a key role, since it is in this temperature range that the rate of reverse reactions increases: $CO + O_2 \rightarrow CO_2 + O$, $CO + O + M \rightarrow CO_2 + M$. At slow enough cooling the gas mixture, passing sequentially through all equilibrium states, will completely pass back to CO_2, therefore, to obtain the required products (carbon monoxide and oxygen) it is necessary to fix the composition of the gas mixture. This can be achieved by rapid cooling (quenching) to a temperature of $\sim$ 1500 K so that reverse reactions do not have time to take place. The quenching rate shall be 10^6–10^7 K/s [4].

Figure 2 shows the degrees of conversion and energy efficiency using different quenching gases for one of the stable regimes of discharge maintenance, and Figure 3 — photographs of the plasma torch (backreaction region) under the same conditions. The flow of each of the quenching gases was maintained at 3 l/min. Without quenching in the selected mode, the conversion rate was 12.2%. When nitrogen was supplied at a rate of 3 l/min as a quench gas, the conversion rate increased more than 2 fold (to 25.7%), while the shape of the plasma torch was significantly deformed and the length decreased to 2–3 cm (Fig. 3, *b*). Similar results were obtained when argon was supplied: the conversion rate was 26% and the torch length was reduced to 1.5–2 cm (Fig. 3, *d*). Under the same conditions, helium turned out to be a less effective quenching gas, as the conversion rate increased only up to 20% and the torch length remained practically unchanged (Fig. 3, *c*).

Argon in comparison with helium provided a greater increase in the degree of conversion because its density is 10 times greater, which means that at the same flows of these gases argon jet has a much greater dynamic effect on the torch and contributes to a more effective heat exchange of the gas mixture from the plasmatron with the atmosphere formed in the chamber.

The density of argon is 43% higher than that of nitrogen, and the deformation of the plasma torch turned out to be more significant when using the denser gas. However, the increase in CO_2 conversion rate (to $\sim$26%) was almost identical in both cases. Note that in the experiments with nitrogen as quench gas, samples were taken for analysis

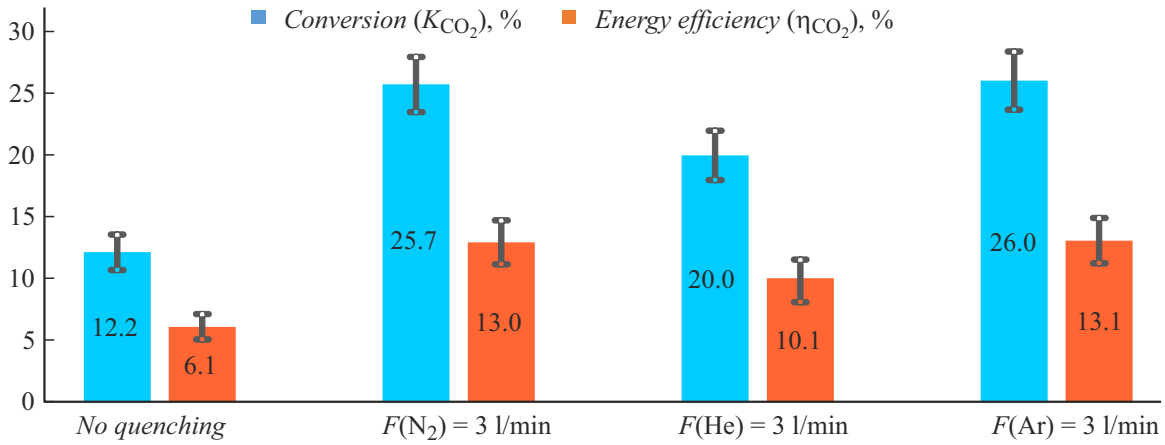

Figure 2. Effect of quenching on conversion rate and energy efficiency. Flows of gases into the plasmatron: $F(\mathrm{Ar}) = 4.25$ l/min, $F(\mathrm{CO_2}) = 0.8$ l/min, microwave power-emission $P = 305$ W, SEI = 5.82 eV/mol.

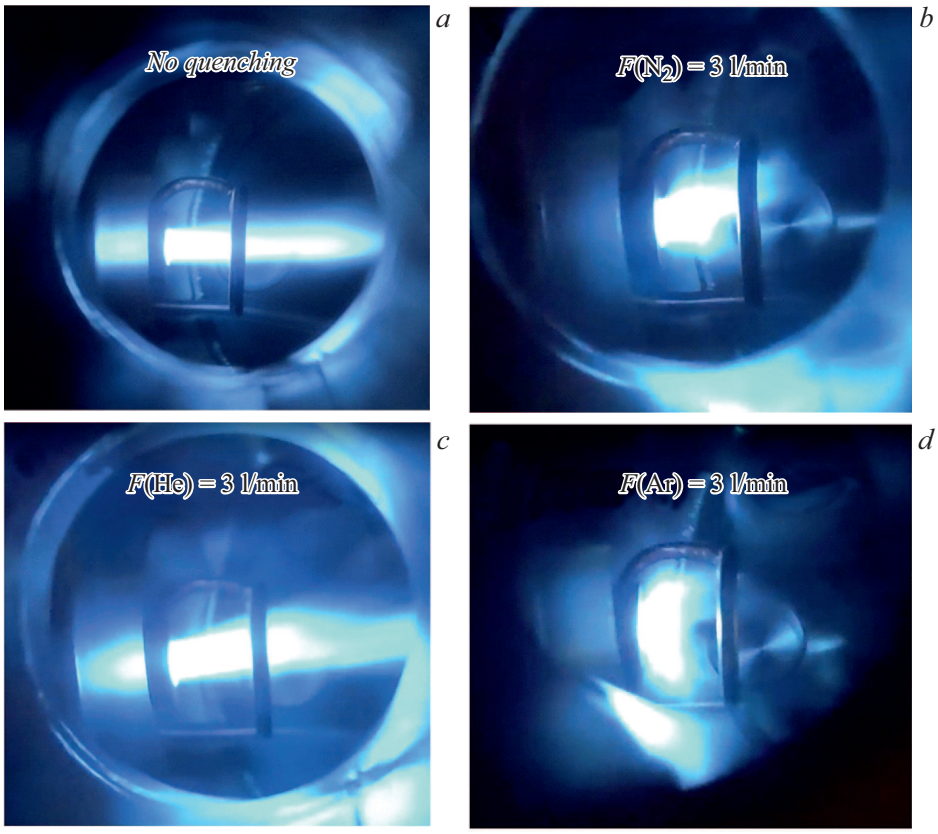

Figure 3. Photographs of the plasma torch when different quenching gases are supplied.

by gas chromatography-mass spectrometry, which showed the absence of nitrogen oxides. The close values of the conversion rate when using argon and nitrogen can be explained by differences in their molar heat capacities. Thus, the molar heat capacity of one-atomic argon at constant pressure is $C_p(\mathrm{Ar}) = 20.8$ J/(mol·K), while that of molecular nitrogen is $C_p(\mathrm{N_2}) = 29.1$ J/(mol·K), and the heat capacity of nitrogen increases with temperature up to $C_p(\mathrm{N_2}) = 37.4$ J/(mol·K) at 3340 K due to the appearance of vibrational degrees of freedom. To estimate the effect of differences in molar heat capacity on the cooling process, we neglect all heat exchange processes except heat transfer between the hot gas stream from the plasma gun and the quenching gas.

The heat balance equation for this process is as follows

$$C_p(\mathrm{Ar})F(\mathrm{Ar})(T - T_{heat}) + C_p(\mathrm{CO_2})F(\mathrm{CO_2})(T - T_{heat}) + C_p(q.gas)F(q.gas)(T - T_0) = 0,$$

where *q. gas* — quenching gas (argon or nitrogen), C_p [J/(mol·K)] — molar heat capacity of the corresponding gases taking into account its temperature dependence due to the effect of degrees of freedom unfreezing, T_{heat} — the temperature of heating of the mixture of Ar and CO_2 by microwave-radiation in the plasmatron, T_0 — the temperature of the supplied quenching gas (argon or nitrogen), T — the final temperature of the mixture.

Assuming $T_{heat} = 4500$ K and $T_0 = 300$ K, heat exchange with argon will reduce the temperature to 3750 K, while the same flow of the more heat-intensive nitrogen will reduce the temperature of the mixture to 2780 K. The above calculation does not take into account convective heat exchange with the chamber atmosphere and the heat effect from exothermic reverse reactions in the postdischarge region; therefore, it allows us to estimate only approximately the influence of the molar heat capacity of the quenching gas on the quenching efficiency.

At present, the plasma chemistry community has focused its efforts to increase the degree of conversion on developing methods of quenching reaction products, including such methods as passing a swirling gas stream through an expanding nozzle [4], lowering the gas temperature by heat exchange in thin water-cooled outlet channels [5]. The use of an expanding nozzle (first method) at a pressure of 0.7 atm increased the conversion rate and energy efficiency from $K_{CO_2} = 5\%$, $\eta = 4\%$ up to $K_{CO_2} = 8\%$, $\eta = 6.5\%$ at SEI = 4 eV/molec and with $K_{CO_2} = 10.5\%$, $\eta = 26\%$ up to $K_{CO_2} = 13\%$, $\eta = 31\%$ at SEI = 1.3 eV/molec. The second method at a pressure of 0.9 atm and SEI = 3.6 eV/molec allowed to raise the conversion rate and energy efficiency from $K_{CO_2} = 13\%$, $\eta = 12\%$ to $K_{CO_2} = 31\%$, $\eta = 37\%$. On the background of the given world results on CO_2 decomposition, the quenching method proposed in the present work looks original and promising.

Thus, the work experimentally demonstrated the possibility of increasing the conversion rate and energy efficiency up to 2.5 times by reducing the role of reverse reactions by rapidly lowering the temperature by cold gas flow. It is shown that quenching efficiency is determined by the flow of quenching gas, its molar heat capacity and density.

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Conflict of interest

The authors declare that they have no conflict of interest.

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