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Carbon dioxide conversion in microwave discharge plasma with counter-flow gas quenching

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Decomposition of carbon dioxide in plasma supported by magnetron radiation with a frequency of 2.45 GHz in the flow of carbon dioxide at atmospheric pressure has been studied. It is shown that quenching of reaction products by a counter flow of gas, more than 1.5 times increases the degree of conversion and energy efficiency of carbon dioxide decomposition. At record values of energy efficiency of 43.9% and conversion of 14.3%, the carbon monoxide yield with productivity of 0.2 kg/h at microwave radiation energy consumption of 6.56.5 kW · h/kg is provided.

Keywords: Microwave heating, atmospheric pressure discharge, carbon dioxide, quenching.

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Various atmospheric pressure discharges, wherein the dissociation of CO_2 molecules proceeds in low-temperature plasma due to the stepwise excitation of vibrational degrees of freedom by electrons and excited molecules [1,2], are currently being used more and more often for conversion of carbon dioxide (CO_2) into high-margin products. Plasma methods do not require chemical precursors and, most importantly, may be applied in the „start/stop“ mode that is typical of renewable energy sources. Being fundamentally electrodeless, a microwave discharge appears to be the most likely underlying physical mechanism for prototype plasma-chemical setups for CO_2 conversion into carbon monoxide [3–5]. As was found in recent studies [6], limit levels of conversion and energy efficiency of the CO_2 decomposition process have been reached in microwave discharge plasma at atmospheric pressure. Reverse reactions of CO recombination into CO_2 ($CO + O + M \rightarrow CO_2 + M$, $CO + O_2 \rightarrow CO_2 + O$) proceeding in plasma are among the factors limiting the efficiency of plasma-chemical methods of CO_2 decomposition in microwave discharge plasma. The most efficient way to increase the CO_2 conversion is rapid (10^6-10^7 K/s) cooling (quenching) of the reaction products, which leads to „freezing“ of the state with maximum conversion [7]. In our recent experiments with plasma of an atmospheric pressure discharge supported by microwave radiation from a gyrotron with a frequency of 24 GHz in a carbon dioxide flow, a threefold increase in the degree of CO_2 conversion and the energy efficiency was achieved due to cooling of the post-discharge region by a counter-flow of gas [8]. In the present study, this quenching method is applied in plasma supported by microwave radiation from a magnetron with a frequency of 2.45 GHz.

Plasma was produced using a microwave discharge method that is often applied in experimental research, in particular for the decomposition of CO_2 [4]. The diagram of the setup is shown in Fig. 1. The discharge was maintained in a flow of carbon dioxide by continuous electromagnetic radiation with a power up to 3 kW. A tangential vortex flow of carbon dioxide was fed to the input of a quartz reactor (a quartz tube with an outer diameter of 20 mm and a wall thickness of 2 mm). The reactor was positioned in the cavity of a microwave applicator and connected hermetically to a diagnostic chamber (a six-way CF 160 vacuum cross). Carbon dioxide was fed into the reactor at atmospheric pressure via Bronkhorst gas mass flow controllers. The flow range was 0–50 l/min. Inside the microwave applicator, the discharge is a plasma column with a diameter of ~ 4 mm stretched along the reactor axis (Fig. 1). With an increase in power and gas flow, the plasma formation extends significantly beyond the microwave applicator. According to estimates from optical measurements of the rotational temperature of CO_2 molecules, the gas temperature in the near-axial discharge region at the center of the applicator may reach 7000 K, which is characteristic of similar discharge types [9]. The chemical equilibrium is shifted strongly toward the reaction products in this zone, and an almost complete decomposition of carbon dioxide ($2CO_2 \rightarrow 2CO + O_2$) is observed. Colder gas from the periphery flows around the central region of direct reactions and, mixing with highly heated plasma, forms a plasma torch at the reactor outlet with a length up to 50 mm and a diameter of approximately 10–15 mm. A region of reverse reactions is thus formed, wherein the reaction mixture cools primarily due to convective heat exchange

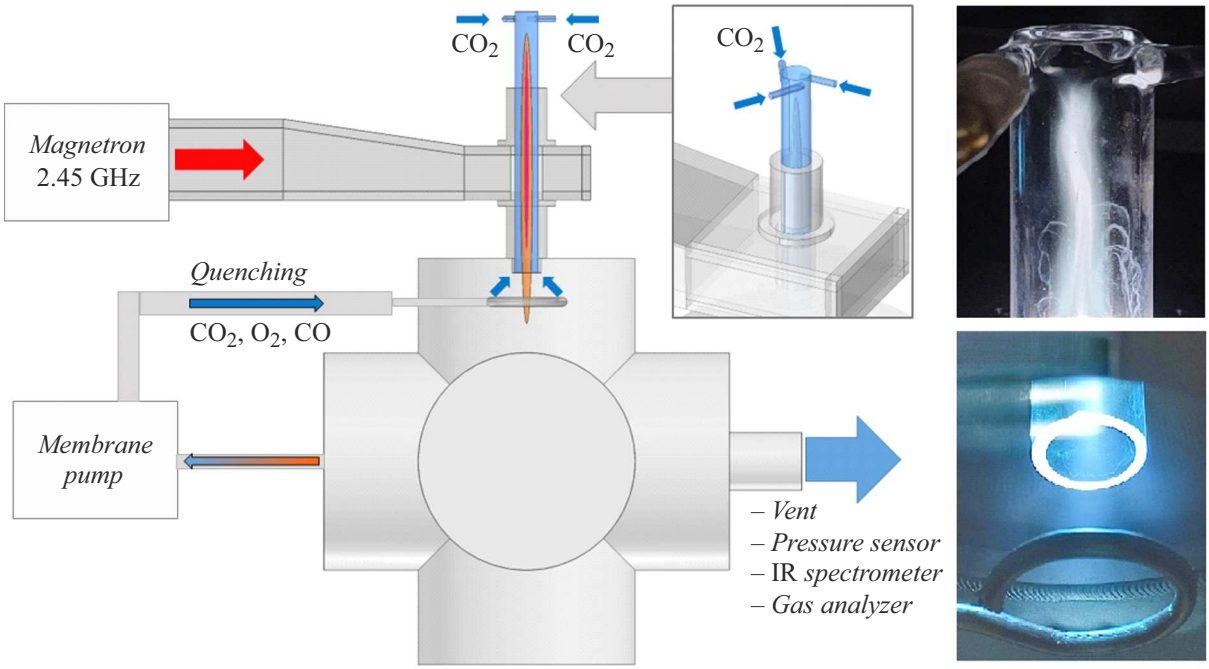

Figure 1. Diagram of the experimental setup. Photographic images of the plasma column (top) and the process of quenching with a counter-flow of gas (bottom) are shown on the right.

with the atmosphere in the chamber, which leads to a shift in chemical equilibrium towards the initial CO_2.

A part of the gas flow leaving the diagnostic chamber was sampled at a rate of 0.5 l/min for subsequent analysis of the reaction products in a TEST-1 gas analyzer, which contains an electrochemical oxygen sensor (O_2; measurement range, 0–21 vol.%; error, 0.5 vol.%) and optical cells for carbon monoxide (CO; measurement range, 0–30 vol.%; error, ±0.3 %) and carbon dioxide (CO_2; measurement range, 0–100 vol.%; error, ±1 %). All sensors were calibrated throughout the entire operating range against test gas mixtures (relative accuracy < 0.3 %). Gas concentrations were measured after steady values were established, which took 10–15 min (depending on the gas flow). The results of additional measurements of CO and CO_2 concentrations via infrared Fourier spectrometry (i-Red 7800u-L spectrometer) match the results of measurements by the TEST-1 gas analyzer within the error limits.

The degree of conversion was calculated based on the readings (φ_{CO}) of the most accurate CO cell in accordance with the formula [10] that takes into account the increase in gas volume in the process of CO_2 decomposition:

$$K = \frac{\varphi_{CO}}{1 - \frac{1}{2}\varphi_{CO}} \cdot 100\%. \qquad (1)$$

The energy efficiency, which is a parameter characterizing the efficiency of decomposition with respect to the standard reaction enthalpy, was determined as

$$\eta[\%] = K\Delta H/\mathrm{SEI}, \qquad (2)$$

where $\Delta H = 2.93$ eV/mol is the specific enthalpy of CO_2 decomposition under standard conditions and SEI is the specific energy input per CO_2 molecule. The latter was calculated as

$$\mathrm{SEI}\left[\frac{\mathrm{eV}}{\mathrm{mol}}\right] = \frac{P[\mathrm{W}] \cdot 60}{F_{CO_2}[\mathrm{l/min}]} \cdot 2.54 \cdot 10^{-4} \frac{\mathrm{eV} \cdot \mathrm{l}}{\mathrm{J} \cdot \mathrm{mol}}, \qquad (3)$$

where P is the microwave radiation power and F_{CO_2} is the CO_2 flow.

Figures 2, *a* and *b* show the dependences of the degree of CO_2 conversion and the energy efficiency on microwave heating power at three different CO_2 flow levels. All the dependencies follow a well-known parity pattern: an increase in heating power leads to an increase in conversion degree and a reduction in energy efficiency, while an increase in gas flow does, on the contrary, lead to a reduction in conversion degree and an increase in energy efficiency. The heating power and gas flow affect directly both the electron temperature, which governs the vibrational excitation of CO_2 molecules and their subsequent dissociation, and the gas temperature. When the latter increases, the efficiency of CO_2 decomposition decreases as a result of collisions of excited molecules with neutral particles (V–T relaxation). In addition, reverse reactions become more prominent at gas temperatures above 1500 K, which also leads to a suppression of CO_2 conversion. This is illustrated clearly at a flow level of 16 l/min (circles in Fig. 2, *a*): with the maximum conversion degree of ~ 10 % reached at a power of 1350 W, a further increase in power leads to a reduction in conversion degree and energy efficiency. As the gas flow increases, the gas temperature in the discharge decreases;

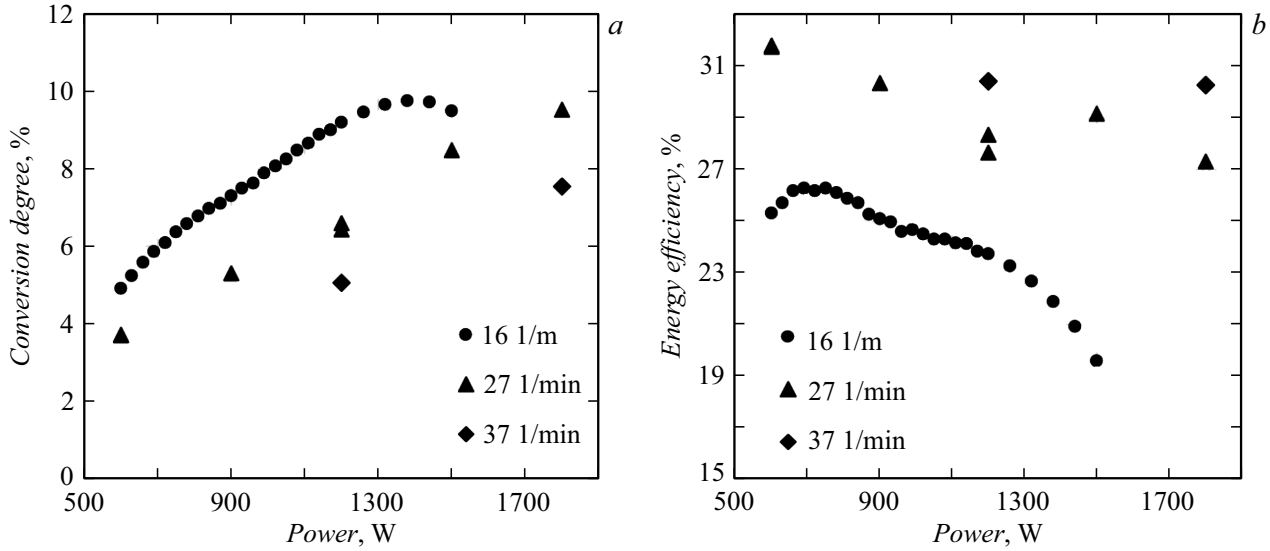

Figure 2. Dependences of the degree of CO_2 conversion (a) and the energy efficiency (b) on power at different CO_2 flows.

the nature of dependences on power remains unchanged, and the maximum degree of conversion is achieved at higher power values.

An increase in heating power and CO_2 flow allows one to obtain the highest carbon monoxide yield while maintaining an optimum conversion degree/energy efficiency ratio. It follows from Figs. $2, a, b$ that the optimum mode (a conversion degree of 8.5 % and an energy efficiency of 29 %) is established at a flow of 27 l/min and a power of 1500 W, which corresponds to a specific energy input of SEI = 0.85 eV/mol. The obtained values are in line with the results of other research groups experimenting with the decomposition of CO_2 in low-temperature plasma of atmospheric pressure discharges (microwave discharge, gliding arc discharge) [6]. However, a conversion degree of at least 15 % is needed for industrial plasma-based processing of CO_2, and the energy efficiency should exceed 50 % [5,11]. Therefore, we used the method of quenching the reaction products with a counter-flow of gas to achieve a significant enhancement of these parameters. Quenching gas was supplied to the base of the plasma torch via a copper tube (with an inner diameter of 3 mm), which was positioned in the diagnostic chamber opposite the reactor outlet, through four symmetrically located apertures with a diameter of 1 mm (Fig. 1). A gas mixture of reaction products (CO_2, CO, O_2) supplied from the diagnostic chamber by a pump with a capacity up to 15 l/min was used as the quenching gas. A similar approach has recently been used to achieve a threefold increase in conversion degree without diluting the reaction products with foreign gases [8].

Figures $3, a, b$ show the dependences of the conversion degree and the energy efficiency on CO_2 flow at the maximum quenching gas flow (15 l/min) and a power of 1350 W. It is evident that quenching of the reaction products provides a more than 1.5-fold enhancement of the conversion and the energy efficiency; notably, the most profound effect (1.8-fold enhancement) was observed at weaker CO_2 flows, which is due to the higher initial gas temperature in the discharge. The energy efficiency increases significantly with increasing gas flow, reaching a maximum of 43.9 % at a CO_2 flow of 21.5 l/min. A further increase in gas flow leads to a significant reduction in conversion degree and, consequently, energy efficiency.

Figure $3, a$ shows the EC values (microwave energy consumption per 1 kg of the reaction product, which is carbon monoxide CO) estimated as

$$\mathrm{EC}\left[\frac{\mathrm{kW}\cdot\mathrm{h}}{\mathrm{kg}}\right] = \frac{1}{K}\frac{P[\mathrm{kW}]}{F_{\mathrm{CO_2}}\left[\frac{\mathrm{l}}{\mathrm{min}}\right]\rho\left[\frac{\mathrm{kg}}{\mathrm{l}}\right]}\frac{1}{60}\left[\frac{\mathrm{h}}{\mathrm{min}}\right], \qquad (4)$$

where $\rho = 0.00114$ kg/l is the CO density. The energy consumption per 1 kg of CO in the optimum mode in terms of productivity and energy efficiency (the corresponding CO_2 flow is 21.4 l/min) is 6.5 kW · h. Taking a CO_2 conversion degree of 14.3 % into account, we find that the maximum yield of carbon monoxide is ~ 0.2 kg/h (or 1.8 tons per year).

Thus, with quenching of the products of the carbon dioxide decomposition reaction with a counter-flow of gas applied in practice, we find ourselves on the cusp of implementing a large-scale process in which, e.g., a magnetron with a power of 30 kW may produce at least 40 tons of carbon monoxide per year. Although the obtained energy consumption values are promising, the total cost of 1 kg of carbon monoxide may exceed significantly the market cost of CO produced in the traditional way. Therefore, we have to solve a number of key problems, such as optimization of the electrodynamic section with the aim of reducing the coefficient of reflection from plasma, optimization of the quenching assembly toward maximizing the cooling rate, and binding or removal of oxygen from the

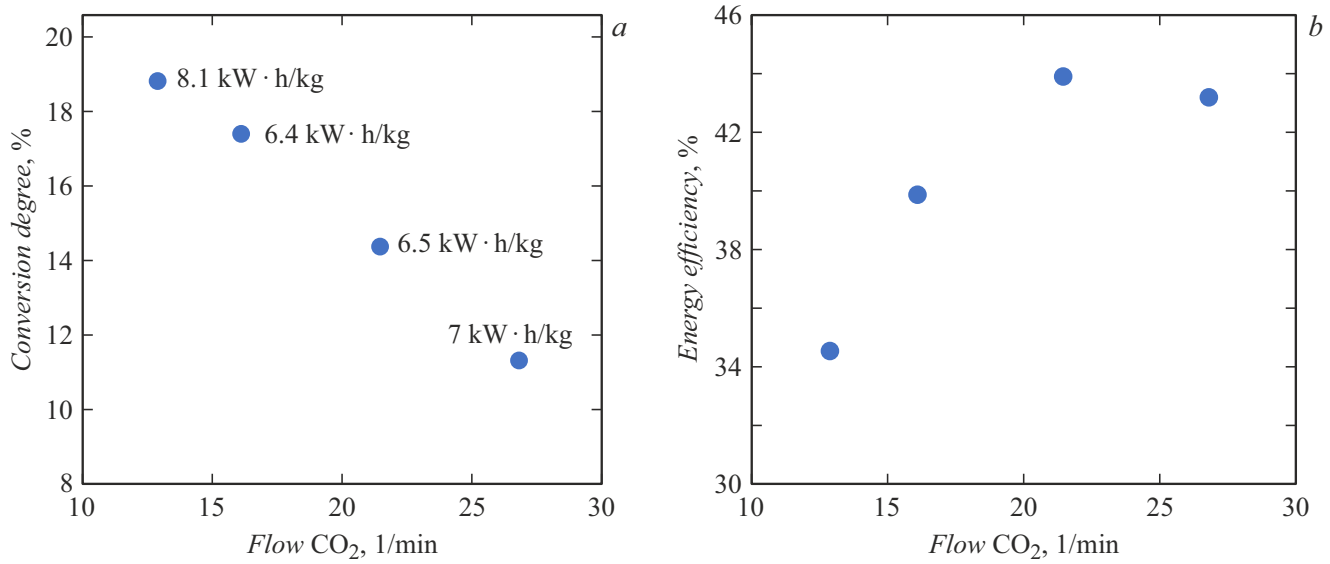

Figure 3. Dependences of the degree of CO_2 conversion (*a*) and the energy efficiency (*b*) on CO_2 flow at the maximum (15 l/min) flow of quenching gas (CO_2+CO+O_2) and a power of 1350 W. The values of energy consumption per 1 kg of CO are indicated in panel *a*.

composition of reaction products for prevention of reverse reactions, in order to raise the degree of conversion and the energy efficiency further. Such studies are made even more relevant by the global trend toward decarbonization of all sectors of the economy, as well as the commitment made by Russia to achieve carbon neutrality by 2060.

Conflict of interest

The authors declare that they have no conflict of interest.

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