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Conversion of CO_2 in microwave discharge in liquid ethanol

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The results of the possibility of decomposing carbon dioxide and obtaining synthesis gas in a microwave discharge in an aqueous solution of ethanol with CO_2 bubbling at atmospheric pressure are presented for the first time. The main products of the discharge are H_2 and CO, the ratio of the main products with increasing power changes insignificantly. The rate of formation of products and the degree of decomposition of carbon dioxide are directly proportional to the incident power. The highest degree of decomposition of carbon dioxide is 43 %.

Keywords: microwave discharge in liquid ethanol, CO_2 decomposition, chromatography of discharge products, synthesis-gas production.

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Several technological problems are currently being solved or are still waiting to be solved. One such challenge is the decomposition of CO_2 or conversion of CO_2 into value-added chemicals and synthetic fuels. Since CO_2 is a product of various technological processes, this is associated with environmental safety issues. In solving these issues, much attention is paid to the use of low-temperature plasma of various types of electrical discharges [1]. The typical degree of decomposition of CO_2 in gas discharges does not exceed 20 %.

It is known that the introduction of methane and hydrogen into a discharge in CO_2 increases the degree of decomposition of CO_2. The positive influence of added CH_4 on the degree of CO_2 conversion was demonstrated experimentally in a barrier discharge [2], gliding arc [3], spark discharge [4], glow discharge [5], microwave discharge in the gas phase [6], etc. The addition of H_2 also enhances the decomposition of CO_2 [2].

In modern research, particular attention is paid to discharges in liquid vapors that are regarded as a promising trend in production of synthesis gas and CO_2 conversion. A new approach to plasma conversion of a mixture of CO_2 and methanol vapor, which provides an opportunity to obtain synthesis gas with simultaneous conversion (up to 20 %) of CO_2, was demonstrated in [7]. By analogy with traditional dry reforming of methane, this process was called dry reforming of methanol.

Improved process efficiency was also demonstrated with the use of alternative gas-liquid mixture compositions. Specifically, a microwave discharge in a mixture of water vapor, ethanol, CO_2, and N_2 was considered in [6]. The maximum degree of CO_2 decomposition was 23 %; an increase in concentration of CO_2 was accompanied by a reduction in hydrogen yield. The influence of the nature of alcohol on the efficiency of hydrogen formation was analyzed in [8], where isopropanol was found to be preferable to ethanol; however, its use is accompanied by the formation of soot.

A high efficiency of CO_2 conversion is also achieved by microwave discharges initiated directly in the liquid phase. One of the key advantages of such systems is the natural implementation of quenching of reaction products, which increases significantly the efficiency of CO_2 decomposition. Specifically, a degree of CO_2 decomposition of up to 60 % with simultaneous production of synthesis gas was demonstrated in [9] at atmospheric pressure with the use of a microwave discharge in liquid hydrocarbons.

In the present study, we report the first results of experiments on decomposition of CO_2 obtained by passing it through a microwave discharge in an aqueous ethanol solution. Hydrogen and methane, which have a positive effect on the CO_2 decomposition process, are among the products of a microwave discharge in liquid ethanol [10]. It should be noted that an in-depth study of the mechanism of a microwave discharge in liquid ethanol was carried out in [11,12].

The experimental setup used for generating and examining the microwave discharge in liquids was discussed in detail in [9,10]. The microwave system includes a magnetron microwave generator (2.45 GHz) and elements needed to control and measure the incident microwave power. Experiments were carried out at an incident microwave power of 380−590 W. The discharge section is a waveguide-coaxial junction with its central conductor serving as an antenna for introducing microwave energy into the reactor. The discharge was initiated near the tip of the antenna in a quartz reactor 55 mm in diameter filled with an aqueous ethanol solution and placed in a protective metal mesh (cell pitch, 0.5 mm). The antenna was constructed from a tungsten tube with an outer diameter of 3.0 mm and a channel diameter of 1 mm. Note that since ethanol and water have a large dielectric loss

tangent, the discharge was ignited at the end of the antenna near the point where it enters the reactor (the antenna protrudes above the dielectric by 1 mm). This is the site of intense evaporation of liquid and ignition of the discharge.

Water was added to ethanol in order to suppress the soot formation process. Thus, an aqueous solution of ethanol with an ethanol concentration of 72 vol.% was used in the experiments. The volume of this solution in the reactor was close to 40 ml, which ensured that the end of the internal electrode of the coaxial line was positioned below the liquid surface.

CO_2 with a flow rate upward of 222 ml/min passed through an RRG-20 flow meter and was introduced into the reactor through a channel in the antenna. The pressure above the liquid surface was near-atmospheric. The approximate duration of the experiment was 1 min. Within this time interval, the gas flow at the reactor outlet was measured, and, when steady-state conditions were established, a gas sample was taken to analyze the composition of products. In one experiment, the composition of liquid in the reactor was not renewed.

A water condenser was used to separate the gaseous products of plasma-chemical reactions from evaporated liquid products. The condensed liquid was returned to the reactor. The flow rate of the gas mixture at the discharge outlet after the water condenser was measured by a mechanical flow meter.

The gas phase composition (CO, CO_2, H_2, C_2H_2, C_2H_4, and CH_4) at the outlet of the reactor with a discharge was determined using a PIA (NPF MEMS, Russia) portable gas chromatograph with a backflush system, a katharometer, and two chromatographic columns with Hayesep N adsorbents and 13X molecular sieves. Argon was the carrier gas.

The main decomposition products are H_2 (50–55 vol.%) and CO (27–31 vol.%). The minor components are CO_2 (9–2 %), CH_4 ($\sim$ 5 %), C_2H_2 ($\sim$ 5 %), and C_2H_4 $\sim$ 3.5 %. The present study is focused on the process of decomposition of CO_2 and the production of synthesis gas.

The degree of CO_2 decomposition (α) and the parameter of synthesis gas important for technical applications (functional f [13]) were calculated based on the flow rates of products at the reactor outlet in accordance with the following formulae:

$$\alpha = \frac{\mathrm{CO}_2^{in} - \mathrm{CO}_2^{out}}{\mathrm{CO}_2^{in}} \cdot 100\,\%, \qquad (1)$$

$$f = \frac{\mathrm{H}_2^{out} - \mathrm{CO}_2^{out}}{\mathrm{CO}^{out} + \mathrm{CO}_2^{out}}, \qquad (2)$$

where H_2^{out}, CO_2^{out}, and CO^{out} are the H_2, CO, and CO_2 flow velocities at the reactor outlet and CO_2^{in} is the CO_2 flow velocity at the reactor inlet.

The key parameters characterizing the efficiency of conversion of an aqueous solution of ethanol and CO_2 are the degree of decomposition of CO_2, the rate of production of synthesis gas, and its composition. The composition of synthesis gas is characterized by the H_2/CO ratio and (more precisely) by ratio (2) that is called the functional (f) [13]. Regardless of the method of production of synthesis gas, it always contains CO_2 in a concentration that may vary within a wide range. One important application of synthesis gas is the production of methanol, which involves both carbon oxides found in synthesis gas (CO and CO_2) [13]. It was established that the optimal value of functional f for methanol synthesis is 2.0–2.2 [13].

Figure 1 presents the dependences of the rate of production of synthesis gas and the degree of decomposition of CO_2 on the incident power. It was determined experimentally that the degree of decomposition of CO_2 and the rate of production of synthesis gas increase with incident power at all the examined CO_2 flow rates. Figure 1 presents these dependences at a CO_2 flow rate of 222 ml/min. Naturally, an increase in the degree of decomposition of CO_2 should induce a change in the H_2/CO ratio and functional f in the product mixture. Figure 2 shows the dependences of ratio H_2/CO and functional f on the incident power. It can be seen that the functional does not assume the values optimal for methanol production, but synthesis gas may be used to obtain other products.

A specific feature of microwave discharges in liquids is that the content and composition of discharge products in an aqueous solution of ethanol without bubbling are virtually independent of power (the ratio of H_2/CO concentrations falls within the range of 2.15–2.4) [10]. When CO_2 is added, the yield of CO increases, and ratio H_2/CO drops to 1.80–1.86, changing only slightly (Fig. 2). Since the degree of decomposition of CO_2 varies significantly with an increase in incident power, the value of the functional changes by a factor of 1.4. The obtained f value is as high as 1.7, which is outside the range of values optimal for methanol production. It is known (see [10]) that the rate of synthesis of products increases with increasing power (Fig. 1). These features of the discharge are associated with its non-steady nature. It is a sequence of individual discharges the lifetime of which is specified by the lifetime of a gas bubble with plasma at the end of the antenna. Under otherwise equal conditions, the rate of occurrence of individual discharges is set by the microwave power.

These dependences may be explained as follows.

With an increase in incident power, the rate of occurrence of individual discharges increases, which translates into a higher rate of decomposition of liquid vapors (primarily ethanol, owing to the difference in boiling points of ethanol and water) and a higher rate of production of hydrogen and methane, which are actively involved in the decomposition of CO_2. This leads to an increase in the degree of decomposition of CO_2 with an increase in incident power at a constant inlet flow of CO_2.

Thus, data on the decomposition of CO_2 with simultaneous production of synthesis gas in a microwave discharge in an aqueous solution of ethanol with bubbling of CO_2 have been obtained for the first time.

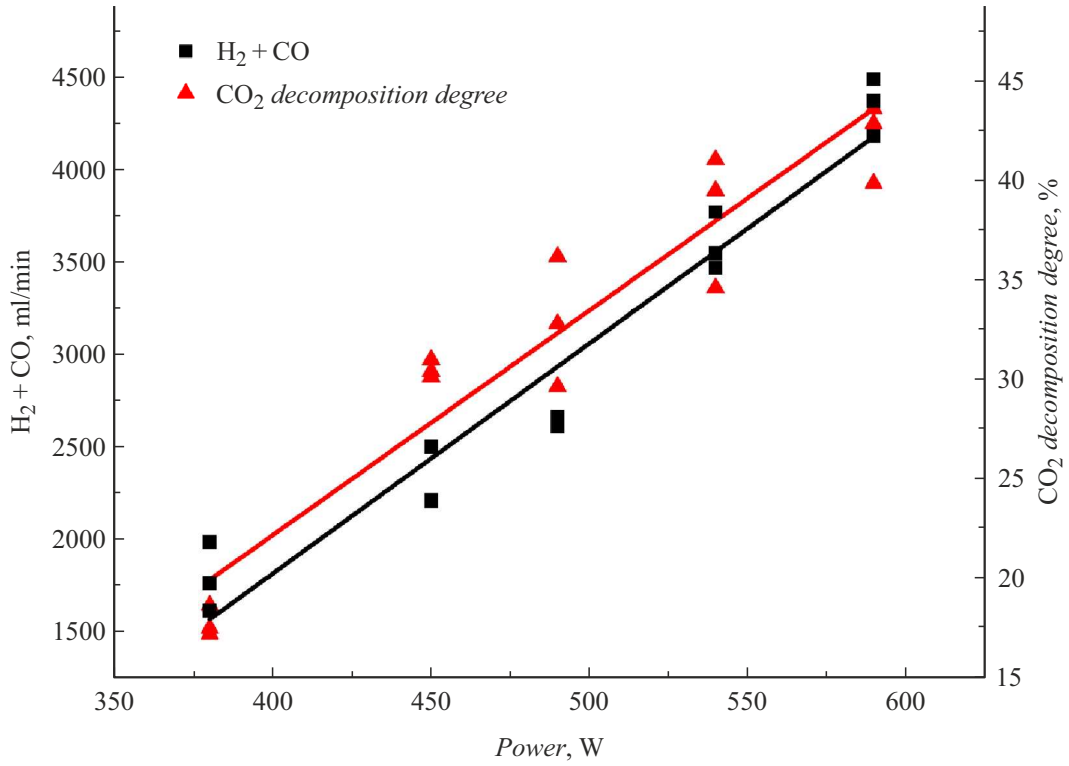

Figure 1. Dependences of the rate of production of synthesis gas and the degree of decomposition of CO_2 on the incident power.

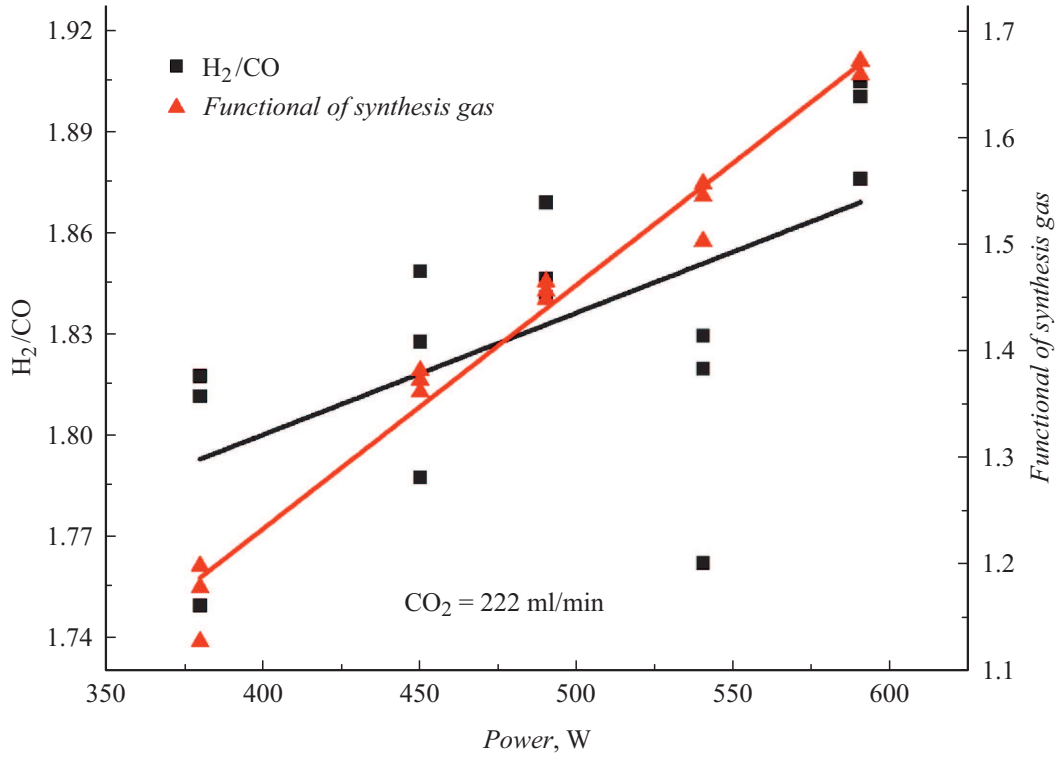

Figure 2. Dependences of the ratio of flows of H_2/CO and the functional of synthesis gas on the incident power.

It was demonstrated that the degree of decomposition of CO_2 reaches 43 %. The first experiments revealed the potential of this method for decomposition of CO_2.

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Conflict of interest

The authors declare that they have no conflict of interest.

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