Disintegration of carbon dioxide in a microwave plasma torch sustained by gyrotron radiation at a frequency of 24 GHz at atmospheric pressure

D. Mansfeld, A. Vodopyanov, S. Sintsov

Institute of Applied Physics of the Russian Academy of Sciences, Nizhny Novgorod, Russia.

Abstract: The study of the carbon dioxide disintegration in CW microwave discharge at atmospheric pressure sustained by the focused microwave radiation was performed. A 24 GHz gyrotron was used as a source of microwave radiation. The conversion of CO2 is in the range 25-40%, while the energy efficiency reaches maximum of 70% at 900 W and decreasing to the value of 20% at power of 4.5 kW

Keywords: gyrotron, microwave discharge, plasma torch, carbon dioxide.

1. Introduction.

Over the past few years, the concentration of carbon dioxide, which is one of the main greenhouse gases in the Earth's atmosphere, has exceeded 400 ppm and continues to grow at an increasing rate. Such a dynamic increase of CO2 in the atmosphere over the coming decades will lead to global climate change with an increase in global temperature by 2ºC at the level of 450 ppm. The enormous efforts of all countries are currently aimed at reducing CO2 emissions by eliminating the burning of fossil hydrocarbons and the transition to renewable energy sources. That is why there is currently a huge demand in the world for the search for carbon dioxide utilization technologies.

To date, traditional methods of electrochemical conversion, solar thermochemical conversion, photochemical conversion, biochemical conversion, catalytic chemistry, each of which has its advantages and disadvantages, are actively developing. The disadvantages are mainly related to the low energy efficiency of the methods and the need to use expensive catalysts that have a limited lifetime due to surface poisoning. Recently, it has been increasingly proposed to decompose CO2 in plasma of various discharges. In a low-temperature plasma, activation (excitation, ionization, dissociation) of highly stable molecules is possible, which increases the rate of reactions and ensures that thermodynamically unfavorable processes of CO2 molecules decomposition. Thermally equilibrium plasma, in which all its components (electrons, gas molecules, excited atoms and molecules, ions, etc.) are characterized by the same temperature, has low energy efficiency in gas conversion applications, since it is necessary to maintain a high temperature of the entire gas volume. At high gas temperatures, the role of reverse reactions also increases in the case of CO2, the limiting degree of conversion and maximum energy efficiency reach a limit of 80% and 47%, respectively, at a gas temperature of 3500 K. That is why the most promising of plasma methods is the use of non-equilibrium plasma, characterized primarily by significantly higher electron temperature, which makes it possible to speed up the flow paths of many plasma-chemical reactions, and possibly realize new ones through the processes of dissociation and excitation of molecules by electron impact.

Non-equilibrium plasma can be created in spark, corona, glow discharges, but the most developed in application to the tasks of gas conversion today are: a gliding arc discharge, a dielectric barrier discharge and a microwave discharge. Studies on the decomposition of CO2 molecules into CO and O2 began in the 1980s with the pioneering work of A.A. Fridman et al., in which record values of CO2 conversion (20%) and energy efficiency (80%) were obtained in a microwave discharge in a subsonic gas flow at pressures of 100–200 Torr [1], however, with an increase in pressure up to atmospheric efficiency and the degree of conversion was reduced to 80% and 10%, respectively [2]. In the past 10 years, interest in the problem has resumed, however, the results obtained in [1,2] in microwave discharges in other laboratories failed to reproduce, only energy efficiency of 40–50% and a conversion rate of 10–20% [3,4] were reported. In the work of Silva et.al energy efficiency was achieved 50-80%, but the degree of conversion did not exceed 10% [5]. All these results were obtained at pressures up to several hundred Torr, at atmospheric pressure, the energy efficiency dropped to 20% at a conversion of 10%, and to 5% at a conversion of 50% [6]. In a gliding arc discharge at atmospheric pressure, good energy efficiency values can be achieved (30-40%), but CO2 conversion is generally limited to a maximum of 10% [7].

To date, the greatest progress in researching stationary microwave discharges in a gas flow has been achieved with the use of compact and inexpensive magnetrons

with a frequency of 2.45 GHz and a power from 50 W to several kilowatts. The implementation of a non-equilibrium microwave discharge using magnetrons is, as a rule, possible under reduced pressure (tens of Torr), which makes it difficult to use for many applications. At atmospheric pressure, as a rule, it is possible to realize only an equilibrium discharge with a gas temperature above 3000 K, and the main attempts associated with an increase in absorbed power and optimization of gas flows lead only to the expansion of the area occupied by the discharge, a slight increase in gas temperature, and a decrease in energy efficiency. That is why, currently, it seems relevant to study the properties and parameters of a non-equilibrium microwave discharge plasma at a pressure close to atmospheric, which becomes possible with increasing frequency of the microwave field and is associated with the development and implementation of new technological sources of centimeter and millimeter radiation of high power. Significant progress in the production of technological gyrotron complexes has allowed for the last 10 years to reach record power levels (up to 20 kW of continuous radiation) with a frequency of ~ 30 GHz with high (up to 60%) efficiency.
The idea of using gyrotrons with a radiation frequency substantially higher than the traditionally used magnetron frequency of 2.45 GHz to maintain a discharge in a flow of carbon dioxide is proposed in this report.

2. Experimental setup

The basis of the setup is a technological gyrotron, generating continuous microwave radiation at a frequency of 24 GHz and a power of up to 5 kW. After exiting the gyrotron, the microwave radiation passes with minimal losses through a water-cooled vacuum window (1) made of boron nitride and then is focused with a help of a system of mirrors (2) at a certain place of the discharge chamber (see Fig. 1). The cylindrical discharge chamber (length 100 cm, inner diameter 26 cm) made of stainless steel has four optically transparent windows DN 160. Two windows are located at the ends of the chamber, two windows with hatches are on the side wall of the chamber. To prevent the microwave radiation from escaping from the chamber, the windows are closed with a copper grid with a cell pitch of 3 mm. Flanges for water inlet are also provided in the chamber. The absorber, made of PTFE tubes, is located at the end of the chamber. Gas inlet is carried out on a stainless tube connected to the focusing region of the microwave beam. The gas supply system allows you to work both in pure gas and in a mixture of gases. The flow of gases is controlled by precision rotameters of various denominations. Flanges are provided on the chamber for pumping the volume with fore-vacuum pumps and measuring residual pressure using barotrons. The pumping system allows for studies in a wide pressure range from 10 ^ -3 to 10 ^ 3 Torr.

Primary (seed) electrons in the discharge region are created as a result of gas pre-ionization using short-pulse high-voltage RF breakdown.

The use of a quasi-optical focusing system made it possible to obtain a power density in the focal waist up to 5 kW per square centimeter. Such record values of the energy density make it possible to maintain non-equilibrium in the plasma torch even at atmospheric pressure. The carbon dioxide at pressure of 1 atm was used as a background atmosphere, while plasma forming gas was carbon dioxide in mixture with argon. The discharge also can be ignited in the pure CO2 with flow rate up to 30L/min.

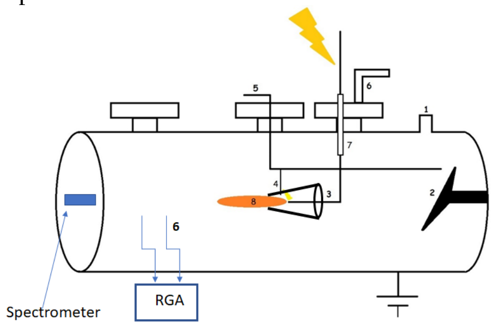

Fig. 1. The scheme of experimental setup. 1 – microwave input window, 2 – focusing mirror, 3- gas tube, 4 - metal cone, gas tube for residual atmosphere, 6 – pumping ports, 7 – isolator, 8- plasma.

While the heating power is less than 1kW the discharge represent itself as an elongated torch, from 1 to 5 cm in length and with a diameter equal to the thickness of the gas tube of 4 mm. In these conditions the plasma absorbs about 30% of heating power and according to the measurements of plasma parameters the discharge is non-equilibrium [9]. The length of the torch increases with microwave power and when the power exceeds 1 kW the discharge becomes voluminous with the dimensions up to 15 cm in length and several cm in diameter. The plasma absorbs 60-70% of the heating power and the discharge tends to be equilibrium with gas temperature of 3000-3500 K.

The best results on the decomposition of carbon dioxide were achieved in flow of gas mixture of argon (25l/min) and CO2 (13l/min). The chemical composition of the gases will be measured using a quadrupole mass spectrometer with differential pumping and a multicomponent gas analyzer. The example of mass-spectrum without plasma is shown in Fig.2. When the plasma is ignited the peak with mass 44, which corresponds to carbon dioxide, is decreasing, while the peaks with masses 28 (carbon monooxide) and 32 (oxygen) are increasing. The conversion efficiency $\boldsymbol{K}$ was estimated by the ratio of CO2 signal with/without plasma.

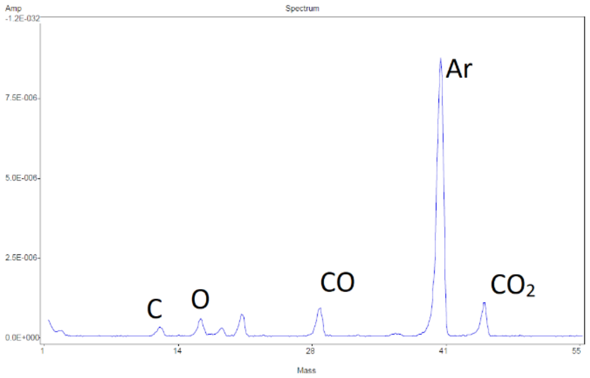

Fig. 2. The mass-spectrum measured by quadrupole spectrometer without plasma.

The energy efficiency was calculated using formula: η = *K*2.9eV/SEI [8]*, where SEI – is specific energy input. For 1 kW of heating power and flow rate of 13 l/min of CO2, the SEI ≈ 1.2 eV/mol. The results are shown in Fig.3, where the squares represent the energy efficiency (left axis), while the circles stand for CO2 conversion (right axis).

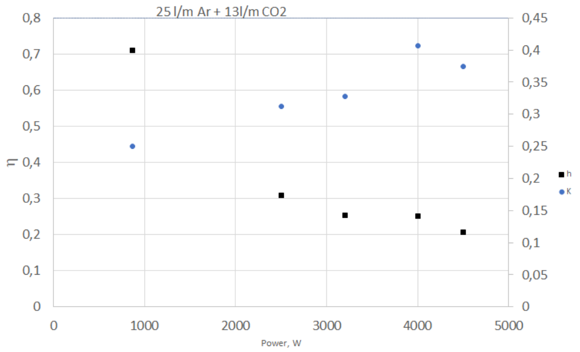

Fig.3. The dependence of the energy efficiency η (left axis - squares) and conversion K (right axis - circles) on the heating power.

It is seen from the fig.3 that CO2 conversion is in the range 25-40%, while the efficiency reaches maximum of 70% at 900 W and decreasing to the value of 20% at power of 4.5 kW. This graph clearly indicates the benefits of non-equilibrium microwave discharge which are related to the moderate CO2 conversion of about 25% but at extremely low energy input (SEI ~ 1 eV/mol). These results are very promising since they are very close to the results obtained by A.A. Fridman et al [1]. The future work will be aimed at optimization of gas conditions and microwave coupling to achieve the best conversion and efficiency in pure CO2 flow.

The work was supported by RFBR grant #18-48-520027.

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