Technical Physics Letters, 2024, Vol. 50, No. 7

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Nitrogen fixation in a microwave discharge supported in the air flow by continuous millimetre radiation

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Received February 22, 2024
Revised March 19, 2024
Accepted March 21, 2024

The first results of experimental investigation of plasma nitrogen fixation in a discharge supported in a „waveguide plasmatron"by continuous radiation of a gyrotron with a frequency of 24 GHz in an air flow at atmospheric pressure are presented. It is shown that specific energy consumption for the synthesis of nitrogen oxides is 3−5.8 MJ/mol, and their content in the spent plasma mixture reaches 1.35%. The obtained qualitative physical regularities can be used for the development of new microwave plasmatrons in the interests of plasma chemistry

Keywords: microwave discharge, gyrotron, plasma chemistry, nitrogen fixation.

DOI: 10.61011/TPL.2024.07.58718.19903

The Birkeland−Eyde process, which allows one the synthesize nitrogen oxides (NO_x) from atmospheric air for the subsequent production of nitric acid [1], is one of the alternative methods for production of nitrogen fertilizers. Studies into the fixation of atmospheric nitrogen in a non-equilibrium gas discharge [2,3] have recently gained momentum. The results of original research in this field have been reported by Polak [4].

With „green" energy sources used, this process will feature minimal greenhouse gas emissions. If one takes the potential production rate requirements into account, plasma nitrogen fixation is viable at atmospheric pressure with air used as a plasma-forming gas. Efficient disruption of the triple covalent bond of a nitrogen molecule is feasible in non-equilibrium plasma where the electron temperature exceeds the gas temperature and is close to the dissociation energy threshold [4,5]. The current best results within this field have been achieved with the use of barrier, arc, and microwave atmospheric-pressure discharges [3]. In experiments, the characteristic concentration of nitrogen oxides in the spent plasma-forming mixture is 0.5−3%, and the energy required for synthesis of 1 mol NO_x is approximately an order of magnitude higher than the corresponding energy in the Haber−Bosch process and varies from 2 to 10 MJ [1].

The use of high-power microwave radiation of the millimeter wavelength range to maintain a discharge is one of the promising trends in development of non-equilibrium sources of atmospheric-pressure plasma [6]. This makes it possible to implement the weakly collisional mode of maintaining a stationary discharge at atmospheric pressure ($\nu_{em} \ll \omega$, where ν_{em} is the rate of electron–neutral collisions and ω is the cyclotron frequency) and establish the conditions for development of a number of physical effects affecting the degree of plasma non-equilibrium [7]. The presence of filamentary plasma structures (efficient sources of ionizing ultraviolet radiation) is a distinguishing feature of such discharges. A plasma halo forms around the filaments under the influence of UV radiation. This halo is a region of non-self-sustaining non-equilibrium discharge that may absorb a significant fraction of energy of a microwave pulse and, consequently, is a medium conducive to plasma-chemical processes [8].

Promising results with regard to non-equilibrium plasma destruction of carbon dioxide have been reported relatively recently in [9], where continuous radiation from a gyrotron with a frequency of 24 GHz was used to maintain a discharge in a gas flow at atmospheric pressure. The present study is a continuation of research into the feasibility of application of non-equilibrium microwave discharges sustained by continuous millimeter radiation in plasma chemistry. The results of experiments on fixation of atmospheric nitrogen with the use of a „waveguide plasmatron" (see the diagram in Fig. 1) are reported. A gyrotron with an operating frequency of 24 GHz, a power up to 7 kW in the continuous mode, and an efficiency of 30−35% was used as a source of millimeter radiation. A microwave TE_{11} wave with linear polarization is transported along a circular superdimensional waveguide with an internal diameter of 32.6 mm. The waveguide plasmatron is coupled to the waveguide via a sealed window made of boron nitride and has two connected structural sections: an electrodynamic waveguide structure with an injection system for plasma-forming gases and a conical nozzle (microwave discharge zone) with a bore diameter of 8 mm. The plasmatron is connected to a gas discharge chamber, which is a 6-way cross with standard CF160 flanges. The conical nozzle, a water-flow calorimeter used to measure the power that was not absorbed by a discharge, a system for removing spent plasma-forming gases, diagnostic ports, and observation ports are located inside this chamber.

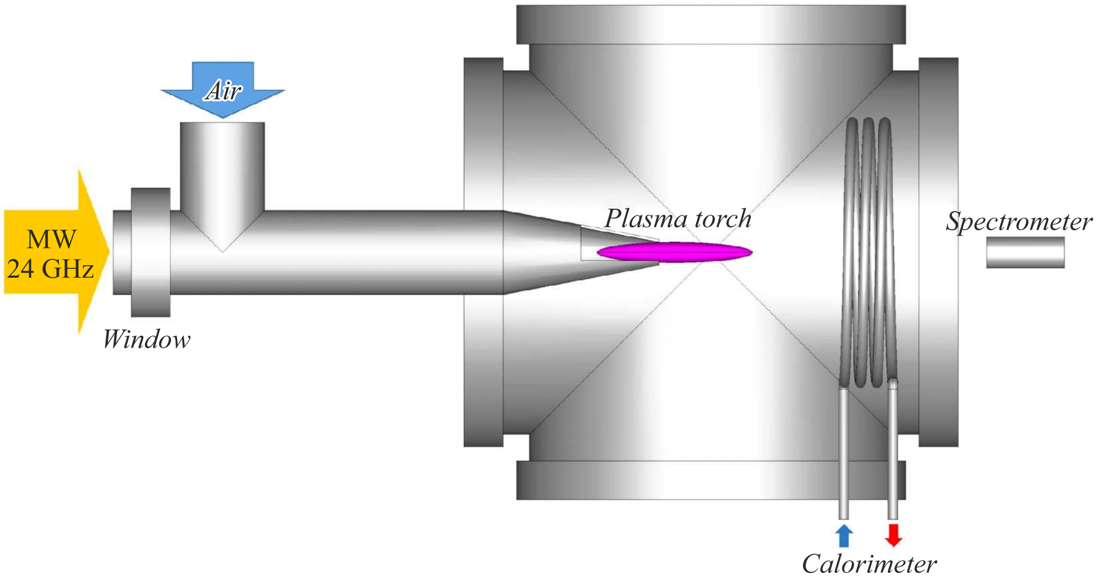

Figure 1. Diagram of a waveguide plasmatron.

Atmospheric air, which was used as a plasma-forming gas, is fed through a waveguide tee positioned after the microwave window. This design helps establish such conditions that prevent the discharge propagation toward microwave radiation. A discharge is initiated in a gas flow at a minimum microwave power of 200 W inside a conical nozzle by introducing a metal wire into it for a short moment. The visible part of a discharge, which is forced out by the flow of plasma-forming gas, is a plasma torch (Fig. 2) with its length proportional to the introduced microwave power and reaching 12 cm. The maximum power at which the discharge could be kept from propagating toward microwave radiation is proportional to the gas flow injected into the plasmatron. For example, the maximum input power reached 320 and 1090 W at an air flow rate of 7 and 15 l/min, respectively. The results of calorimetric measurements demonstrated that the plasma torch absorbs 54–71% of the input microwave power; notably, the efficiency increases with increasing power.

Emission spectra of the plasma torch were recorded using an S150 duo spectrometer (SOL Instruments). A diffraction grating with a period of 400 mm^{-1}, which provides a resolution of 0.6 nm, was installed in the monitoring channel of the instrument. The integral translational temperature was estimated from the spectral continuum corresponding to Planck radiation of the heated gas. The obtained estimate varied within the 3050−4600 K range depending on the discharge mode. It should be noted that the gas temperature decreases continuously with increasing microwave radiation power. For example, with an air flow rate of 15 l/min and an input power of 290 W, the translational temperature is 4600 K; if the power is raised to 1000 W at the same flow rate, the temperature drops to 3500 K. This variation is attributable to the fact that an increase in microwave

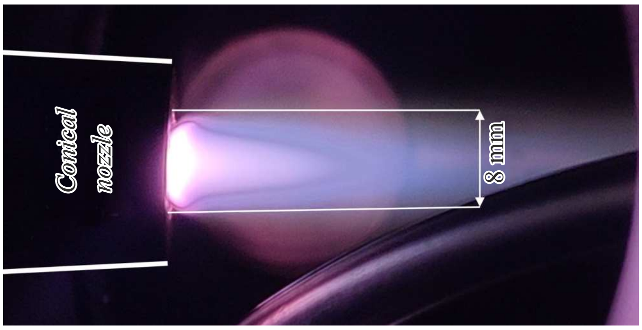

Figure 2. Photographic image of a plasma torch emerging from a conical nozzle. The air flow rate is 7 l/min, and the input power is 320 W.

radiation power leads to a disproportionate increase in plasma volume inside the conical nozzle, since the region with an electric field strength sufficient to maintain a discharge expands. Note that in the context of maintaining a discharge, cooling of the gas (i.e., increase in its density) is compensated by an increase in electric field strength.

Spent plasma-forming mixtures were sampled to determine the concentration of nitrogen oxides (NO and NO_2) in discharge modes corresponding to different microwave heating powers (from 230 to 1090 W) and air flow rates (7, 10, and 15 l/min). This analysis was performed using an Agilent 6890/MSD 5973N gas chromatograph/mass spectrometer with various capillary columns. Having determined the percentage of nitrogen oxides and the power absorbed by the discharge in each mode, we estimated the specific energy cost of synthesis. Note that these estimates were obtained without regard to nitrogen oxides deposited on the inner walls of the chamber. Figure 3 presents the

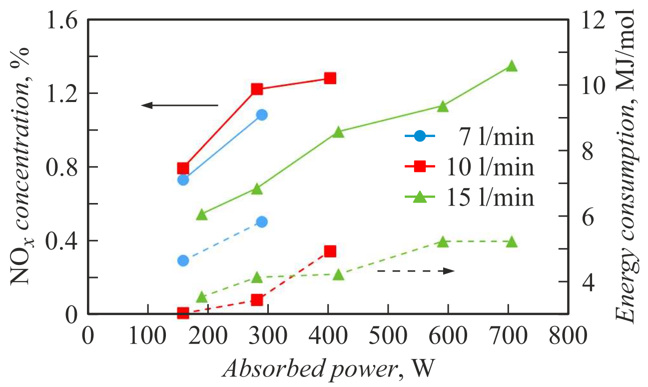

Figure 3. Dependences of the concentration of nitrogen oxides in the spent plasma-forming mixture (solid curves) and the specific energy consumption for synthesis of NO_x (dashed curves) on power absorbed by the discharge at different air flow rates.

results of measurements. The power limits of the presented dependences correspond to the minimum and maximum values at which a stable discharge could be maintained with a given air flow. It is evident that the concentration of nitrogen oxides in the spent plasma-forming mixture increases uniformly in all modes and reaches 1.35% with an increase in power absorbed by the discharge. A change in flow rate has an ambiguous effect on the conversion rate, providing indirect evidence of the presence of an optimum. The obtained patterns suggest that the NO_x concentration may be increased by raising the microwave heating power and the air flow rate simultaneously. In contrast, the best results in terns of energy efficiency (3–3.5 MJ/mol) were obtained at minimum heating powers. Thus, the power of microwave radiation grows faster than the percentage of nitrogen oxides in the spent mixture, ultimately leading to an increase in the energy cost of synthesis. It should be noted that the actual energy cost of synthesis of NO_x determined with account for the gyrotron efficiency and the efficiency of radiation absorption by plasma is approximately 5 times higher.

The presented first results of plasma synthesis of nitrogen oxides are promising at the global level. Specifically, the obtained values of specific energy consumption for synthesis of NO_x in discharges in a flow of atmospheric air are close to record-low ones [3], suggesting that the used type of discharge holds promise for plasma chemistry applications. The efficiency of the examined process may be raised significantly by optimizing the discharge conditions. For example, tangential input of components of the plasma-forming mixture was used in our previous study [9] to form a swirling gas flow inside the waveguide plasmatron and increase the discharge stability. Optimization of the shape and size of the conical nozzle may also expand the power range within which plasma is feasible to be maintained. The qualitative physical relations obtained in this study may be used to design new microwave plasmatrons for plasma chemistry applications.

Funding

This study was supported financially by the Russian Science Foundation (project 22-72-00073).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Safin