Plasma-chemical kinetics in an atmospheric pressure parallel plate capillary jet operated in argon-water vapour mixtures

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Abstract: Plasma driven biocatalysis is of interest as a lower-cost, environmentally friendly alternative to conventional chemical conversion. To successfully drive biocatalytic reactions, precise control of reactive species delivery is required. In this work, the plasma-chemical kinetics of a capillary plasma jet operated in argon-water vapour mixtures is investigated for applications in this area. Plasma-properties and reactive species formation in argon-based mixtures are also compared to those in helium-based mixtures.

Keywords: 0-D simulation, biocatalysis, plasma jet, hydrogen peroxide

1. Introduction

Radio-frequency driven atmospheric pressure plasma jets are suitable sources for a range of applications such as biomedicine and chemical conversion due to their ability to produce a variety of reactive species. These reactive species can also act as precursors for applications in biocatalysis, an enzyme-based, environmentally friendly alternative to conventional chemical conversion [1]. Here, low temperature plasmas can allow for non-invasive delivery of a reactant, such as hydrogen peroxide, to enzymes immersed in liquids. Together, the enzyme and the reactant act to drive the biocatalytic conversion of a substrate molecule into a value-added product [1]. Selective and energy-efficient production of reactant species is essential to further develop and optimise plasmadriven biocatalysis.

In this work, a parallel plate electrode plasma jet containing a dielectric capillary is used as plasma source. While this, and similar sources have often operated in helium with molecular admixtures [2, 3, 4], argon is favourable in many applications as it is less expensive and more sustainable. However, the plasma properties and reactive species production in argon-based mixtures are expected to differ from those in helium-based mixtures due to the different ionization potentials and electron impact cross sections in the two gases. Therefore, this work investigates the plasma properties and reactive species formation in argon-based mixtures and compares them to the same source operated under equivalent power deposition and molecular admixtures in helium.

The overall goal is to identify the optimum conditions for the generation of hydrogen peroxide, for use as a reactant in biocatalysis, while minimising the delivery of enzyme-damaging reactive species such as OH or O. To do this, variation of molecular gas admixtures, flow rates and plasma power deposition are investigated. Simulations will be compared to experimentally measured concentrations of hydrogen peroxide in plasma-treated liquids.

2. Capillary Jet

The capillary jet [6] is an alteration of the wellinvestigated COST-Jet [7], extended with an additional borosilicate glass capillary between the plane parallel stainless-steel electrodes.



Fig. 1. Schematic of the capillary jet source showing the dimensions of the plasma forming region, the effluent, and the location of the liquid surface to be treated.

The glass capillary, with an inner square cross-section of 0.1 cm^2 , a wall thickness of 0.02 cm and an additional length below the end of the electrodes of 1 cm, serves as dielectric and allows for the utilisation of a wide range of operating conditions, such as higher gas admixtures and higher applied power in comparison to the COST-Jet. The two electrodes have a length of 4 cm. One electrode is driven by a radio-frequency power generator at a frequency of 13.56 MHz, while the other is grounded. The source is operated in helium or argon as feed gas with water vapour content added using an ice-cooled bubbler. Measurements are performed with a minimal distance of 2.4 cm between the end of the electrodes and a liquid surface.

The results of the simulations are validated with experimental measurements. The hydrogen peroxide concentration is measured in the liquid by absorption spectroscopy using an ammonium metavanadate assay. The measurements are taken 0.8 cm below the liquid surface.

3. Simulation

The 0-D plasma-chemical kinetics code GlobalKin [8] is used to simulate the capillary jet in this work. GlobalKin solves the mass continuity equation for charged and neutral species and the electron energy conservation equation. The mass continuity equation is solved including gas-phase and surface loss processes, while the electron energy equation solves for the electron temperature accounting for elastic and inelastic collision processes and the deposited power. Moreover, the solution of the two-term approximation of the Boltzmann-equation is used to calculate the electron energy distribution function and electron impact rate and transport coefficients. The gas temperature is derived by solving an energy balance equation for the neutral gas. In addition, a pseudo-1D plug flow model is used to convert the temporal solution of the species densities to spatiallydependent values along the length of the plasma source using the gas flow velocity as a conversion factor.

The basic plasma-chemical reaction scheme for water vapour is described in detail in [2, 3]. In those works, helium was used as the background gas. Here, the previously published reaction scheme is extended to include argon based on the reaction scheme published by Van Gaens and Bogaerts [5].

4. Results

Fig. 2 shows the electron density for the capillary jet operated in argon and helium with varying water vapour content for a power deposition of 6 W. Here, it can be observed that argon-based mixtures have substantially higher electron densities for low water vapour admixtures. However, after a few hundred ppm of water vapour is added, the electron density in argon-based mixtures



Fig. 2. Electron densities for argon- and helium-based mixtures as a function of water vapour admixture, for a power deposition of 6 W.

decreases rapidly, becoming lower than those of heliumbased mixtures. This is consistent with the simulations carried out by Liu *et al.* [9] for argon-water vapour mixtures in a similar plasma source.

Fig. 3 shows the simulated electron temperature in argon- and helium-based mixtures for the same conditions as Fig. 2. Here, the electron temperature in argon-based mixtures are consistently above those in helium-based mixtures. The values and trend for electron temperatures are again broadly consistent with Liu *et al.* [9]. Those for helium-based mixtures are similar to those of Schröter *et*



Fig. 3. Electron temperatures for argon- and heliumbased mixtures as a function of water vapour admixture, for a power deposition of 6 W.

al. [3], who also operate with a similar plasma source, albeit without a dielectric capillary. Due to the relatively significant differences in electron densities and temperatures, as well as in the electron energy distribution functions (not shown), the two working gases also differ in their charged and neutral particle kinetics. These will be discussed further during the conference contribution, as will comparisons with experimentally measured hydrogen peroxide concentrations.

5. Conclusion

A plasma-chemical reaction scheme has been developed and applied to an atmospheric pressure capillary plasma jet source. It is found that the electron, charged particle and neutral kinetics differ significantly when the source is operated in argon instead of helium. The implications for these differences for applications in plasma-driven biocatalysis will be discussed.

6. Acknowledgement

The authors thank Prof. Kushner for providing the GlobalKin code and the DFG for the financial support via SFB 1316 (project number 327886311), project B11.

7. References

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