Chemical and Physical Characterization of Nano-second Pulsed Electrical Discharges Propagating along a Gas-Liquid Water Interface

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Abstract: Plasma discharges propagating along a gas-liquid interface are analysed in a small tubular flow reactor with two different nano-second power supplies and one microsecond power supply and various carrier gases (helium, argon, air, nitrogen). Characterization of the major stable chemical products include in the liquid phase hydrogen peroxide, nitrate, and nitrite and in the gas phase molecular hydrogen and oxygen as well as nitrogen oxides has been accomplished. Time resolved and average optical emissions spectroscopy showed the variation of electron density with the electrical pulse. A simple zero-dimensional mathematical model is developed to interpret experimental results on reaction stoichiometry.

Keywords: plasma-liquid interactions, hydrogen peroxide, hydrogen, nitrogen oxides.

1. Introduction

Analysis of plasma generated by electrical discharges in gas-liquid systems is of significant fundamental and practical interest in biomedical, environmental, materials, agricultural and chemical applications [1, 2]. We have conducted experiments to analyse the chemical reaction pathways in electrical discharge plasma channels that propagate along the interface of a flowing gas and a liquid film [3]. In this reactor, a small capillary tube is used with inlet and outlet flow nozzles that also function as the electrodes [3]. The gas-liquid two-phase flow hydrodynamics were found to follow annular flow patterns such that the gas flows through a central core in the reactor surrounded by a water film on the walls [4]. In this configuration the reactor has continuous flows of both gas and liquid with residence times of 2 to 5 ms and 100 to 200 ms, respectively. The plasma channel propagates along the gas-liquid interface across the full width of the electrode gap. This reactor has been characterized with respect to hydrocarbon oxidation and formation of aldehydes, alcohols and other compounds from alkanes [5], organic dye decomposition with and without the addition of Fenton catalysts [6], and hydroxyl radical generation using gas (CO) and liquid (ethanol) chemical probes [7] in the case of a microsecond pulsed power supply based upon an automobile ignition coil. We have also characterized the plasma generated with a variety of carrier gases (e.g., helium, argon, air, nitrogen) with the microsecond power supply [8] as well as a commercial nano-second pulsed power supply (Eagle Harbor, Seattle, Washington, USA) [9, 4]. We have found that the fast rise time of the nano-second pulsed power supply readily allows for operation to near sea-water conductivity [10], that the hydroxyl radical generation (in helium and argon) is affected by the plasma gas temperature and electron density, and that net hydrogen peroxide production is limited by degradation reactions from radicals and plasma electrons [8]. Efficient degradation of 1, 4 dioxane dissolved in the liquid phase was demonstrated through combination of the plasma reactor followed by a bioreactor [11]. In pure N_2 and N_2/argon mixtures, the generation of nitrogen oxides in the gas was found to be limited by atomic oxygen formation from water and the subsequent reactions to form liquid soluble products, nitrate and nitrite are limited by hydroxyl radicals from the liquid [12].

2. Methods

The present work focusses on analysis of the same gas-liquid plasma reactor utilizing a custom-made nanosecond pulsed power supply (Airity, San Francisco, California, USA) that operates to 60 kHz. In this work we measure the formation of stable molecular products in the gas and liquid (gas phase: H_2, O_2, NO, NO_2; liquid phase: H_2O_2, NO_2^-, NO_3^-, pH, conductivity) for various gas compositions and selected frequencies. In addition, we characterize the plasma through averaged and time resolved optical emissions spectroscopy. A simple zero dimensional mathematical model is developed to assess the formation of these stable products as a function of the measured electron density, plasma gas temperature, and pulsed power characteristics.

3. Acknowledgements

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4. References

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