Falling liquid film plasma reactor to study plasma-liquid interactions with highly controlled convective transport: comparison of model and experiment

T. K. Srivastava¹, C. C. Rich², R. Frontiera², P. J. Bruggeman¹

¹ Department of Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, USA ² Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, USA

Abstract: Understanding liquid-phase transport limitations is important to improve many applications. We report a falling liquid film plasma reactor which allows us to control liquid phase convection and enables us to describe the decomposition of formate in a plasma environment with a simple 2D convection-diffusion model. We furthermore show significant larger conversion of formate at high pH which can be explained by enhanced transport due to drift and/or volume reactions enabled by long-lived species (at the elevated pH) such as HO₂⁻.

Keywords: plasma-liquid interaction, transport, convection, diffusion, reaction kinetics .

1. Introduction

Plasma-liquid interactions have various applications [1] including wound healing [2], bacterial inactivation [3], nanoparticle synthesis [4] and wastewater treatment [5,6]. The reactors developed for these applications rely on reactive species generated by the plasma in the gas phase entering the liquid phase [1]. Due to the short lifetime of many plasmaproduced reactive species, their penetration depth in the liquid phase ranges between 10s of nanometers to a few micrometers [7,8]. Therefore, many reactions are confined to the near plasma-liquid interface and plasma-liquid reactors used for the above-mentioned applications often heavily rely on liquid-phase transport such as convection and diffusion of chemical compounds towards the plasma-liquid interface to react with the short-lived species. Most plasma reactors used for water treatment applications involve the treatment of bulk volumes of liquids, in which the transport timescales are on the order of seconds to minutes [9], much slower than the timescales of reactive processes occurring at the plasmaliquid interface [1,8]. This results in recombination of shortlived species which can significantly impact of the effectiveness of such reactors.

In spite of the importance of transport on the overall plasma-induced liquid phase chemistry, only a few experimental studies so far have focused on gaining a quantitative understanding transport limitations. For instance, Oinuma et al. [10] have shown that the decomposition of formate in a plasma-droplet reactor is limited by diffusion for 38 μ m droplets on the timescale of 10 ms. The impact of liquid-phase convective transport has been mostly studied through numerical studies, with Delgado et al. [11] suggesting that interfacial liquid flow velocities of the order of 100 m/s would be needed to minimize the recombination of short-lived species in the liquid phase and thereby minimize transport limitations. Furthermore, most

studies have focused on the effects of overall bulk chemistry upon plasma treatment over a time scale of minutes. A falling liquid film reactor allows for simultaneous control over convective and diffusive timescales in the liquid phase by controlling the liquid flow velocity and varying the film thickness. In this work, we have used a falling liquid film reactor to study the impact of convective transport on conversion of formate as a model compound at different pH. We will show that the controlled plasma-liquid interaction conditions for this setup also allow to investigate new unexplored plasma-induced liquid phase chemistry occurring at timescales equal or larger than transport timescales (1 ms) in the reactor.

2. Methods

For these experiments, we use a falling liquid film reactor coupled to a plasma jet, inspired by the work of Tauber et al. [12]. The setup consists of a wire loop, between which the flowing liquid originating from a reservoir (not shown) forms a film due to surface tension. The wire loop is resting on a glass slide which acts as a drip guide and guides the liquid to a lower reservoir. Unlike Tauber et al. [12], we did not recirculate the liquid. The thickness of the film was adjusted by controlling the solution flow rate using a stopcock valve connected to the reservoir.

The plasma jet had the same geometric parameters as in [13]. We used a helium flow of 0.5 standard liter per minute (slm) of through the capillary tube of the jet. We used a negative dc high voltage supply to excite the needle electrode of the jet while keeping the discharge current constant at 6.4 mA throughout the work. We measure the liquid film thickness using *in-situ* optical absorption spectroscopy on the liquid film using a broadband light source and a fiber optic spectrometer. The film thickness was measured using a ferricyanide solution of 30 mM for films < 100 μ m and 10

mM for films > 100 μ m motivated by the strong absorption of ferricyanide at 420 nm. Nonetheless, we focus in this study on the conversion of formate as it does not have a reversible redox chemistry as ferricyanide. We assume that the thickness of the films are the same for both formate and ferricyanide solutions.

We measured the decomposition of formate *ex-situ* using Ultra-Violet High Performance Liquid Chromatography (UV-HPLC) using a Supelco Supelcosil C-18 column (250 mm x 4.6 mm diameter, 5 μ m particle size). For the mobile phase, we used a composition of 97% of 20 mM KH₂PO₄ solution at pH of 2.5, which was maintained using H₃PO₄, and 3% methanol flowing at 1 mL/min for 5 minutes along with a sample injection volume of 10 μ L. We maintained the column at 22 °C and set the UV detector at a wavelength of 220 nm [14].



Fig 1. Schematic representation of the falling liquid film reactor and the *in-situ* optical absorption spectroscopy across the liquid film

3. Results and Discussion

We first modelled the conversion of 2 mM of using a 2-D convection diffusion model of the film considering that convection dominated the vertical transport and the transport across the film is due to diffusion. We further assumed that the plasma-induced reactions occurred only at the plasma-liquid interface and accounted for by assuming that the concentration of formate at the plasma-liquid interface was negligible. This was previously shown to be a good approximation to model formate decomposition in droplets [15]. The governing equation for the model used is :

$$V\frac{\partial[K]}{\partial x} = D_k \frac{\partial^{2}[K]}{\partial y^2} \qquad (1)$$

where *V* represents the liquid velocity in the film, which was determined from the measured film thickness and liquid flow rate (time taken for a given volume of liquid to flow through the film) and assuming a rectangular cross section of the film. D_k is the diffusion coefficient of formate [16], [*K*] represents the concentration of formate at a given spatial location (*x*,*y*) with *x* and *y* the liquid flow direction and the direction along the thickness of the film, respectively. The conversion percentage was found to be dependent on the non-

dimensional Peclet number *N*, which represents the ratio of convective and diffusive time scales:

$$N = \frac{VH^2}{D_k L} \qquad (2)$$

where *H* represents the film thickness and *L* the plasma spot size along the flow direction. A typical solution in nondimensional terms for *N* corresponding to thin film (50 µm) is shown in figure 2. The figure show the formation of a decomposition boundary layer near the plasma-liquid interface. For $N \sim 480$ (corresponding to a film thickness ~ 50 µm and a solution flow velocity of 0.7 m/s), the model predicts the decomposition boundary layer to be limited to within 10-20% of the liquid film and an overall formate conversion of 5.1%. The conversion reduces significantly with increasing Peclet number and increase film thickness as shown in figure 3 for a 320 µm film thickness ($N \sim 21000$).



Fig 2. Decomposition boundary layer solution of a 2-D convection-diffusion model for a falling liquid film reactor for $N \sim 480$ in non-dimensional terms ($[K_0] = 2 \text{ mM}$)

The conversions modelled for the two film thicknesses (50 and 320 μ m) were compared with the experimentally measured conversion of 2 mM formate in figure 3.

The experimental and modeling results are in excellent agreement for both the 50 and 320 μ m film. Formate solutions have a limited conductivity resulting in a highly resistive liquid layer for films ~ 50 μ m which at times causes the plasma to spread out towards the guiding wires of the film. Hence, we also increased the conductivity for the 50 μ m film up to ~ 20 mS/cm by adding 0.1 M NaOH (pH ~ 13) and 0.27 M H₃PO₄ (pH < 1). For the low pH case, i.e. H₃PO₄ addition, the conversion was measured to be 6 ± 2% consistent with conversion in the model and the experimental measurement without H₃PO₄ addition (figure 3). However, in the high pH case (NaOH addition) a factor 2 higher conversion was found compared to the low pH case.





The pKa of the conversion of formic acid to formate has been reported to be ~ 3.75 [17]. Therefore, for the low pH case formate is likely to be in the formic acid form (HCOOH) , whereas at high pH, it is likely to be entirely in its ionic form (HCOO⁻). Based on the reaction rates with OH radicals reported by Imoberdorf and Mohseni [18], the reaction rate of formic acid with OH radicals is an order of magnitude lower compared to that of formate with OH radicals. Nonetheless, reaction times remain in both cases well below the convective and diffusive transport timescale for the reactor. This confirms that the reactor is transport limited and therefore the near interfacial reaction rates should have minimal impact on the amount of conversion, given that the liquid-phase transport processes are the rate-limiting step.

For the high pH case, since formate exists predominantly in its ionic form, there is a possibility of drift influencing the transport time scales in the solution. Furthermore, at high pH, Katafias et al. [19] have shown that deprotonated forms of H_2O_2 (HO_2^- and $O_2^{2^-}$) can drive reduction reactions and that the reaction rates of the limiting step of the mechanism is dependent on the pH of the solution, especially for pH > 13. Given that the pKa of H_2O_2 converting into HO_2^- is 11.7, these species can potentially contribute to the decomposition of formate. Interestingly, we have detected $HO_2^$ concentrations up to ~1 M in this reactor at high pH. We will discuss the possible role of pH and HO_2^- in detail in the presentation.

4. Conclusion

We show the well-defined convection in the liquid film reactor can be used to quantitatively describe plasma-induced formate decomposition using a convection-diffusion model assuming transport limited conversion. This 2-D convection-diffusion model shows that the conversion of formate depends on a non-dimensional Peclet number N, which represents the ratio of convective to diffusive time scales in the liquid phase. At high pH, an increase in conversion was observed, which can be caused by two phenomena: a significant impact of drift transport in the film and enhanced conversion by volume reactions due to long-lived species (enabled by the elevated pH) such as HO₂⁻.

5. Acknowledgement

This work was partially supported by the US Department of Energy, Office of Science, Office of Fusion Energy Sciences, General Plasma Science program, under Award Number DE-SC- DE-SC-0020232 and the Army Research Office under Grant Number W911NF-20-1-0105.

6. References

[1] P J Bruggeman et al. 2016 Plasma Sources Sci. Technol. 25 053002

[2] B K H L Boekema et al. 2015 J. Phys. D: Appl. Phys. 49 044001

[3] P Shaw, N Kumar, H S Kwak, J H Park, H S Uhm, A Bogaerts, E H Choi, P Attri 2018 *Scientific Reports* **8** 11268

[4] V S S K Kondeti, U Gangal, S Yatom, P J Bruggeman 2017 J. Vac. Sci. Technol. A. **35** 061302

[5] J Foster 2017 Physics of Plasmas. 24 055501

[6] S M Thagard et al 2017 J. Phys. D: Appl. Phys. 50 014003

[7] P Rumbach, D M Bartels, D B Go 2018 *Plasma Sources Sci. Technol.* **27** 115013

[8] C C W Verlackt, W Van Boxem, A Bogaerts 2018 Phys. Chem. Chem. Phys. 20 6845-6859

[9] H Taghvaei, V S S K Kondeti, P J Bruggeman 2019 Plasma Chemistry and Plasma Processing **39** 729-749

[10] G. Oinuma, G Nayak, Y Du, P J Bruggeman 2020 Plasma Sources Sci. Technol. **29** 095002

[11] H E Delgado, G H Brown, D M Bartels, P Rumbach, D B Go 2021 J. Appl. Phys. **129** 083303

[12] M J Tauber, R A Mathies, X Chen, S E Bradforth 2003 *Rev. Sci. Instrum.* **74** 4958-4960

[13] Y Yue, S Exarhos, J Nam, D Lee, S Linic, P J Bruggeman 2022 *Plasma Sources Sci. Technol.* **31** 125008

[14]<u>https://www.phenomenex.com/applications/single?ap</u> <u>pid=14666</u>

[15] G Nayak, J Wang, R Li, D Aranzales, S M Thagard, P J Bruggeman 2023 *Plasma Process. Polym.* (accepted)

[16] P Vanýsek: *Ionic conductivity and diffusion at infinite dilution, Handbook of Chemistry and Physics*, CRC Press, 1992/93 edition. Boca Raton, 1992. pp. (5-111)-(5-113).

[17] Smith, Robert M.; Martell, Arthur E. (1989). *Critical Stability Constants Volume 6: Second Supplement*. New York: Plenum Press. p. 299. <u>ISBN 0-306-43104-1</u>.

[18] Imoberdorf G and Mohseni M 2011 Chem. Eng. Sci. 66 1159–67

[19] A Katafias, O Impert, P Kita 2008 *Trans. Met. Chem.* **33** 1041-1046