

Chemical Conversion in Atmospheric Pressure Plasmas Sustained in Packed Bed Reactors

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Abstract: Chemical conversion by low temperature plasmas has many potential advantages in using renewable electricity in environment and energy applications. The most rapid implementation will be by augmenting current industrial infrastructure with plasma enhanced processes. Selective chemical conversion using plasmas is an unmet challenge, particularly when being applied to current technologies. In this paper, we discuss results from a modeling study of chemical selectivity in a plasma enhanced packed bed reactor.

Keywords: plasma chemical conversion, atmospheric pressure plasma, modeling.

1. Introduction

The use of atmospheric pressure plasmas for chemical conversion will be a critical component for using renewable electricity for environmental and energy applications. Given the huge industrial infrastructure for chemical conversion, the most rapid implementation of plasma enhanced processes will likely be by augmenting currently used technologies. One such technology is the packed bed reactor (PBR) which is widely used for industrial chemical processes. A PBR consists of catalytic dielectric beads, often impregnated with additional metal catalyst particles, that thermally chemically convert gases flowing through the system. In a plasma enhanced packed bed reactor (PE-PBR), a discharge sustained between the dielectric beads additionally produces radicals and activates the catalyst particles, enabling synergies between thermal and plasma processes [1].

Key research issues in plasma enhanced chemical conversion include efficiency and whether plasma enhancement can selectively produce reactants. These issues in turn depend on the character of the plasma propagating through the PE-PBR and the flow patterns of the reactants produced. For example, the plasma in PE-PBRs consists of microdischarges (MDs) between the near contact points of the dielectric beads, surface ionization waves (SIWs) along the surface of the beads and volumetric discharges in the volumes between the beads [1,2]. Each variety of discharge produces different proportions of radicals and excited states in different locations. Combined with the flow patterns of gas through the reactor, with its own stagnation points and eddies, the PE-PBR is a complex chemical system which is challenging to optimize to produce a selective output.

In this paper, we discuss results from a computational investigation of a 2-dimensional atmospheric pressure PE-PBR sustained in flowing humid air. The intent of the investigation is to highlight how geometry and flow combine to produce spatially dependent sources of reactants,

which during repetitive operation produce a complex chemically reacting system.

2. Description of the Model

The model used in this investigation is *nonPDPSIM*, a 2-dimensional plasma-hydrodynamic simulator utilizing an unstructured mesh [2]. *nonPDPSIM* uses time-slicing techniques to combine solutions of Poisson's equation, charged particle transport, radiation transport and Navier-Stokes equations, while considering surface chemistry and charging. The PE-PBRs of interest can be many tens of cm long which exceed the current capability to model while including the spatial resolution required to resolve plasma-surface interactions. Given that the long-term flow through the reactor is important to the chemical conversion process, *nonPDPSIM* was improved for this investigation with the ability to have periodic boundary conditions. That is, flow out the right boundary is injected through the left boundary. *nonPDPSIM* was also improved with a neutral-plasma option to speed the calculation of the interpulse period and repetitive operation.

3. Repetitively Pulsed PE-PBR

The model geometry and initial gas flow speed are shown in Fig. 1. The portion of the PE-PBR explicitly addressed is 10 mm long, 6.5 mm high, containing an array of 0.7 mm dielectric beads having relative permittivity $\epsilon_r = 8$. Gas flow is from left-to-right with periodic boundary conditions. Gas leaving through the right boundary is injected through the left boundary. The dielectric beads were located sufficiently far from the boundaries so that the discharge through the array was not affected by the boundaries. Flow is 500 sccm of humid air ($N_2/O_2/H_2O = 78/21/1$), with a -30 kV pulse applied to the top electrode at repetition rates of 100 Hz to 1 kHz. Gas flow tends to stagnate in the array of beads, with the fastest flow being around the array.

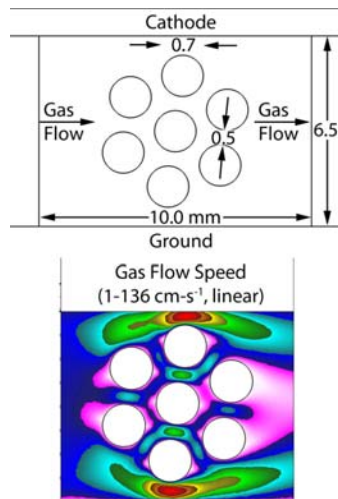


Fig. 1. (top) Geometry of the PE-PBR reactor and (bottom) gas flow speed through the array of beads.

The densities of OH and H₂O₂ are shown in Fig. 2 after pulsing for 0.1 s at 1 kHz (100 pulses). H₂O₂ is dominantly produced by reactions between OH radicals. Electron impact dissociation of H₂O is largely responsible for production of OH, and this occurs where the discharge is most intense as it propagates through the array – in SIWs along the surface of the beads and in MDs at the vertical poles of the beads. The lifetime of the OH is relatively short, being consumed in production of H₂O₂ and, after several pulses during which NO_x species are formed, in production of acids HNO_x. The flow tends to stagnate between beads, increasing residence time which enables both radicals to be locally consumed and some buildup of products.

The layout of the beads is important with respect to the structure of the discharge propagating through the array. The layout is also important with respect to long term

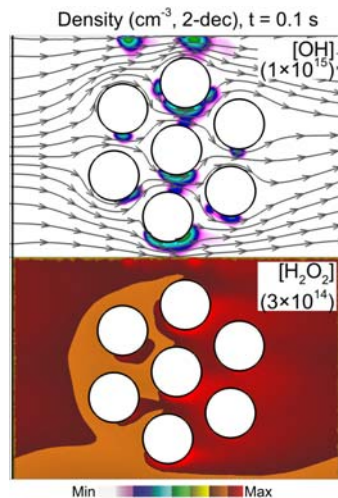


Fig. 2. Densities of (top) OH with flow streamlines and (bottom) H₂O₂ after pulsing for 0.1 s at 1 kHz.

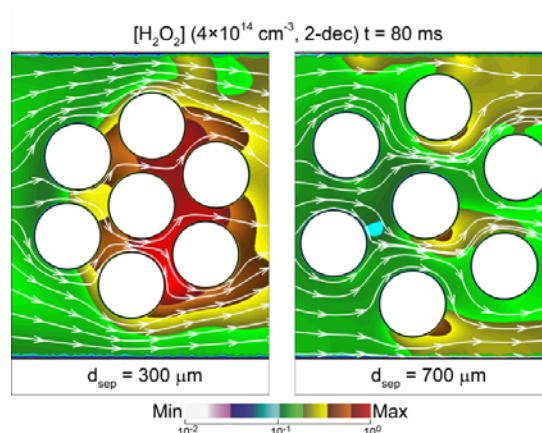


Fig. 3. Densities of H₂O₂ with flow streamlines for bead separations of (left) 300 μm and (right) 700 μm.

chemistry. For example, H₂O₂ densities are shown in Fig. 3 for bead separations of 300 μm and 700 μm. The smaller spacing produces more stagnation of the flow between the beads, increasing residence time of all species between the beads and increasing the average residence time. This increased residence time enables reactions between primary radicals that would otherwise be swept away with the flow, in this case producing a higher density of H₂O₂. Note that with the larger spacing, the production of H₂O₂ is dominated by where the discharge initially produces larger densities of OH. These locations are near the poles of the beads where MDs are produced, and along the surface where SIWs propagate. Plumes of H₂O₂ then flow from these locations.

Repetition rate is another important process variable. With a given flow rate, lower repetition rate enables primary radicals directly produced by the discharge to flow out of the discharge volume prior to the next discharge pulse. Higher repetition rates tend to expose radicals and products produced by a prior discharge pulse to radicals produced by the next pulse. For example, O and O₃ densities at the end of the 20th pulse are shown in Fig. 4 for repetition rates of 100 Hz and 1 kHz. At both repetition rates, the O atoms are largely restricted to the path of the discharge as it propagates through the array. The lifetime for O radicals is shorter than the interpulse period for both cases, and so O atoms do not flow significantly away from where they are produced. At 1 kHz, the interpulse period is short, and the O₃ density builds up inside the array where the discharge propagates. For these conditions, the next discharge pulse produces radicals that can rapidly react with the O₃. At 100 Hz, the O₃ has largely flowed out of the array out of the path of the next discharge pulse.

4. Concluding Remarks

As atmospheric pressure plasmas begin to be industrially deployed, particularly for chemical conversion in energy and environmental applications, a more systems perspective of the process will be required. In this paper, the

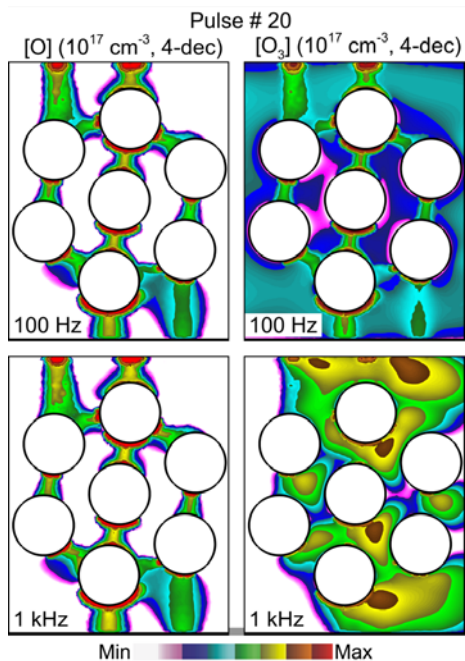


Fig. 4. Densities of (left) O and (right) O₃ at the end of the 20th pulse for repetition rates of (top) 100 Hz and (bottom) 1 kHz.

consequences of system parameters on reactant production in a flowing PE-PBR have been discussed, with emphasis on repetition rate and bead separation. Lifetimes of radicals, flow speeds and location of where radicals are produced in the PE-PBR array combine to determine the final selectivity of the process.

5. Acknowledgements

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6. References

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