

Numerical Study of Liquid Phase Hydrogen Peroxide Decomposition in Catalytic Micro-reactors

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Abstract- Hydrogen peroxide has recently been considered as a monopropellant in micropropulsion systems for the next generation of miniaturized satellites ('nanosats') due to its high energy density, modest specific impulse and "green" characteristics. Efforts at the University of Vermont have focused on the development of a MEMS-based microthruster that uses the catalyzed decomposition of hydrogen peroxide to generate thrust and impulse-bits commensurate with the intended micropropulsion application. The present study is a computational effort to investigate the initial decomposition of the monopropellant as it enters a catalytic chamber. Two-dimensional numerical models of the monopropellant in microchannel geometry have been developed and used to characterize the performance of the monopropellant before vaporization occurs. The results of these studies show that in the absence of a non-diffusive mixing mechanism at the microscale, decomposition of the monopropellant occurs very slowly. A method for enhancing decomposition via the introduction of gas bubbles into the flow is studied, and found to increase decomposition for a given length by over 57%.

Keywords: Micropropulsion, heterogeneous catalysis, micro-reactor, hydrogen peroxide.

1. Introduction

A recent focus of the aerospace community has been on the development of small sized satellites (>10 kg) due to the potential for reduced launch and operational costs. Proposed missions involving these small satellites called "nanosats", have ranged from traditional scientific endeavours with the redundancy of having many nanosats for the costs of a single large satellite, to complex missions involving formation flying of many satellites to enable missions that are not currently possible. While the shrinking size of computer and energy storage systems are promising developments for nanosats, it is the progress of Micro-ElectroMechanical Systems (MEMS) design and manufacture that offer the promise of a fully functional, miniaturized satellite.

One of the major challenges facing the development of nanosats is the development of small scale propulsion technologies capable of providing the reduced thrust, specific impulse and impulse-bit requirements while meeting size, mass and power constraints. Current efforts to meet these challenges include passive, electric and chemical systems with each facing its own set of scaling challenges. One promising technology is the miniaturization of monopropellant thrusters based on rocket grade hydrogen peroxide (HTP). Hydrogen peroxide is a desirable monopropellant due to its modest specific impulse ($I_{sp}=150s$), high storage density (1450 kg/m^3) and its "green" characteristics (Whitehead, 1998). Hydrogen peroxide decomposition is a highly exothermic reaction, with an adiabatic flame temperature of 886° - 1251° K, but the activation energy of this reaction is high enough to prevent spontaneous reaction in storage. When exposed to a catalyst, which may include silver, platinum, various iron compounds or a range of other metals, the activation energy is lowered sufficiently to allow the reaction to proceed at room temperature.

The aerospace community has a long history with HTP-based rockets, so it is a natural choice when investigating the development of micro-scale thrusters. Cervone et al. (2009) developed a small-scale thruster with thrust levels of $\approx 5N$ using silver gauze and pellets as a catalyst. Attempts to shrink this design to smaller scales ($O[500\mu m]$) were unsuccessful due to pressure drop issues associated with the

packed bed. A microscale thruster, developed at NASA Goddard Space Flight Center (GSFC) used MEMS-manufacturing techniques to develop a thruster capable of meeting design requirements recommended by Thomas (2000) including a thrust level of 500 μN , impulse bit of 1-100 μNs and a specific impulse of 160s. This thruster included a catalytic chamber with an array of square silver-coated pillars oriented at 45° to the flow (Hitt et al, 2001). While this system was an effective demonstration of a microscale monopropellant microthruster, it suffered from performance degradation as the silver coating flaked off the pillars at high temperatures.

A new monopropellant microthruster has been proposed at the University of Vermont, which serves to build upon the GSFC system to offer improved performance. This proposed microthruster is a three-section system, as shown in Fig. 1. The first subsystem is a fuel delivery system that provides discrete slugs of fuel to the catalytic chamber, which has been reported on by McDevitt and Hitt (2009). The second subsystem is the catalytic chamber that consists of an array of micropillars coated in ruthenium oxide (RuO_2) nanorods, which has been reported on by Widdis et al. (2013), and is the focus of the current study. The third subsystem is the linear micronozzle, which has been reported on by Louisos and Hitt (2008).

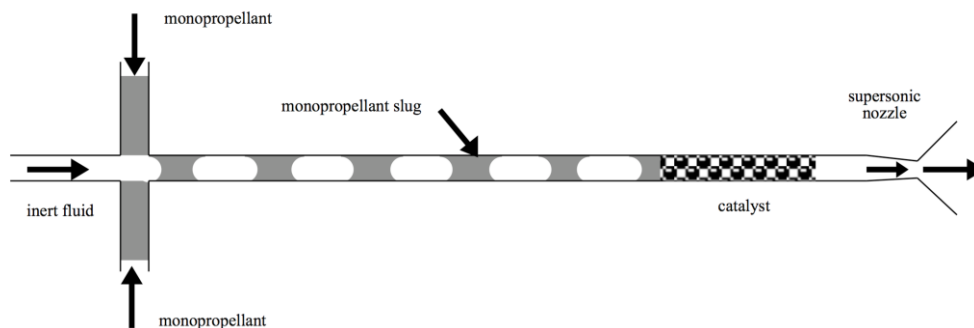


Fig. 1. Schematic of the proposed "discrete" monopropellant microthruster at UVM.

Proper sizing of the catalytic chamber is critical to the proper operation of the microthruster; if the chamber is too short, there is incomplete decomposition, wasting energy and decreasing thrust. If the chamber is too long, the water vapor may condense into droplets, which will also decrease thrust. The development of a predictive model capable of assessing critical reactor dimensions is an ongoing undertaking at the University of Vermont.

In studies by Zhou and Hitt (2003, 2004, 2005), various simplifications for the decomposition process of hydrogen peroxide have been reported, with an estimated reactor length of 1-3mm. In Widdis et al. (2013), a 2D model was developed, which simulates the decomposition process that begins once all of the reactants and products are in a gaseous state. This model has provided valuable information about the effects of thermal and mass diffusivities at the MEMS-scale, but was limited in its ability to predict reactor dimensions as it could not account for the length required to vaporize the hydrogen peroxide, or the importance of inlet boundary condition on system performance.

In this study, the performance of the catalytic chamber pre-vaporization is evaluated. This study serves as a natural complement to the work performed by Widdis et al. (2013), as it investigates effects associated with the monopropellant in its liquid form. The impact of microscale effects on the decomposition of the liquid monopropellant is investigated, and a method for enhancing the performance of the catalytic chamber via the introduction of discrete slugs of monopropellant is proposed.

2. Computational Methodology

To study the effect of liquid phase HTP entering the catalytic chamber, a computational model was developed to characterize the decomposition of hydrogen peroxide. The model tracks the species

formation and heat generation associated with the decomposition. The model is allowed to run to 423 K, the vaporization temperature of hydrogen peroxide, at which point it terminates as phase change is not included. The specific details of the model are delineated below.

2. 1. Governing Equations

2. 1. 1. Chemical Reaction

The chemical kinetic rate constant k and reaction rate r are modeled according to first-order Arrhenius kinetics:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

$$r = kC_{H_2O_2} \quad (2)$$

where E_A is a catalyst-dependent activation energy. Zhou and Hitt (2005) calculated the activation energy of an effective catalyst as 52.5 kJ/mol. The pre-exponential factor (A) has units of s^{-1} and acts as a scaling factor that varies with surface area to volume ratio. In a previous study, Zhou and Hitt (2005) estimated $A=10^9 s^{-1}$, which is consistent with value according to collision theory.

The reacting flow associated with the decomposition of hydrogen peroxide is governed by the unsteady, compressible Navier-Stokes equations, along with the transport equations for species and energy:

$$\frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c = \nabla \cdot (D_i \nabla c_i) + R_i \quad (3)$$

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \cdot \nabla T = \nabla \cdot (k \nabla T) + Q \quad (4)$$

Initial material properties are determined from the bulk concentration on a molar average. The mass diffusivity of liquid hydrogen peroxide is taken as $4E-9 m^2/s$. It is worth noting that this value is much lower than the gas diffusivity of hydrogen peroxide, which will be explored in more detail in the Results section below.

In this model, the surface effects arising from the catalytic nanorods are ignored and instead regarded as a perfect surface coating. Given the scale of the nanostructures, this is likely a good approximation. If necessary, however, their impact could theoretically be accounted for by adjusting the pre-exponential factor to match experimental results.

The equations governing the reacting flow are either the unsteady Navier-Stokes, or the multiphase unsteady Navier-Stokes. Each of these sets of equations is described in the following section.

2. 1. 2. Lamellar Flow

The unsteady Navier-Stokes equations were solved to find the flow field within the computational domain. Due to the extremely low Re number ($\sim O[1]$), the flow is laminar at all points in the simulation. The momentum and continuity equations, respectively are presented here:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-pI + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u})I] + \mathbf{F} \quad (5)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (6)$$

where \mathbf{u} is the velocity field of the fluid, ρ is the fluid density, p is the pressure, μ is the dynamic viscosity and \mathbf{F} is the surface tension force.

2. 1. 3. Slug Flow

The two-phase flow field is governed by the incompressible Navier-Stokes Equations:

$$\rho_i \frac{\partial \mathbf{u}_i}{\partial t} + \rho_i (\mathbf{u}_i \cdot \nabla) \mathbf{u}_i = \nabla \cdot [-p\mathbf{I} + \mu_i (\nabla \mathbf{u}_i + (\nabla \mathbf{u}_i)^T) - \frac{2}{3} \mu_i (\nabla \cdot \mathbf{u}_i) \mathbf{I}] + \mathbf{F} \quad (7)$$

$$\nabla \cdot \mathbf{u}_i = 0 \quad (8)$$

where the variables are the same as in Equation (5)&(6), but the subscript \mathbf{i} corresponds to the appropriate gas or liquid phase. To track the interface between the two phases, the level set method was used. In the level set method, the discontinuity between two discrete phases is represented with the level set function Φ , a continuous function bounded by zero and unity that represents the normalized distance from the interface at all points in the domain (Osher and Sethian 1998). As the flow field is calculated, the movement of the interface is calculated by:

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \phi(1 - \phi) \frac{\nabla \phi}{|\nabla \phi|} \quad (9)$$

The discontinuity in density and viscosity are smoothed across the interface using Equations:

$$\rho = \rho_1 + (\rho_2 - \rho_1)\phi \quad (10)$$

$$\nu = \nu_1 + (\nu_2 - \nu_1)\phi \quad (11)$$

The surface tension equation can then be recast in terms of the surface tension coefficient and the level set function:

$$\mathbf{F}(x) = \sigma \kappa(x) \hat{\mathbf{n}}(x) \quad (12)$$

In this formulation, the surface tension represents a volume force that is spread across the width of the interface. The new force is only equal to the surface tension in the limit as the thickness of the interface goes to zero, which places an upper bound on the maximum width of the interface. If the interface gets too small, however, the discontinuity in density and viscosity cannot be properly smoothed, which yields difficulties in computing the solution. The governing equations were solved in COMSOL 4.4, a FEA-based multiphysics solver.

2. 2. 2D Model of a Catalytic Wall

A slender straight channel was first modeled to apply the reaction kinetics to a fluid flow in order to determine system performance at mass flow rates consistent with the micropropulsion application. The flow is assumed to be unidirectional and the geometry lacks all complexities of the pillar-based catalyst bed design. This geometry is shown in Fig. 2. The inlet is a laminar inflow condition, and has been set to a prescribed temperature of 293 K and a flow rate of 1.2 m/s. Species inflow is prescribed at 100% concentration of H_2O_2 . The walls in the first 200 μm of the channel have been set as an insulated wall, with the remainder acting as a catalytic surface. This has been done to prevent heat from being conducted upstream through the boundary. The outlet is a pressure outlet (1 atm). This is the only mode for heat to exit the system. A grid convergence study of this domain was performed to verify grid insensitivity.

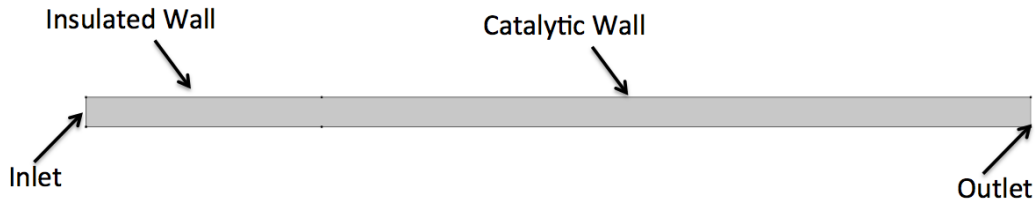


Fig. 2. Computational Geometry of the Straight Microchannel.

2. 3. 2D Model of Catalytic Pillar Geometry

Using results from the simplified straight channel, a section of the pillar array was studied, as shown in Fig. 3. This section is intended to model flow through the middle of the pillar array, and uses symmetry along the top and bottom planes. The pillars are assumed to be evenly coated in the nanorods, and serve as the reaction sites. The inlet is a laminar inflow, while the outlet pressure condition is 1 atm.

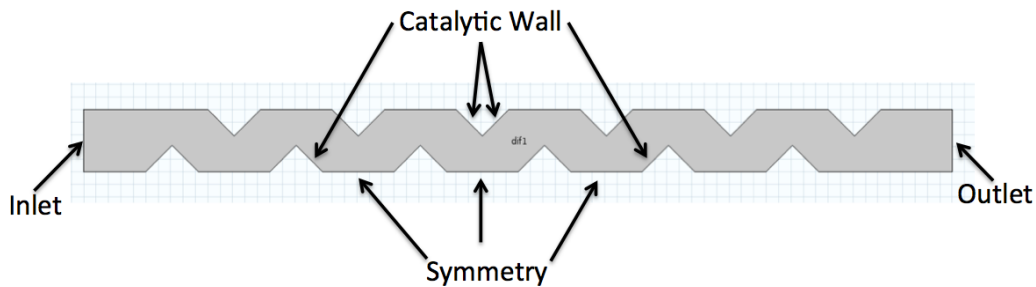


Fig. 3. Catalytic Pillar Computational Domain.

2. 4. 2D Model of a Catalytic Wall with Slug Flow

To study the effects of multiphase flow entering the catalytic chamber, the 2D slender channel was modified to provide the necessary conditions to generate slug flow. This can be accomplished at the microscale by having two immiscible fluids meeting at a cross-junction. In this model, two of the inlets are hydrogen peroxide, while the third inlet is air, with each inlet set to a flow rate of 0.4 m/s. The outlet is set at 1 atm. The wall after the junction is set as a reacting wall.

3. Results

3. 1. 2D Catalytic Wall – Laminar Flow

A sample image of the concentration of hydrogen peroxide in the straight channel is shown in Fig. 4. In the computational domain, only the region of fluid in contact with the wall, or very nearby, is decomposed. This is because at the microscale, diffusion is the only mechanism transporting the hydrogen peroxide to the catalyst. The much lower mass diffusivity of liquid hydrogen peroxide than in its gaseous state, means that a reactor sized for optimal vapor phase performance will suffer from poor performance before vaporization occurs. The results observed in this model are similar to the straight channel experimental results presented in Widdis et al. (2013). In those experiments, incomplete decomposition of the hydrogen peroxide was observed in a straight microchannel with reactive walls. The results of this computational model support that experimental effort, as they show that the low mass diffusion in the liquid-phase make vaporization, and complete decomposition, challenging.

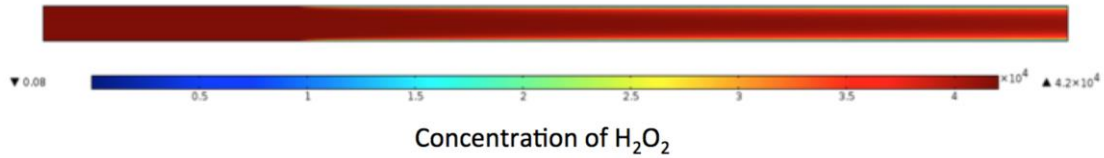


Fig. 4. Surface plot of hydrogen peroxide concentration in the straight channel.

3. 2. 2D Pillar Geometry

Having examined decomposition in the simplified catalytic wall model, the geometric impact of a pillar configuration was next considered. For these studies, the pillars are 40 μm pillars with 20 μm spacing. Representative results are shown in Fig. 5. The purpose of the nanorod-coated pillars is to enhance decomposition when compared to a straight channel. While differences in channel lengths make a direct comparison difficult, qualitatively, it can be observed that there are regions near the wall, where decomposition is much better than in the straight channel. The addition of the pillars serves to increase the reactive surface in contact with the flow for a given channel length. In a geometry that is nearly a quarter of the length, the average hydrogen peroxide concentration is slightly lower than the straight channel; presumably, over an equivalent domain length that performance would be improved even further. One challenge associated with the introduction of the pillars is the pressure drop associated with obstructing the flow. This sets an upper limit on the number of pillars that can be in the channel, if a desired mass flow rate is to be achieved. Therefore, for a given channel length, increasing the pillars can only be part of the solution for enhancing performance.

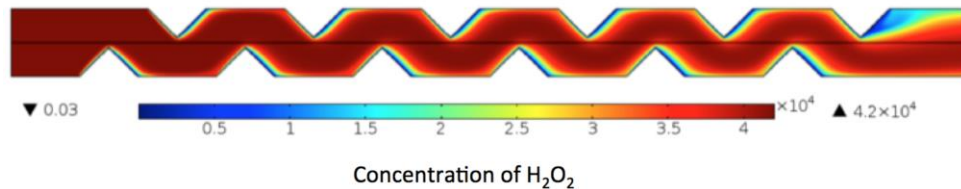


Fig. 5. Surface plot of hydrogen peroxide concentration in the pillar array.

3. 3. 2D Catalytic Wall – Slug Flow

In McDevitt and Hitt (2013), species transport in a microchannel was found to be enhanced in the slug flow regime. This enhancement is a result of the internal recirculation of the slugs that pulls the species from the center of the slug toward the exterior of the slug. While reviewing the poor performance exhibited by the catalytic chamber in these simulations, it was theorized that a similar enhancement would be found in the heterogeneous catalytic chamber if slug flow were used instead of laminar flow.

Fig. 6 shows representative results of the simulations of hydrogen peroxide decomposition in the slug flow regime. When compared to the straight channel, the concentration of hydrogen peroxide at the outlet has decreased by over 36%. A thruster using slug flow could have a catalytic chamber that is less than half as long to achieve equivalent decomposition. As theorized, this enhancement comes from the internal recirculation within the slugs, which can be clearly seen in Fig. 7. As the slug moves down the channel, it pulls unreacted hydrogen peroxide from the center of the channel toward the wall, where it can come into contact with the catalyst. This mechanism is much more effective than diffusion, which accounts for the dramatically improved performance.

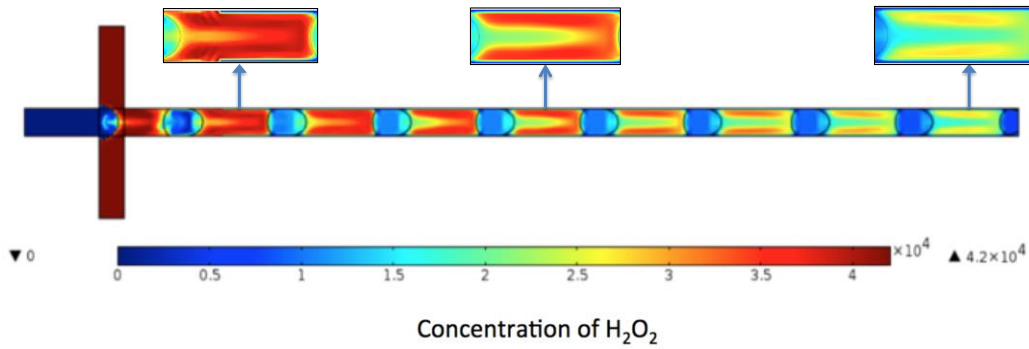


Fig. 6. Representative results of the decomposition in the microchannel with slug flow. The callouts highlight the enhancement offered by the internal recirculation of the slugs.

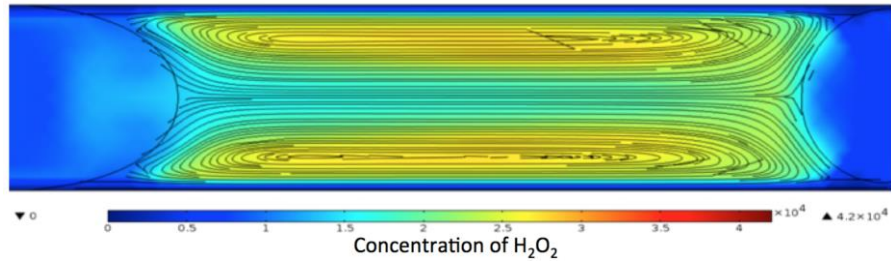


Fig. 7. Plot of the streamlines within the slug, emphasizing the internal recirculation that enhances decomposition.

To characterize the improvement, the average concentration across the microchannel was calculated at several downstream locations for both the laminar and slug flow systems. The results of these calculations are plotted in Fig. 8. Beyond the absolute improvement in performance, it is worth noting that the rate of decomposition is decreasing in the laminar system while in the slug flow system it is remaining constant. Presumably, over a longer domain this would result in a greater relative improvement for the slug flow system.

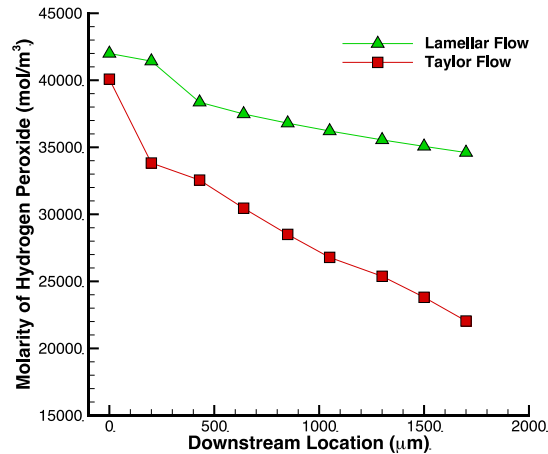


Fig. 8. Comparison of the average concentration at downstream locations in the slug flow and laminar flow systems.

4. Conclusion

In this study, a numerical model of hydrogen peroxide decomposition in a microreactor with a micropropulsion application was developed. This model builds upon the work of Widdis et al. (2013) by

focusing on performance of the catalytic chamber before vaporization begins. This adds to the development of the model, as it provides information about the engineering challenges present before the hydrogen peroxide begins to vaporize.

The major findings of this work are twofold: at the microscale, the lack of a non-diffusive mixing mechanism inhibits the performance of the catalytic chamber, and that performance can be enhanced by forcing the flow regime into a slug flow pattern. The effect of mass diffusion in the vapor phase has been studied previously, by Widdis et al (2013) and the findings here support those findings; in purely laminar flow, the low mass diffusivity of hydrogen peroxide leads to incomplete decomposition, or extremely long decomposition lengths that are not appropriate for the micropropulsion application.

The second finding is that for a given channel length, decomposition can be enhanced by improving mixing within the channel. In this study, the flow in a microchannel is forced into the slug flow regime through the addition of an immiscible gas. As these slugs flow down the microchannel, an internal recirculation pulls unreacted flow from the center of the slug toward the reacting walls. This convective mixing mechanism is much more effective than diffusion, and results in a much higher rate of decomposition at equal channel lengths.

Acknowledgements

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