Numerical model for concentration measurement during decomposition of H_2O_2 over silver catalyst

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Abstract. Minimal thrust of the order of few Newton is produced using micro thrusters, which are used for controlling the orientation and trajectory of the satellite or spacecraft. Controlled thrust production of the order of milli Newton is still a challenging task. Green propellants like Hydrogen peroxide are utilized in such applications. The products of this green fuel after decomposition are water in the form of steam and oxygen. The present work involves the simulation of hydrogen peroxide decomposition on silver catalyst which can be used in space propulsion. The simulations are done for flow of 30% hydrogen peroxide concentration when flowing inside a mini channel of size 3.4mm. Helical shaped silver catalyst is positioned inside the tube to enhance the decomposition. The model involves the concentration measurement of the reactants and products and after passing over the catalyst surface. The results will help in choosing the geometry and position of the catalyst to have effective decomposition of the monopropellant.

1 Introduction

In space propulsion, minimal thrust is required for propelling a spacecraft due to the absence of drag forces. As the technology keeps developing, many researchers and organisations have moved towards developing green fuels that are efficient and provide the same amount of thrust produced by conventional fuels. Hydrogen peroxide is such a type of green fuel that provides controlled amount of thrust for manoeuvring and trajectory setting in outer space. Hydrogen peroxide has found applications in different fields like medicine where 6% H_2O_2 is used as an antiseptic and in industries as a bleaching agent. Hydrogen peroxide is also eco-friendly and is used in advanced oxidation process (AOP), in textile industry to give high degree of brightness to the fibres without compromising their mechanical properties, as a monopropellant or bipropellant. High concentration of hydrogen peroxide is used for rocket propulsion along with other fuels. Hydrogen peroxide of varying concentrations is important for many applications. In propulsion where the concentration will be varying after passing through the catalyst, the formed products decide the amount of thrust. Hence the concentration measurement becomes important. Some of the works reported on hydrogen peroxide based propulsion systems and concentration measurements are detailed below.

Widdis et al. [1] developed a model based on MEMS-based micro propulsion using a monopropellant hydrogen peroxide. It was observed that the incomplete decomposition of hydrogen peroxide was because of the less wetted area on the catalytic walls. Adam et al. [2] evaluated the performance of hybrid sounding rockets in which hydrogen peroxide was used as an oxidizer. The study was done for optimal burn duration and selection of nozzle. Goszner et al. [3] studied the decomposition of hydrogen peroxide on silver and gold alloys for concentrations from 5 to 0.05 mol/lit and found that the catalyst behavior was basically determined by the oxygen affinity. It was concluded that gold and silver had similar properties as a catalyst. Bao-Jin et al. [4] measured 30% concentration of hydrogen peroxide using an optical device with the help of refractive index variation. Ryan et al. [5] developed a numerical model to study the hydrogen peroxide decomposition in catalytic micro reactors. It was found that due to the absence of non-mixing mechanism in micro scale the decomposition was slow in micro channels. A new technique was developed by introducing gas bubbles which significantly increased decomposition by 57% for the given length. Berna et al. [6] developed a COMSOL model and applied it to isothermal, steady state and 3D PEM fuel cells to observe parameters like concentration profiles, current density profiles and polarization curves. Duncan et al. [7] detailed the measurement of oxygen (O_2) concentration in its gaseous form with a paramagnetic analyzer. Baldikova et al. [8] used non-woven fabric fibers, which easily absorbed the manganese dioxide micro particles. The composite

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material of low-cost was used as a recoverable catalyst for hydrogen peroxide decomposition. Mohith et al. [9] measured the concentration of hydrogen peroxide experimentally based on the change in optical property and refractive index. An IR transceiver circuit was used to measure the concentration. Kang et al. [10] studied high concentration hydrogen peroxide to design high-speed underwater jet engines. Hydrogen peroxide decomposition was the primary fluid used for propulsion and a huge amount of propulsive force was successfully generated and could be used for unmanned underwater vehicles. Lennon et al. [11] worked on the multiphase catalytic decomposition of H_2O_2 into H_2O and O_2 and investigated a way to reduce the risk of thermal runaway. Thirumalikumaran et al. [12] analysed the products after catalytic decomposition of hydrogen peroxide with silver catalyst inside mini channels. The above literature details the various works reported on decomposition of hydrogen peroxide using silver as a catalyst. Many types of sensors are reported in literature for concentration measurement when the fluid does not undergo catalytic decomposition. However works done for online measurement of concentration during catalytic decomposition is limited. In the present work a numerical model is developed using COMSOL Multiphysics to analyze the effects of geometry of the catalyst silver on decomposition rates. The concentration variation during the flow process is also detailed. Such a numerical model is essential for understanding the decomposition phenomenon, which in turn will control the thrust required for micro propulsion devices used in Nano satellites.

2 Numerical model

The numerical model is developed using COMSOL Multiphysics software. Initially as a validation exercise the catalytic decomposition process is carried out in a batch process. Later a 2D and a 3D model is developed with the same package to analyse the variations during the flow process.

2.1 Zero Dimensional Model

The zero dimensional model assumes a batch type reactor process with constant volume. The rate expression is of first order for the given reaction and Arrhenius expression is used as given in Goszner [3] et al. The values for activation energy are given as 52200 J/mol and frequency factor of collision as 0.18 x10^9 (m^3/s mol). The reaction is taken from the experiment done by Thirumalikumaran et al. [12] The decomposition reaction is,

$$H_2O_2 \xrightarrow{decomposition\ by\ catalyst(Ag)} H_2O + 0.5O_2 \quad (1)$$

The surface species (catalyst) is kept with locked concentration. The governing equations in reaction engineering are,

$$\frac{dc_i}{dt} = R_i + R_{ads,i}\frac{A_r}{V_r} \quad (2)$$

Here for a species i, C_i is the concentration, R_i is the rate of the species, $R_{ads,i}$ is the rate effect of surface species on i, A_r is the surface reaction area and V_r is the reactor volume. The study is carried out with time steps of 0.1 to 1 second, the results are plotted in a 1D graph.

2.2 2D Model Straight Channel

After verifying the energy balance and volume based reactant and products, the model is further developed to simulate the decomposition in a mini channel. Here the hydrogen peroxide will flow over a 2D catalytic wall for a specific length. The dimensions are same as that of Widdis et al. [1]. The flow velocity is set as 1.2 m/s and unidirectional, the concentration of hydrogen peroxide is set as 100%. Part of the channel is insulated with wall type boundary condition and the remaining with catalytic walls. The catalytic walls are set with open boundary. The outlet pressure is set as 1atm. The physics used in the geometry is similar to the one used in the 3D model explained in the next section. The mesh is given as normal mesh. The geometry is given below,

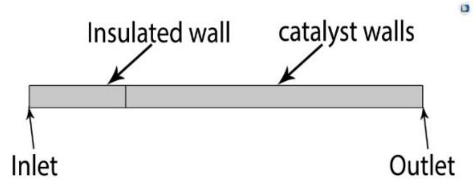

Fig. 1. Geometry of the straight channel.

2.3 3D Model with Helical Catalyst

After validation of the process involved using a 2D model, a 3D model is developed. The main geometry is developed in COMSOL Multiphysics software which consists of a cylindrical mini channel having diameter of 3.4 mm and length of 60 mm. The catalyst is of helical structure (spring) having 10 turns and has a diameter of 3 mm. The helix is positioned about 20 mm from the inlet. Silica glass is the chosen material for the mini channel walls and the catalyst is silver (Ag).

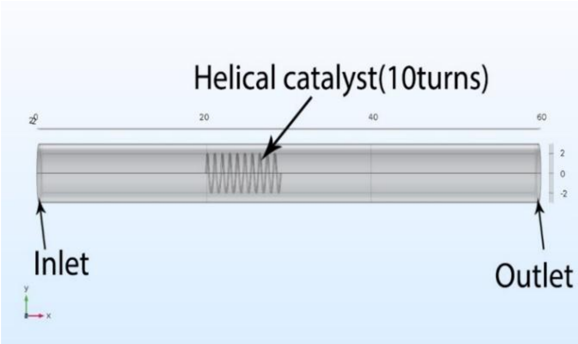

Fig. 2. Numerical model of 3D geometry with helical catalyst.

The 3D component is developed using the following physics. Transport of diluted species is used to compute the concentration field. The governing physics involves the use of Fick's law for transport by diffusion and adsorption as the adsorption happens on the catalytic surface. The products are formed when they are desorbed from the catalyst surface. The equations governing the transport of diluted species are,
Fick's law,

$$\nabla \cdot (-Di\nabla Ci) + u \cdot \nabla Ci = Ri \quad (1)$$

$$Ni = -Di\nabla Ci + uCi \quad (2)$$

Here for the species i, N_i is molar flux, D_i is the diffusion coefficient, u is the velocity of the fluid and C_i is the concentration. Transport mechanisms also include convection. Diffusion coefficients for the species are specified as 4 x 10^{-4} m/s. No flux is given for the outer walls of the channel. Initial values are given as concentration of the species. Inlet concentration of hydrogen peroxide is given as 8823.52 mole/m^3(for 30% concentration), water as 38888.89 mole/m^3, and oxygen as 0 mole/m^3. The flux discontinuity is specified over the catalyst boundary for the surface reaction of hydrogen peroxide to happen. Heterogeneous catalysis takes place in this type of catalytic decomposition. The same reaction and values used in the zero dimensional model is taken and the species from the reaction are H_2O_2, H_2O, Ag and O_2. This physics acts over all the domains. The governing equations in chemistry are,

Reaction rate,

$$R_i = \sum_j R_{ij} \quad (3)$$

Reaction rate over the surface,

$$R_{ads} = \sum_j R_{ads,j} \quad (4)$$

Arrhenius equation,

$$k = A(\frac{T}{T_{ref}})^n \cdot e^{\left(-\frac{E}{RT}\right)} \quad T_{ref} = 293K \quad (5)$$

In this R_i *and* R_{ads} denote the rates of the reactants and rate with the surface species. In Arrhenius equation k is the reaction rate, A represents the frequency factor for the reaction, T represents the temperature, T_{ref} represents the reference temperature, n represents the forward temperature exponent, E denotes the activation energy, R denotes the gas constant with value 8.314 J/mol. Navier-Stokes equation and continuity equation are employed in this physics. The inlet velocity is specified as 0.01m/s and in the outlet it is given as suppressed backflow and pressure is set as zero. The governing equations are,

Navier-stokes equation,

$$\rho\left(\frac{\partial u}{\partial t} + u \cdot \nabla u\right) = -\nabla p + \nabla \cdot \left(\mu(\nabla u + (\nabla u)^T) - \frac{2}{3}\mu(\nabla \cdot u)I\right) + F \quad (6)$$

Continuity equation,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \quad (7)$$

Here p is the pressure of the fluid, u is the velocity of the fluid, ρ is the fluid pressure and μ is the fluid dynamic viscosity. In the Navier-stokes equation the various terms corresponds to the (left side) pressure force, (right side) viscous forces and the external forces applied. Mesh is given as finer. The 3D model is studied as time dependant from 0 to 1s with time steps of 0.1.

3 Results and discussion

3.1 Zero dimensional Model

The concentration distribution from the reaction engineering in zero dimensional plot is shown in a 1D plot. The graph is plotted considering the inlet concentration of hydrogen peroxide and other species. The reaction has proceeded in the expected way and the products are formed as shown in the graph. The study is time dependant and starts from 0 to 1 second with time steps of 0.1. The graph with the concentration variation with respect to time from reaction engineering is shown below,

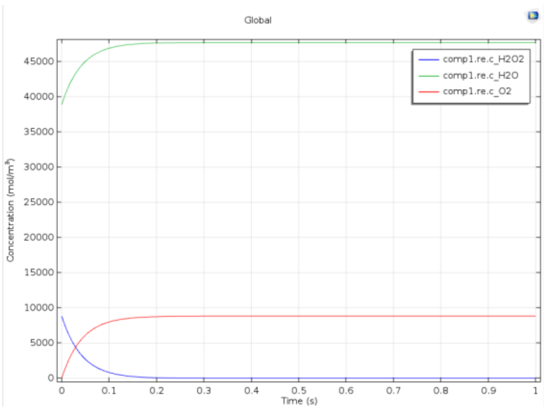

Fig. 3. Concentration plot in 1D for 30% concentration of hydrogen peroxide.

From the reaction-engineering graph, it is found that the concentration of hydrogen peroxide decreases in a parabolic trajectory to lower concentrations and reaches a zero value indicating a complete decomposition. Similarly the concentrations of water and oxygen has increased in a parabolic trajectory to higher concentrations. The concentration of hydrogen gets exhausted in 0.2 s and goes to near zero for the rest of the time, similarly for water the main change has happened in 0.2 s. From the reaction, the amount of water concentration coming out is higher.

3.2 2D Model Straight Channel

The catalyst reaction is modelled with the wall as the catalyst and the fluid that is in contact with the wall is only decomposed. In microscale, the transport is only due to diffusion. The results that are from this model are similar to the straight channel model by Widdis et al. [1] which validates the present numerical model developed.

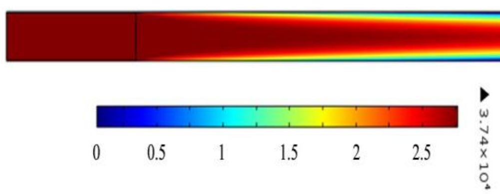

Fig. 4. Hydrogen peroxide concentration (mol/m^3) in straight channel (surface plot).

In this channel, the decomposition of hydrogen peroxide is very much less. As the decomposition in this channel is incomplete, a better geometry of catalyst can improve this discrepancy. A better computational model is developed with the help of COMSOL Multiphysics in 3D geometry.

3.3 3D Model with Helical Catalyst Reaction

The results from the 3D component are studied as time dependant and the 3D plots are plotted for the concentrations of H_2O_2, H_2O and O_2 and velocity after 1s.

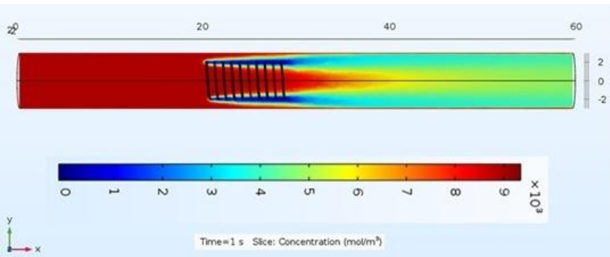

Fig. 5. Concentration of H_2O_2 (mol/m^3)

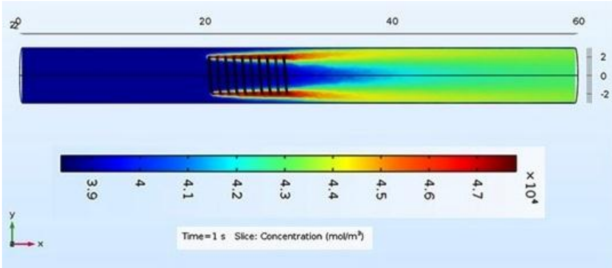

Fig. 6. Concentration of H_2O (mol/m^3)

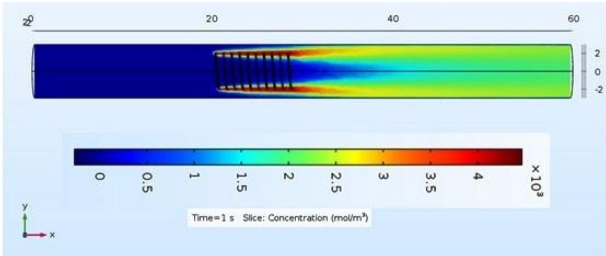

Fig. 7. Concentration of O_2 (mol/m^3)

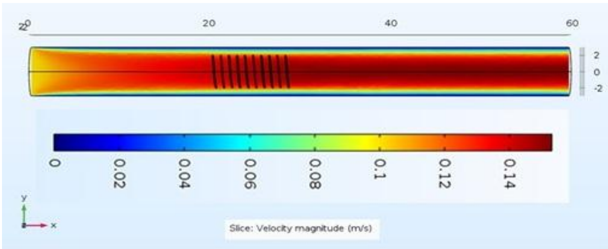

Fig. 8. Velocity plot in (m/s).

From the plots, it is seen that there is a significant decrease in the concentrations of H_2O_2, and concentration of H_2O and O_2. The decomposition is much better in this model with a helical silver catalyst and this serves as a better model for the decomposition of hydrogen peroxide. The helical catalyst improves the surface area that is exposed to the hydrogen peroxide thereby improving the reaction and solving the discrepancy. The increase in number of turns of the helix will increase the reaction further. The velocity in the channel has increased and has reached nearly 0.15 m/s. The pressure drop is also significant.

4 Conclusion

A numerical simulation model is developed using COMSOL Multiphysics software. The model that is developed is validated with the model by Widdis et al.[1] A 3D model is developed to simulate the decomposition reaction of hydrogen peroxide on a silver catalyst for the measurement of the reactants and products. The percentage of unused hydrogen peroxide concentration coming out after reaction from the catalyst is also known and this can help in placing the number of helical catalysts or increasing the number of turns in the catalyst so that maximum reaction of hydrogen peroxide can happen. This model can be used for concentration measurement. Future work is to match the numerical values with the experimental values of concentration.

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