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Simulation of decomposition of sulfur trioxide gas on a self-catalytic material

Kiran Kumar Muramalla
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SIMULATION OF DECOMPOSITION OF SULFUR TRIOXIDE GAS ON A
SELF-CATALYTIC MATERIAL

by

Kiran Kumar Muramalla

Bachelor of Technology in Mechanical Engineering
Jawaharlal Nehru Technological University, India
2003

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Mechanical Engineering
Department of Mechanical Engineering
Howard R. Hughes College of Engineering

Graduate College
University of Nevada, Las Vegas
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Simulation of Decomposition of Sulfur Trioxide Gas on a Self-Catalytic Material

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Dean of the Graduate College

ABSTRACT

Simulation of Decomposition of Sulfur Trioxide Gas on a Self-Catalytic Material.

by

Kiran Kumar Muramalla

Dr. Yitung Chen, Examination Committee Chair
Associate Professor, Department of Mechanical Engineering
University of Nevada, Las Vegas

This thesis deals with the development of a two-dimensional numerical model to predict the wall-catalyzed homogeneous decomposition of sulfur trioxide gas in tubular component geometry for the production of hydrogen by the sulfur-iodine thermochemical water splitting cycle, a candidate cycle in the U.S. Department of Energy Nuclear Hydrogen Initiative. Cross flow type of heat exchanger concept is chosen for the analysis. The reacting fluid is a mixture of sulfur trioxide gas and water vapor inside the tubes of a heat exchanger. The heat exchanger tubes are made of Incoloy alloy 800H with ALFA-4 coated on the inner walls which acts as a catalyst for the chemical decomposition of sulfur trioxide into sulfur dioxide and oxygen. Decomposition of sulfur trioxide depends on many different parameters such as catalyst used, wall surface temperature, mole flow rate of the reacting mixture, diameter of the reactor tube, length of the reactor tube, operating pressure and inlet temperature of the reacting mixture. The effects of variation of wall surface temperature, diameter of the reactor tube, length of the tube and mole flow rate of the incoming mixture on the decomposition of sulfur trioxide were

investigated using a two-dimensional numerical model using computational fluid dynamics (CFD) techniques. It is observed that smaller diameter reactor tubes, higher temperatures and lower flow rates allow having higher decomposition. Sulfur trioxide decomposition reaction in the presence of catalyst platinum is also analyzed using a three-dimensional numerical model where helium acts as a hot fluid that supplies thermal energy required for the endothermic sulfur trioxide decomposition reaction.

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NOMENCLATURE

A_r	Pre-exponential factor, s^{-1}
C_p	Coefficient of heat capacity, J/kg-K
D	Diameter of the reactor tube, mm
D_{AB}	Binary mass diffusion coefficient, m^2/s
E_r	Activation energy, J/kg-mol
K	Rate of the reaction, 1/s
K	Thermal conductivity of the fluid, W/ m-K
L	Length of the reactor tube, mm
M	Molecular weight, kg/kg-mol
P	Pressure, Pa
ΔP	Pressure drop, Pa
Q	Volumetric flow rate, m^3/s
R	Universal gas constant J/kg-mol-K
Re_D	Reynolds number
R_i	Net rate production of species, 1/s
S_i	Rate of reaction by addition from the dispersed phase, $kg\text{-mol}/m^3\text{-s}$

T	Temperature, K
T_w	Wall temperature, K
U	Velocity, m/s
Y_i	Mass fraction of the species
$\sum v$	Atomic diffusion volumes

Greek Symbols

η	Pump efficiency
μ	Dynamic viscosity, kg/m-s
ρ	Density, kg/m ³

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Hydrogen is the latest in the succession of energy providers, with many social, economic, and environmental benefits to its credit. Although hydrogen (H_2) is ubiquitous, it does not exist by itself naturally, so it must be generated out of substances such as water or natural gas. Current hydrogen separation processes use fossil fuels to raise the temperature enough to produce H_2 from either water or natural gas. Producing hydrogen with these processes releases greenhouse gases. In addition, carbon dioxide is also released into the atmosphere as a by-product of natural gas separation. Therefore, replacing the heat source with nuclear energy would help to relieve climate change concerns. Three major ways of producing hydrogen from water are electrolysis, thermochemical water splitting, and high-temperature electrolysis or hybrid electrolysis-thermochemical water-splitting. Splitting water through the thermochemical process offers the potential for clean, efficient and cost effective large scale production of hydrogen. In addition, the separation of water into hydrogen and oxygen using thermochemical water splitting cycles would occur at a much lower temperature than a direct decomposition of water which needs a temperature more than $2500^{\circ}C$. Figure 1.1

shows how the hydrogen production plant is connected to the nuclear power plant according to Department of Energy (DOE).

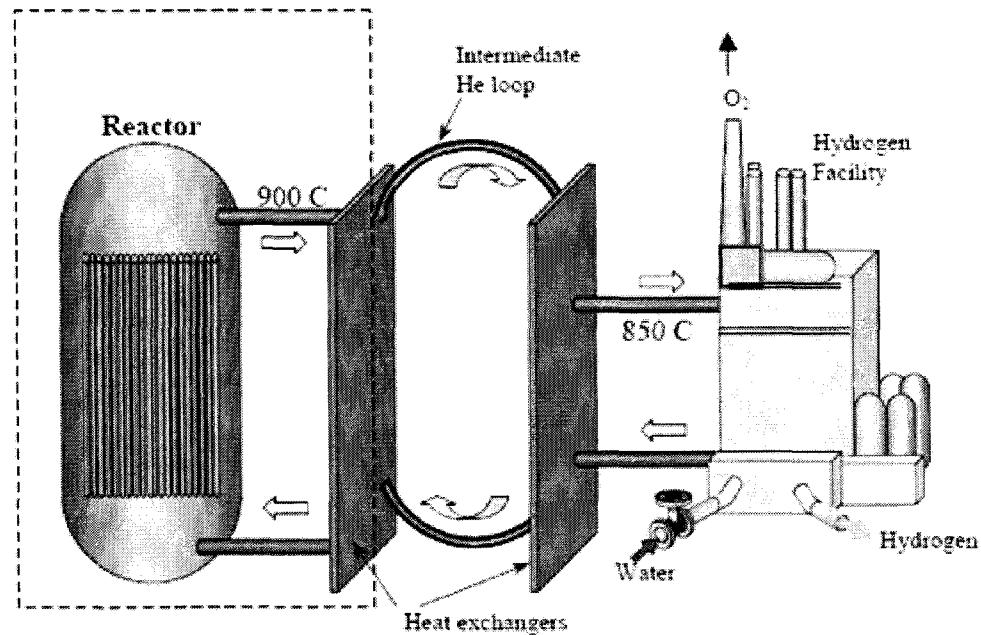


Figure 1.1. Schematic diagram of the nuclear hydrogen production plant according to DOE

Thermochemical water-splitting is the conversion of water into hydrogen and oxygen by a series of thermally driven chemical reactions. Energy, as heat, is input to a thermochemical cycle via one or more endothermic high temperature chemical reactions. Heat is rejected via one or more exothermic low temperature reactions. All the reactants, other than water, are regenerated and recycled. Among different thermochemical water splitting cycles, the sulfur-iodine cycle is a prime candidate as it offers a highly efficient process that can be achieved under practical reaction environments which helps to keep the final cost of hydrogen down. The Sulfur-iodine (S-I) cycle was developed at General Atomics in the mid 1970s; different reactions involved in the cycle are shown below.



In this cycle, iodine and sulfur dioxide are added to water, forming hydrogen iodide and sulfuric acid in an exothermic reaction (1.1). Under proper conditions, these compounds are immiscible and can be readily separated. The sulfuric acid can be decomposed at about 850°C releasing the oxygen and recycling the sulfur-dioxide (1.2). The hydrogen iodide can be decomposed at about 350°C, releasing the hydrogen and recycling the iodine (1.3). The net reaction is the decomposition of water into hydrogen and oxygen (1.4). In the S-I cycle most of the input heat goes into the dissociation of sulfuric acid, (1.2). The whole process takes in only water and high temperature heat and releases only hydrogen, oxygen and low temperature heat. All reagents are recycled; there are literally no effluents. Figure 1.2 represents the schematic diagram of how different chemical involved in different reactions in the S-I cycle.

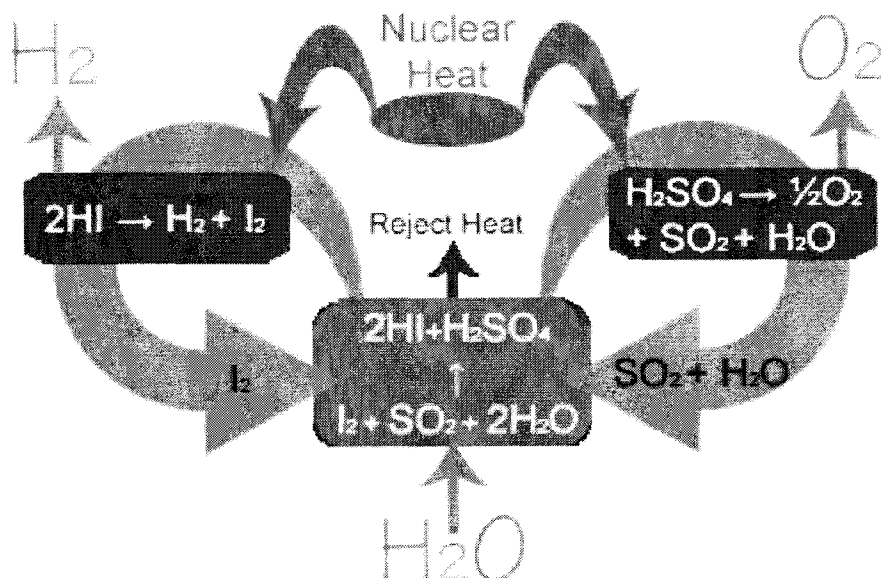


Figure 1.2. Recycling of different chemicals involved in different reactions in S-I thermochemical cycle [adopted from Reference 8]

1.2 Research Objectives

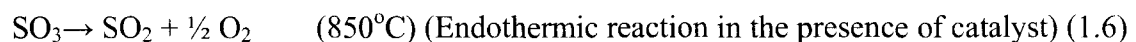
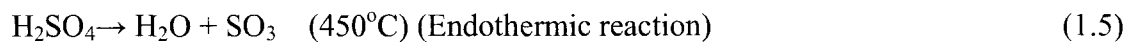
The Department of Energy (DOE) gave the motivation for this work in support of the Next Generation Nuclear Plant (NGNP) program that deals with the production of hydrogen. Some of the research objectives that have been outlined are

- Model the decomposition of sulfur trioxide on a catalytically coated surface
- Analyze the performance of catalyst at different temperatures on a two-dimensional numerical model
- To study the effect of variation of different parameters, diameter of the reactor tube, length of the reactor and mole flow rate at the inlet of the reactor tube on the decomposition of sulfur trioxide using a two-dimensional numerical model
- Compare the simulation results with available experimental data

- To investigate the decomposer performance on a three-dimensional numerical model

1.3 Literature Review

Over past three decades a large amount of experimental work has been conducted in understanding not only the chemical reactions involved in the decomposition of sulfuric acid but also in analyzing the performance of the catalyst involved in the acid decomposition. In most of the cases a shell and tube configuration with a packed catalyst bed either on the shell side or on the tube side was considered for the experiments. For example, General Atomics (G A) [1] is one of the companies that worked on understanding the decomposition of sulfuric acid in the presence of a catalyst by conducting the experiments on a laboratory scale sulfuric acid decomposing plant. General Atomics has designed, built and tested a high-pressure catalytic metal reactor for the purpose of estimating the behavior and operating characteristics of large reactors for solar applications. The overall system is made up of two identical systems each having a different catalyst to decompose sulfuric acid. Each system consists of a boiler, a super heater, a decomposer, a condenser, and a vapor/liquid separator. The feed to the reactor is sulfuric acid. The decomposition of sulfuric acid, (1.2), further consists of two different reactions as shown below.



The first step is the vaporization and super heating of the sulfuric acid and its products. It happens when sulfuric acid is fed into a boiler where liquid sulfuric acid decomposes into sulfur trioxide gas ($\text{SO}_3(\text{g})$) and water vapor ($\text{H}_2\text{O}(\text{g})$) at around 450°C and 5atm. The gaseous mixture is fed into a super heater whose sole purpose is to raise the temperature of the gaseous mixture from 450 to 600°C so as to avoid recombination of decomposed products. The second step is to decompose the sulfur trioxide further into sulfur dioxide and oxygen. The hot reacting gaseous mixture coming from the super heater is fed into a decomposer where sulfur trioxide further decomposes into sulfur dioxide and oxygen in the presence of a catalyst. A schematic representation of the flow of sulfuric acid and its components through the different parts of the plant is shown in Figure 1.3.

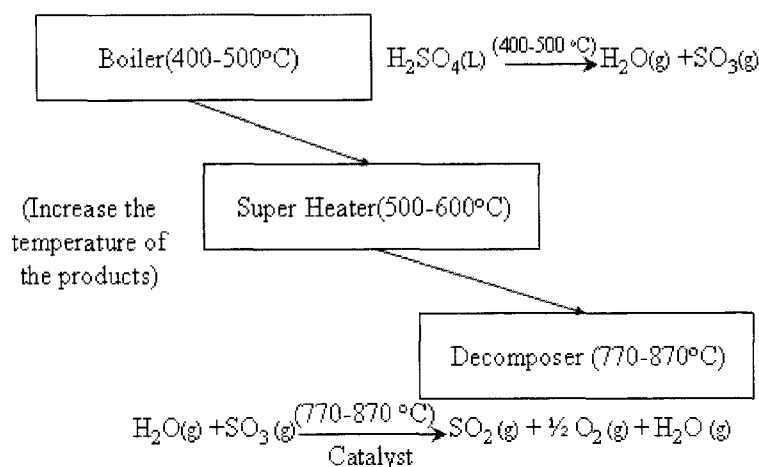


Figure 1.3. Schematics of sulfuric acid flow through different components in S-I production plant.

The decomposer further consists of three different parts, non-reactive inlet, reactor panel, non reactive outlet. The model of the decomposer created in SOLID WORKS according to the description in the General Atomics report [1] is shown in Figure 1.4. The reactor panel is constructed entirely of incoloy alloy 800H. Flow of hot reacting mixture, H_2O and SO_3 , enters the reactor panel through the non reactive inlet manifold and from there the steam splits into 5 different reactor tubes which consist of catalyst in the form of a packed bed to support the decomposition of sulfur trioxide. Then the decomposed mixture is collected into a non-reactive outlet manifold.

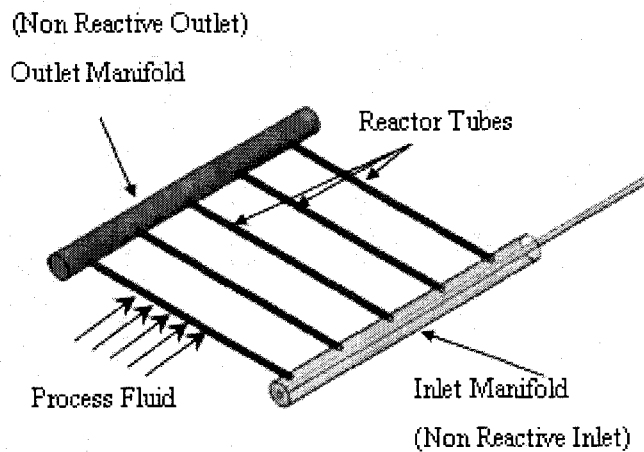


Figure 1.4. Schematic of decomposer created in SOLID WORKS based on G A report [1]

Two different sets of experiments were done for two different catalysts, platinum and iron oxide. But in both cases the catalysts are used in the form of pellets. The reactor tubes were filled with a platinum catalyst supported on zirconia and similarly for the other panel an iron oxide catalyst supported on alumina. G A conducted the experiments for the temperature range from 700°C to 900°C at different pressure conditions 5atm, 7.5atm and 10atm and for different mole flow rates 3mol/min, 4mol/min and 5mol/min.

The percentage decomposition of sulfuric acid at different mole flow rates at 7.5atm for platinum catalyst and for iron oxide catalyst is shown in Figures 1.5 and 1.6, respectively [1].

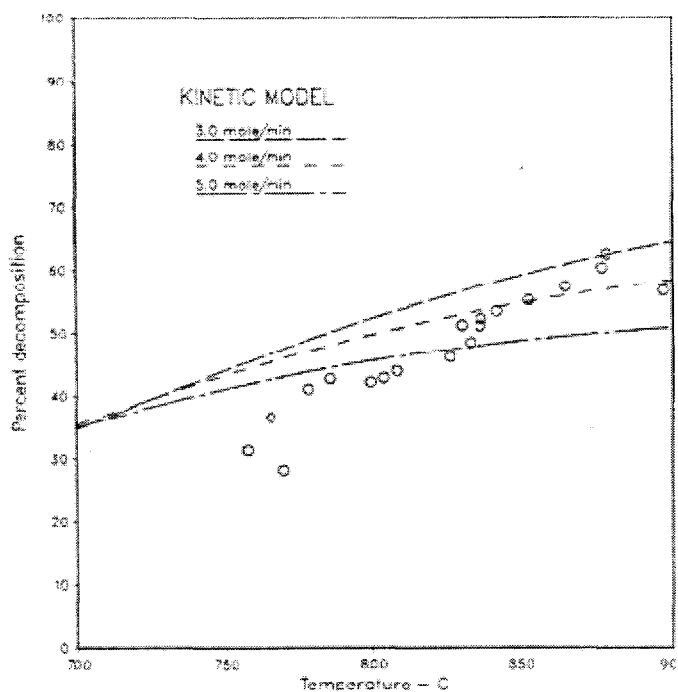


Figure 1.5. Percentage decomposition of sulfuric acid at different temperatures for a platinum catalyst

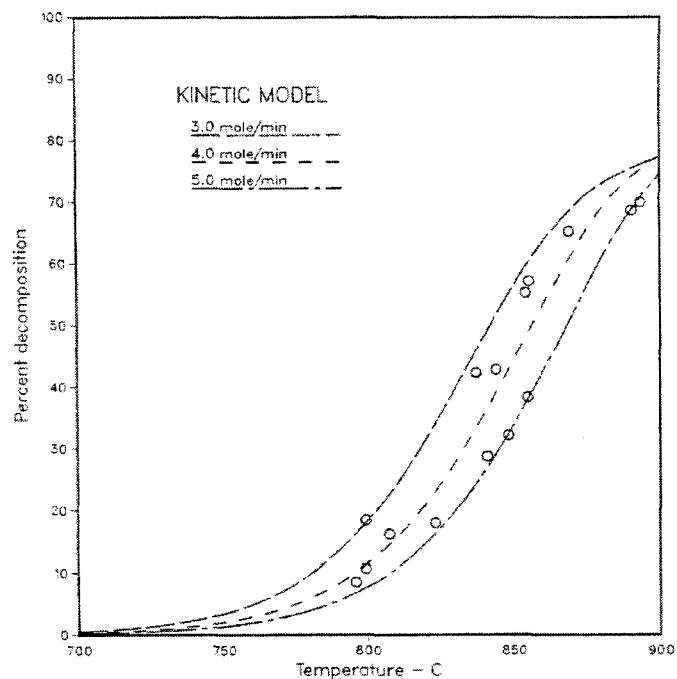


Figure 1.6. Percentage decomposition of sulfuric acid at different temperatures for an iron oxide catalyst

They concluded that the performance of iron oxide is good at higher temperatures but it is very poor at lower temperatures where as there is not much variation in the platinum catalyst over the same temperature range. Percentage decomposition of sulfuric acid in the presence of catalyst is around 35% even at temperatures close to 700°C where as for the catalyst iron oxide there is no decomposition observed at that temperature.

Cunping Huang, Ali T-Raissi [2] used Aspen Technologies' HYSYS chemical process simulator (CSP) to develop flowsheets for sulfuric acid decomposition that include all mass and heat balances. Based on the HYSYS analyses, two new process flowsheets have been developed. These new sulfuric acid decomposition processes are simpler and more stable than previous processes and yield higher conversion efficiencies for the sulfuric acid decomposition and sulfur dioxide and oxygen formation. The

developed flowsheets are on the assumption that WX-2 is used as a catalyst in enhancing the decomposition of sulfur trioxide. The activation energy and pre-exponential factor used for the flowsheet development are 17.46 kcal/mol/k and $2.45 \times 10^8 \text{ h}^{-1}$. Different flowsheets are developed for different sulfur trioxide decomposer temperatures starting from 500 to 850° C and there is a 100 % decomposition of sulfur trioxide for the flowsheets developed even at 500° C. This indicates the fact that the sulfur trioxide decomposition can be efficient even at lower temperatures with selection of appropriate catalyst.

S.S. Lin and R. Flaherty [3] the design studies of the sulfur trioxide decomposition reactor encompassing the thermodynamics, reaction kinetics, heat transfer and mechanical considerations, are described along with a brief description of the test units. Experiments were to find out the percentage decomposition of sulfuric acid for different decomposer temperatures for different sulfuric acid concentrations. They designed a pressurized test unit (PTU) to carry out the experiments at 20 atm using ALFA-4 as catalyst for decomposing the sulfur trioxide. The choice of catalyst was made based on the experiments carried out at Westinghouse. ALFA-4 has been selected due to its satisfactory performance and low cost. The PTU consists of three major units that help in decomposing the sulfuric acid via vaporizer, pre-heater and acid decomposer. Helium is used as a heat transport medium to provide the heat for endothermic decomposition of sulfur trioxide, both preheating and decomposing the acid vapor, and to provide the heat from the final stage of acid vaporization. The acid decomposer is a shell and tube type heat exchanger where the catalyst ALFA-4 is located in the shell-side of the decomposer, with helium flowing through the tubes. The preheating section of the reactor is loaded

with a packed bed of spheres or rings containing no catalyst but intended solely for increasing the rate of heat transfer. On the shell side of the decomposer cylindrical catalyst beads consisting of ALFA-4 on alumina substrate were used. The tube side consists of 21 tubes of inner diameter 0.5in. Decomposition of SO_3 at 20 atm and various temperatures vs feed composition is shown in Figure 1.7. The percentage decomposition of SO_3 was very low at temperatures below 1000 K. However satisfactory conversions were obtained at temperatures greater than 1073 K.

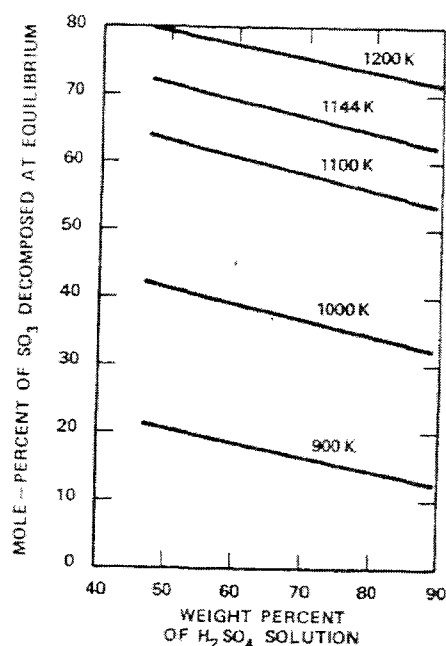


Figure 1.7. Percentage decomposition of SO_3 at 20 atm. and various temperatures vs feed composition.

1.4 Outline of Thesis

This thesis research focuses on designing and simulating the flow of chemical decomposition of sulfur trioxide in wall catalyzed reactor tubes using computational fluid

dynamics (CFD) analysis. Performance of catalyst ALFA-4, coated on the inner walls of the reactor tubes is tested at different temperatures and the study also focuses on the effect of variation of several parameters, diameter of the reactor tubes, length of the reactor tubes and mole flow rates at the inlet of the reactor tubes, on sulfur trioxide decomposition. Chapter 2 shows the details of description of the problem, geometry of the two-dimensional numerical model, inputs calculation and governing equations. Chapter 3 describes the numerical method for solving the problem involved with both heat transfer and wall catalyzed chemical reaction. The grid independent study and validation of model by comparing the results with experimental results are shown in Chapter 4. Chapter 5 discusses the two dimensional numerical modeling results for performance of catalyst and also for the different parameters variations. Chapter 6 deals with three-dimensional numerical model and results for catalyst platinum. Conclusions based on both 2D and 3D modeling, and some suggestions for future work are discussed in chapter 7.

CHAPTER 2

DESCRIPTION OF THE PROBLEM, CALCULATION OF INPUTS AND GOVERNING EQUATIONS

2.1 Description of the Problem

The sulfur trioxide decomposition is a very important reaction which has an effect on hydrogen production so SO_3 decomposer should be designed with care to attain highest possible decompositions for given operating conditions. There is no specific design that has been proposed for the sulfur trioxide decomposer. It can be a counter flow or a parallel flow or cross flow type heat exchanger. However the decomposer considered for two-dimensional modeling is a shell and tube heat exchanger. The reactor tubes carrying the reacting mixture consists of four different chemical species in their gaseous state, H_2O , SO_3 , SO_2 and O_2 , which enter the reactor tubes at around 875 K. Where as the shell side fluid could be either helium or liquid salt coming from the high temperature heat exchanger (HTHX) at around 1145K. The tube side fluid, reacting mixture acts as a cold fluid where as shell side fluid acts as a hot fluid which provides the thermal energy required for SO_3 decomposition. The pressure on the hot fluid side and on the cold fluid side is 7 MPa and 0.7 MPa respectively. The inner walls of the reactor tubes on the cold fluid are coated with the catalyst which is essential for sulfur trioxide decomposition

The decomposer should be capable of decomposing 24 kg/hr (~245 mol/hr) of sulfuric acid. The initial geometry selected for the analysis is similar to the laboratory scale decomposer designed by General Atomics which is shown in Figure 1.4. Length and diameter of the reactor tubes are 500 mm and 12.7 mm, respectively. A total of five reactor tubes of the above mentioned dimensions accommodate the total flow rate of 24 kg/hr of sulfuric acid. Inner walls of the reactor tubes are coated with ALFA-4 which acts as a catalyst in decomposing sulfur trioxide gas. Hot fluid which acts as a heat source for the endothermic reaction is replaced with a constant wall surface temperature. Constant wall surface temperature allows understanding the performance of the catalyst at different temperatures which is a difficult task in case of a fluid flowing over the tubes. The problem can be described using a schematic diagram as shown in Figure 2.1.

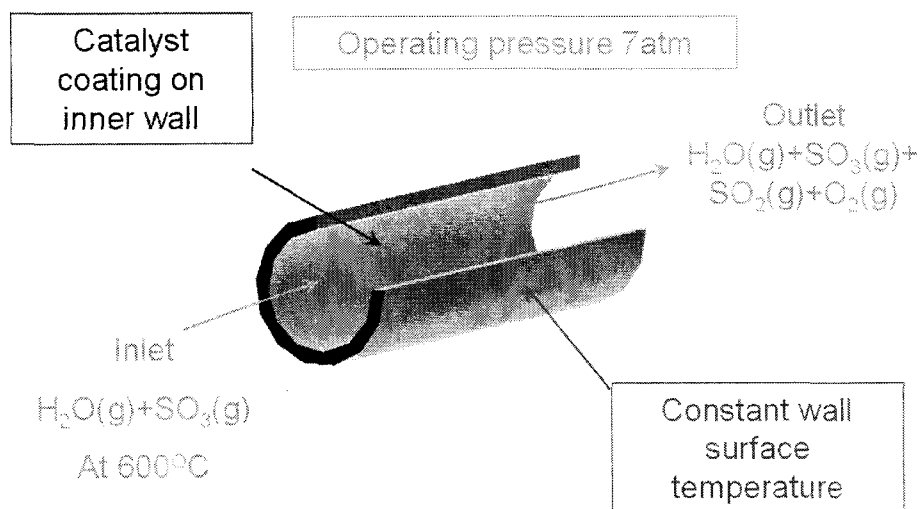


Figure 2.1. Schematic diagram of the tubular decomposer

2.2 Modeling Approach

Initially the decomposition of sulfur trioxide is analyzed using the two-dimensional model with constant properties; at later stages variable properties are introduced. ALFA-4 is used as a catalyst for initial work. At later stages platinum is used as a catalyst to validate the model with available experimental results and also for three-dimensional analysis. Investigation is carried out on a 12.7 mm diameter reactor tube with length equal to 500 mm. The two-dimensional grid for the above mentioned reactor tube is generated using GAMBIT with 30,000 nodes. The reactor tube aspect ratio is very high so it is difficult to view the mesh for the entire reactor tube at once. The magnified view at the inlet portion of the reactor tube is shown in Figure 2.2.

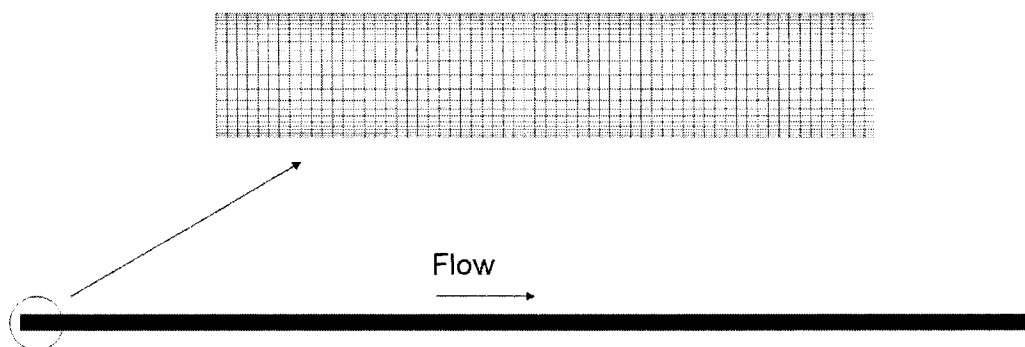


Figure 2.2. The computational mesh at the inlet of the reactor tube

The mesh density variation from wall to the center of the reactor tube can be seen clearly from Figure 2.2. The sulfur trioxide decomposition is modeled as a wall surface reaction so very fine mesh has been used near to the wall surface where the high gradients of concentrations occur. Since the gradients of concentrations along the length

of the reactor tube is very less when compared to the gradients of concentrations in radial direction, the mesh density along the length of the reactor tube is kept constant.

2.3 Inputs Calculations

To simulate the reaction mechanism there is a need for different properties which include both individual species as well as the mixture. Properties such as density (kg/m^3), specific heat (J/kg-K), thermal conductivity (W/m-K) and viscosity (kg/m-s), at 870°C for both individual species as well as the mixture are taken from G A report [4]. Similarly other inputs such as standard state enthalpy (J/kg-mol), standard state entropy (J/kg-mol), reference temperature (k) and molecular weight (kg/kg-mol), are taken from NASA report [5]. Inputs such as inlet and outlet mass fractions for (N-1) species i.e. 3 species are calculated according to the G A report [1]. Binary mass diffusion coefficients for all the six pairs of species are calculated at 700°C and at 7 atm using the Fuller, Schettler, and Giddings relation, equation (2.1), [6].

$$D_{AB} = \frac{10^{-3} T^{1.75} [(M_A + M_B) / M_A M_B]^{1/2}}{P[(\sum \nu_A)^{1/3} + (\sum \nu_B)^{1/3}]^2} \quad (2.1)$$

Thermal diffusion coefficients are calculated by FLUENT material properties panel using kinetic theory. Apart from the fluid properties FLUENT also needs information about the chemical reaction and the type of catalyst. Inputs required to represent the reaction such as stoichiometric coefficients for reactants, stoichiometric coefficients for products, rate exponent for reactants and rate exponent for products are calculated using the dissociation of sulfur trioxide Equation (1.6). Similarly the inputs

required to represent the catalyst, pre-Exponential factor ($1.041\text{E}+10 \text{ S}^{-1}$) and activation energy ($1.964\text{E}+08 \text{ J/kg mol}$) are taken from International Journal of Hydrogen Energy [3].

Boundary conditions required for reacting flow calculations such as temperature of the mixture at inlet, wall surface temperature (T_w), operating pressure condition are taken from the G A report [1]. Velocity of reacting mixture at the inlet of the reactor tubes is calculated according to the conceptual design of sulfur trioxide decomposer. A total of 5 reactor tubes accommodate 24 kg/hr of reacting mixture/sulfuric acid to pass through the decomposer so velocity at the inlet of the reactor tube is equal to 1.91 m/s which is calculated using ideal gas relationship. Numerical values of the inputs and boundary conditions are shown in Table 2.1, 2.2 and 2.3.

Table 2.1. Properties of both individual species and mixture at 1143 K

	H ₂ O	SO ₃	SO ₂	O ₂	Mixture
Density (kg/m ³)	0.251489	0.85218	0.758153	0.7582	-
Specific heat Cp (J/kg-K)	2344.608	102.1579	791.3052	501.159	2923.433
Thermal conductivity (W/m-K)	0.105572	0.0642	0.049844	0.08393	0.0709587
Viscosity (kg/m-s)	0.0000384	0.0004464	0.000047	0.00011	1.79E-05
Molecular weight	18.01534	80.058	64.0648	31.999	-
Standard state enthalpy (J/kg mol)	-2.04E+08	-3.9E+08	-2.97E+08	0	-
Standard state entropy (J/kg mol-K)	188829	256547	248222	205149	-
Reference temperature (K)	298.15	298.15	298.15	298.15	-

Table 2.2. Boundary conditions values.

	Inlet	Outlet	Wall
Velocity magnitude (m/s)	1.91	-	-
Temperature (K)	873	-	1143
Mass fraction of SO ₃	0.8164	0	-
Mass fraction of H ₂ O	0.1836	0.1836	-
Mass fraction of SO ₂	0	0.6531	-
Gauge pressure (Pa)	-	700000	-

Table 2.3. Reaction inputs

	H ₂ O	SO ₃	SO ₂	O ₂
Reactants stoichiometric coefficients	1	1	-	-
Reactants rate exponents	1	1	-	-
Products stoichiometric coefficients	1	-	1	0.5
Products rate exponents	0	-	0	0

At later stages of the investigation the constant properties of the both individual fluids and mixture at 873 K are replaced with variable properties. Similarly variable binary mass diffusion coefficients for all the six pairs of species are included in the numerical model instead of constant binary mass diffusion coefficients at 973 K. The methods employed to calculate the variable properties for individual species and mixture are described in Chapter 3.

2.4 Governing Equations

The governing equations considered in this chemical reaction model are the basic continuity equation, and momentum equations and species equation for each specie involved in the reaction. For steady flow, the governing equations for mass, momentum and energy in tensor forms in the master cylindrical coordinate system can be written as follows

2.4.1 Continuity Equation:

$$\frac{\partial}{\partial r_i}(\rho u_i) = 0 \quad (2.1)$$

2.4.2 Momentum Equation:

$$\frac{\partial}{\partial r_j} \left[\mu \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right) + \rho u_j u_i + \delta_{ij} p \right] + \rho g_i = 0 \quad (2.2)$$

2.4.3 Energy Equation:

$$\frac{\partial}{\partial r_j} \left(k \frac{\partial T}{\partial r_j} - \rho u_j C_p T \right) + \mu \phi_v = 0 \quad (2.3)$$

where u_i is the velocity in different coordinate directions, ρ is the density, μ is the dynamic viscosity, p is the pressure, T is the temperature, C_p is the specific heat capacity, k is the thermal conductivity, $\mu \phi_v$ represents the viscous heating term in the energy equation, δ_{ij} in the kronecker symbol and ϕ_v is defined as

$$\phi_v = \frac{\partial u_i}{\partial r_j} \left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} - \frac{2}{3} \mu \frac{\partial u_i}{\partial u_j} \delta_{ij} \right) \quad (2.4)$$

2.4.4 Species Modeling:

The governing equation for different species involved in the reaction modeling can be written as follows

$$\frac{\partial}{\partial r_j} \left(D_{i,m} \frac{\partial Y_i}{\partial r_j} - u_j Y_i \right) + R_i + S_i = 0 \quad (2.5)$$

where Y_i is the mass fraction for the i th of species, R_i is the net rate of production of species i by chemical reaction and S_i is the rate of reaction by addition from dispersed phase, $D_{i,m}$ is the diffusion coefficient for species i in the mixture.

2.4.5 Chemical Kinetics:

The wall surface reaction model was implemented to determine the mole fraction of SO_3 , SO_2 , H_2O and O_2 . The reaction rate was defined by equation (2.6).

$$K = A_r \exp (-E_r/RT) \quad (2.6)$$

The species involved in the chemical reactions were included in the material panel of FLUENT. The activation energy and pre-exponential factor were specified in the reaction panel of FLUENT for the specific catalyst that is considered for the analysis. The reaction rate was calculated, using FLUENT, in each cell with the respect to that particular cell temperature value.

CHAPTER 3

NUMERICAL METHOD, ALGORITHM AND BOUNDARY CONDITIONS

A mixture of chemical species undergoing chemical reactions while flowing through reactor tubes, coated with catalyst on the inner walls to support the chemical reaction, make the flow complex. In this case the actual physical device is replaced by a discrete number of points that represent the entire geometry of the cell where not only the production and destruction of species are found but also the pressure, temperature, etc. are also found. These equations will be solved only at the discrete points representing the geometry of the cell where the distributions of pressure, temperature, etc. are found. The approach requires defining the mathematical equations that govern the physical process. These equations will be solved only at the discrete points representing the geometry. FLUENT, a commercial computer program, based on a finite-volume method is among the most powerful packages of existing commercial software for solving fluid flow, heat transfer and chemical reaction problems [7]. The purpose of this research study is to determine the performance of the catalyst at different temperatures in decomposing the sulfur trioxide and the effect of different parameters on sulfur trioxide decomposition.

3.1 The Finite Volume Method

The finite volume method (FVM), often called control volume methods, are

formulated from the inner product of the governing partial differential equations with a unit function, \mathbf{I} . This process results in the spatial integration of the governing equations. The integrated terms are approximated by either finite differences or finite elements, discretely summed over the entire domain. Physically, the conservation of mass, momentum, and energy are assured in the formulation of FVM via the finite difference method (FDM) itself. The finite difference scheme approximation is done for the program used in this study.

3.1.1 Solution Method

The segregated solver was used to solve the governing integral equations for the conservation of the mass, momentum, energy and species equations. The solution is obtained by using a control-volume-based technique which consists of:

- Division of the domain into discrete control volumes using a computational grid
- Integration of governing equations on the individual control volumes to construct algebraic equations for the discrete dependent variables (“unknowns”), such as velocity, pressure, temperature, species mass fractions, reaction rates and conserved scalars
- Linearization of discretized equations and solution of the resultant linear equation system to yield updated values of the dependent variables

3.2 Segregated Solution Algorithm

In this approach the non-linear governing equations are solved sequentially using the iterative technique. Each step in iteration is as follows:

1. Fluid properties are updated, based on the current solution (or the initial conditions if just starting)
2. The u , v , and w momentum equations are each solved in turn using current values of pressure and face mass fluxes, in order to update the velocity field
3. Since the velocities obtained in step 2 may not satisfy the continuity equation locally the “Poisson-type” equation for the pressure correction is derived from the continuity equation and the linearized momentum equations. This pressure correction equation is then solved to obtain the necessary corrections to the pressure and velocity fields and the face mass fluxes, such that the continuity is satisfied
4. Where the appropriate equations for scalars such as turbulence, and energy are solved using the previously updated values of other variables
5. A check for the convergence of the equation set is made

The governing equations which are discrete and non-linear are linearized to produce a system of equations for the dependent variables in every computational cell. The resultant linear system is then solved to yield an updated flow-field solution. The governing equations were linearized by the “implicit” method with respect to the set of dependent variables. By this method the unknown value in each cell is computed using a relation that includes both existing and unknown values from neighboring cells. Therefore, each unknown appearing in more than one equation such as the velocity v and these equations will be solved for simultaneously to give the velocity and pressure values. A point implicit Gauss-Seidel linear equation is used in conjunction with an algebraic multigrid (AMG) method to solve the resultant scalar system of equations for the

dependent variables in each cell. Thus, the solver solves for a single variable field like pressure, at one time considering all cells. The next variable, like velocity, is solved using the same technique.

3.3 Discretization

FLUENT uses a control-volume-based technique to convert the governing equations to algebraic equations that can be solved numerically. This control volume technique consists of integrating the governing equations about each control volume, yielding discrete equations that conserve each quantity on a control-volume basis. The integral of the governing equations is applied to each control volume, or cell, in the computational domain and discretized. By default the solver stores the discrete values of the scalar quantities at the cell centers. However, when the face values of the scalar quantities are required the values are interpolated from the cell center values. This is accomplished using an “upwind” scheme. Upwinding means that the face values are derived from quantities in the cell upstream, relative to the direction of the normal velocity.

A first order upwind scheme was used for acquiring first-order accuracy. When this scheme is selected, the face value of a scalar quantity is set equal to the value in the upstream cell. Since the flow is aligned to the grid here i.e., flow in a hexahedral grid, the first order discretization scheme was found to be acceptable.

3.3.1 Discretization of the Momentum Equations

Since the pressure fields and face mass fluxes are not known a priori and must be obtained as a part of the solution. FLUENT uses a co-located scheme, whereby pressure

and velocity are both stored at cell centers. An interpolation scheme is formulated to compute the face values of pressure from the cell values.

Pressure Interpolation Scheme

The default scheme in the standard solver interpolates the pressure values at the faces using momentum equation coefficients, since the variation between the cell centers is considerably smooth without any large gradients.

3.3.2 Discretization of the Continuity Equation

In the sequential scheme as described earlier the continuity equation is used as an equation for pressure. But for incompressible flows pressure does not appear explicitly since density is not directly related to pressure. The SIMPLE (Semi-Implicit Method For Pressure-Linked Equations) is used to introduce pressure into continuity equations.

Pressure-Velocity Coupling

The SIMPLE algorithm uses the relationship between velocity and pressure corrections to enforce mass conservation and to obtain the pressure field. The momentum equation is solved using a guessed pressure field to obtain the face flux. If the resulting face flux does not satisfy the continuity equation a correction face flux is added to obtain the corrected face flux, thus satisfying the continuity equation.

The SIMPLE algorithm substitutes the flux correction equations into the discrete continuity equation to obtain the discrete equation for the pressure correction p' in the cell. The pressure-correction equation may be solved using the AMG method.

3.4 Boundary Conditions

3.4.1 Velocity Inlet Boundary Conditions

Velocity inlet boundary conditions are used to define the flow velocity, along with all other relevant scalar properties of the flow, at the flow inlets. The total (or stagnation) properties of the flow are not fixed, so they will rise to whatever value necessary to provide the required velocity distribution. This type of boundary condition at the inlet is intended to be used in incompressible flow. It requires the specification of velocity magnitude and direction, the velocity components, or the velocity magnitude normal to the boundary. In this case the velocity normal to boundary specification method was used.

3.4.2 Pressure Outlet Boundary Conditions

The pressure outlet boundary condition requires the specification of gauge pressure at the outlet. Flow quantities are extrapolated from the interior. A set of the “backflow” conditions are also specified, should reverse flow occur at the exit during the solution process. Specifying realistic values of backflow quantities reduced convergence difficulties. To set the static pressure the appropriate gauge pressure should be entered. Backflow temperature and turbulence parameters were set normal to the boundary with a realistic value. At the pressure outlets FLUENT uses the boundary condition pressure input as the static pressure of the fluid at the outer plane, and extrapolates all other conditions from the interior of the domain.

3.4.3 Thermal Boundary Conditions

When choosing to solve an energy equation, it is required to define the thermal boundary condition at the walls. Since the wall zone in three-dimensional modeling is a

“two-sided wall” (a wall that forms the interface between two regions, such as the fluid/solid interface) a conjugate heat transfer problem is encountered. The code allows user to choose whether or not the two sides of the wall are “coupled”. When the “coupled” option is chosen no other additional thermal boundary conditions are required, because the solver will calculate heat transfer directly from the solution in the adjacent cells.

3.4.4 Wall Boundary Conditions

Wall boundary conditions are used to bound fluid and solid regions. Since the flow is modeled as viscous flow, the no-slip boundary condition is enforced at walls. A zero-gradient condition for all species is assumed at walls and the wall surface reaction is enabled at the wall which allows fluid to react when it comes in contact with the wall. Constant wall surface temperature boundary condition allow to maintain constant temperature at the walls independent of the reaction heat liberation or absorption taking place at the walls because of the wall surface reaction.

3.4.5 Fluid Boundary Conditions

A fluid zone is a group of cells for which all active equations are solved. The only required input for a fluid zone is the type of fluid material. In the present case the fluid is a mixture of four different species. The type of fluid is specified in the material panel and the fluid properties of the all individual fluids as well as the mixture properties are first defined in the material properties panel of FLUENT.

3.4.6 Solid Conditions

A “solid” zone is a group of cells for which the heat conduction problem is solved; no flow equations are solved. The only required input for the solid zone is the material of solid which is input into the material conditions panel of the FLUENT code.

3.4.7 Axis Boundary Conditions

The axis boundary condition is specified as axis-symmetric which allows the user not to have to specify any other boundary condition at the axis. FLUENT uses the adjacent cell values to determine the appropriate physical values for a particular variable at any point on the axis.

3.5 Physical Properties Model

An important step in the set up of the numerical model is the definition of the physical properties. For the fluid materials the values of density, thermal conductivity, viscosity, specific heat capacity for the individual species and also for the mixture are required for the calculation purposes. The physical properties may be dependent or independent of temperature depending upon the type of approach chosen.

When there is a large temperature difference between the fluid and the surface the assumption of constant fluid transport properties may cause some errors, because the transport properties of most fluids vary with temperature. In the present case the properties of the mixture depend not only on the temperature at that location but also on the individual species concentration at that location. These property variations will then cause a variation of velocity and temperature throughout the boundary layer or over the

flow cross section of the geometry so variable properties for the fluid as well as mixture were considered for investigation.

The properties, thermal conductivity, viscosity and specific heat for all individual species (H_2O , SO_3 , SO_2 and O_2) are dependent on temperature and are calculated by FLUENT material panel using the kinetic theory. Mixture properties such as thermal conductivity, viscosity and specific heat are dependent on both temperature and the individual species concentrations and so they are calculated using mass weighted mixing law. Density of the mixture is calculated using incompressible-ideal gas relationship.

3.6 Setting the Under-Relaxation Factors for the Solution

The segregated solver uses under-relaxation to control the update of the computed variables after every iteration. The solver initially has a set of default under-relaxation factors for all variables that are set to near optimal values for most cases. However for calculating reacting mixtures the under-relaxation factors vary from default values (optimal values). The under-relaxation factors used for different parameters are shown below

Pressure – 0.1

Temperature – 0.1

Species – 0.1

The higher the under-relaxation factors the faster the convergence, so after running the simulation for some time at the above mentioned values then the values are increased to 0.9 which resulted in faster convergence.

CHAPTER 4

GRID INDEPENDENT STUDY AND VALIDATION OF TWO- DIMENSIONAL NUMERICAL MODEL

4.1 Mesh Dependency Investigation

The main objectives of the mesh independence investigation are

- 1) Examination of the solution sensitivity and computational time from the mesh changes (refinement and coarsening)
- 2) Selection of the optimal mesh for analyzing the problem using CFD techniques.

Investigation of decomposition of sulfur trioxide in a wall catalyzed reactor tube using numerical models requires an appropriate mesh density. To find out the type of mesh, which provides stable and accurate results, analysis is to be carried out with different mesh densities varying from course to fine and the results should be compared with the base mesh. A reactor tube of diameter 2 mm and length 500 mm is considered for the investigation. Five different types of meshes with variation in mesh densities at the center as well as at the walls are considered for the investigation and are shown in Figure 4.1. Since in the present problem the decomposition of sulfur trioxide reaction is a wall surface reaction, all the five different grids were created with fine mesh close to walls when compared with center of the reactor tube to capture the species formation and

destruction at the walls. Number of nodes vary from 26,000 to 43,000 for mesh quality 5 (course mesh) to mesh quality 1 (fine mesh) respectively. Mesh density decreases (number of nodes decreases) from quality 1 to quality 5 not only in the radial direction but also in axial direction.

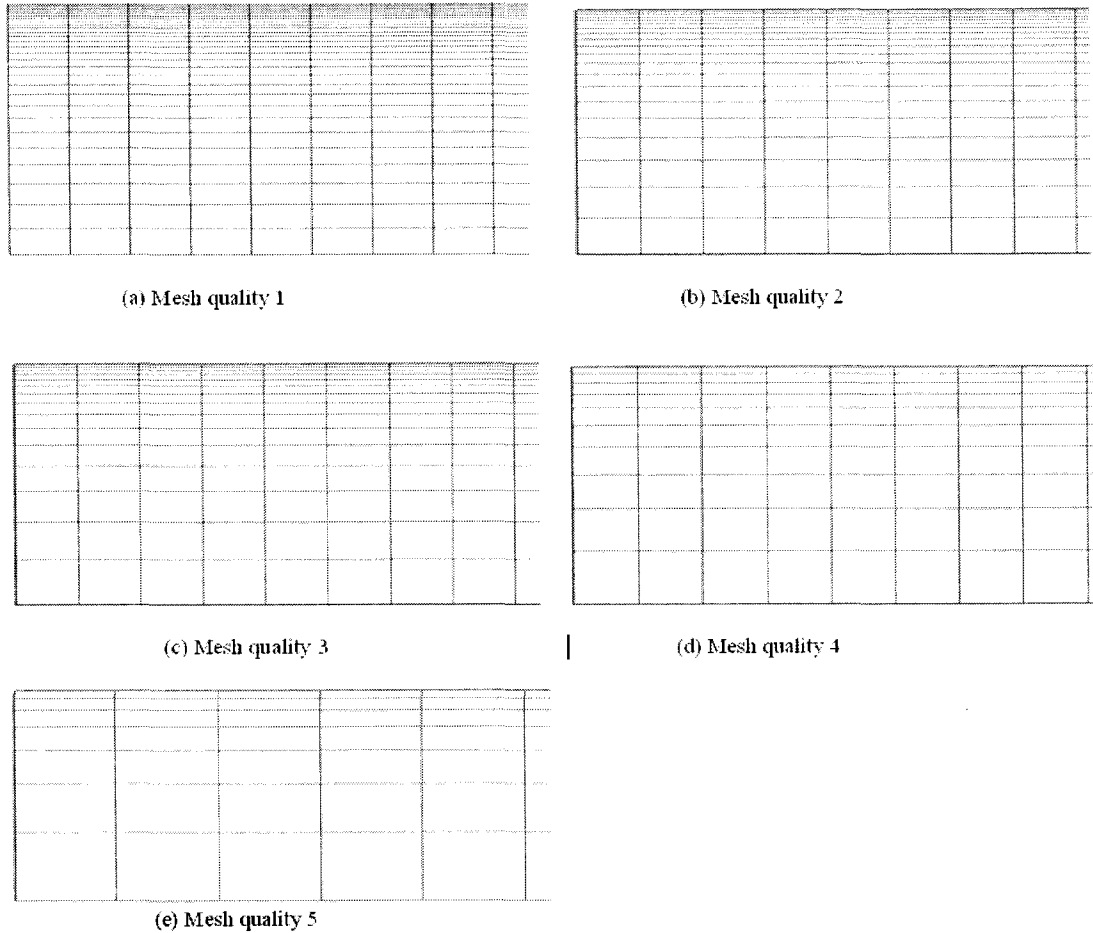


Figure 4.1. Five different mesh qualities considered for grid independent studies.

Five simulation cases are carried on all the five mesh qualities at 1000 K wall surface temperature and at 2 m/s inlet velocity of the mixture. The percentage change in the percentage decomposition of sulfur trioxide and number of iterations taken for

solution convergence are considered very important while making decision on mesh quality. Number of iterations taken for solving the problem represents time taken to compute the problem for a given accuracy. Both above mentioned variables are tabulated for all five mesh qualities in Table 4.1.

Table 4.1. Percentage change in percent decomposition of SO_3 and the number of iterations taken to solve the problem for different mesh qualities

Mesh quality.	Number of iterations	Percent change in results
1	3700	0
2	3270	0.5
3	2150	2
4	1900	3
5	1100	9.8

From Table 4.1 it is more than clear that the percentage change in results increases with decrease in mesh quality from 1 to 5 because the coarser the mesh the more inaccurate the results are. On the other hand when the mesh becomes coarse, there are less number of nodes, and this results in less computational time. So there should be a tradeoff between the number of iterations and the accuracy of results. It looks like the number of iterations increased drastically from mesh quality 2 to 3 with a smaller decrease in percentage change in results. So a decision has been taken to use the mesh quality 3 for future investigations which would contribute for better results with less computational time. The percentage change in percent decomposition of sulfur trioxide and number of iterations for different mesh qualities are shown in Figure 4.2.

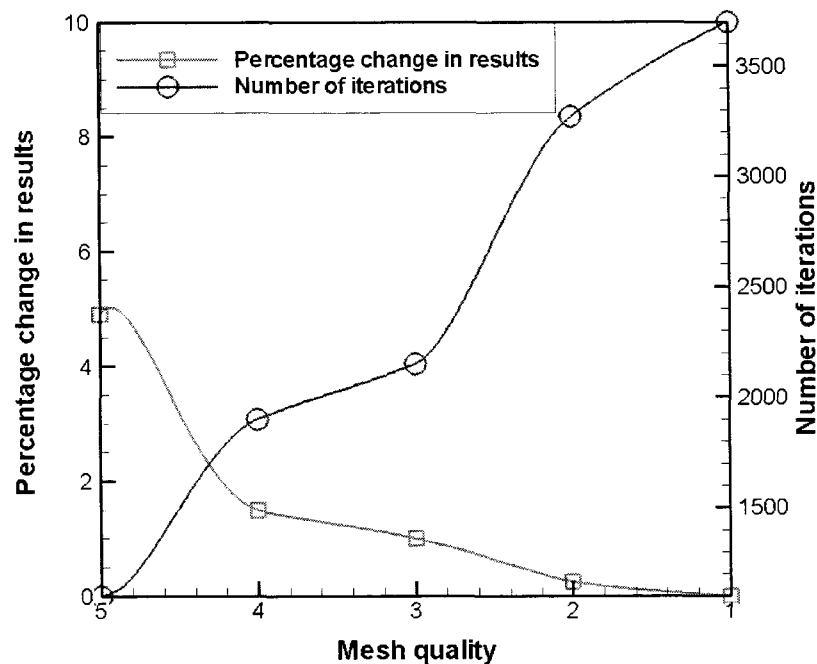


Figure 4.2. Percentage variation in the results and number of iterations taken vs mesh quality.

4.2 Comparison of Results with Experimental Data

The decomposition of sulfur trioxide modeling involves flow modeling, chemical reaction modeling and modeling species transport. So to validate the model the results from the simulation results should be compared with known experimental data. Unfortunately there is no experimental data available for catalyst ALFA-4. However experimental results using platinum as a catalyst are available for comparison. These experiments were conducted at the Idaho National Engineering Laboratory (INEL).

Sulfuric acid (95.5wt %) flowing at 49 g/hr through a tube consisting of a 0.032 m² surface made of platinum is considered for the experimental results. Experiments are conducted for different temperatures ranging from 750° C to 900° C. Initial experiment

are conducted at 850° C and at alter stages experiments are conducted for other temperatures starting from 750° C. Properties of catalyst such as activation energy and pre-exponential factor should be known in order to perform simulation of sulfur trioxide decomposition in the presence of catalyst platinum. Activation energy (E_r) ($8.8034E+07$ J/kg-mol) and pre-exponential factor (A_r) (0.6218 mol/sec) for catalyst Platinum are calculated from the experimental results conducted at INL. Using the calculated data simulation cases for different temperature ranging from 500° C to 1400° C are carried out keeping operating conditions same as the experiments. Percentage decomposition of sulfur trioxide for both simulation results and experimental data is shown in Figure 4.3 and are tabulated in Table 4.2.

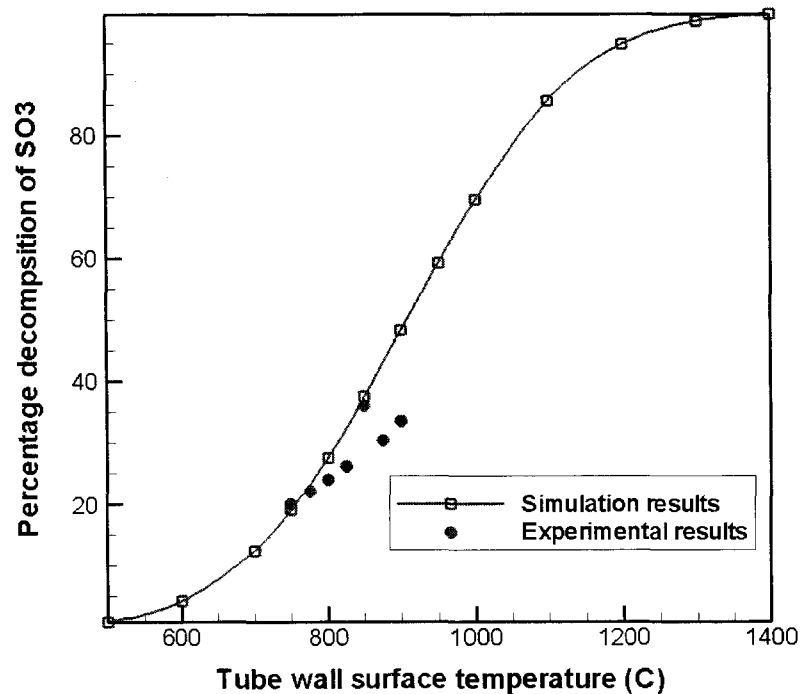


Figure 4.3. Comparison of percentage decomposition of sulfur trioxide between numerical and experimental results.

From Figure 4.3 it is clear that the numerical results at temperatures 850° C and 750° C match closely with the experimental results. The remaining points from the experimental data deviate from the numerical results and the reason as explained by the source of experimental results is: Platinum could not withstand on the surface of the material at elevated temperatures and so the decomposition rates at the elevated temperatures are less than the expected values. From Figure 4.3 it is evident that there is very close similarity between the experimental results and numerical results and so the two-dimensional numerical model of wall catalyzed sulfur trioxide decomposition reaction is working well.

Table 4.2. Percentage decomposition of SO₃ for both experimental results and numerical results at various temperatures

Wall surface temperature		Percentage decomposition of SO ₃	
K	C	Experimental results	Numerical results
1023	750	20.1	19.09
1048	775	22	-----
1073	800	23.9	27.54
1098	825	26.2	-----
1123	850	36	37.46
1148	875	30.4	-----
1173	900	33.5	48.28
1223	950	-----	59.21
1273	1000	-----	69.47
1373	1100	-----	85.66
1473	1200	-----	94.83
1573	1300	-----	98.61
1673	1400	-----	99.73

CHAPTER 5

TWO-DIMENSIONAL NUMERICAL CALCULATIONS

The two-dimensional numerical studies are carried out on one of the reactor tubes among the five as shown in Figure 1.4. The diameter and length of the reactor tube are 12.7 mm and 500 mm, respectively. The inlet portion of the grid considered for the analysis is shown in Figure 2.1. The wall surface reaction of sulfur trioxide decomposition in the presence of catalyst ALFA-4 is incorporated in the numerical model. Appropriate boundary conditions are enabled and required inputs are provided for calculations. Simulation cases are carried out and the results are observed to see how well the wall surface reaction modeling is working. Since the aspect ratio of the reactor tube is very high it is difficult to see the variation in parameters along the length of the reactor tube at once. A zoomed view of the reactor tube at its inlet showing the contours of mass fraction of sulfur trioxide is shown in Figure 5.1.

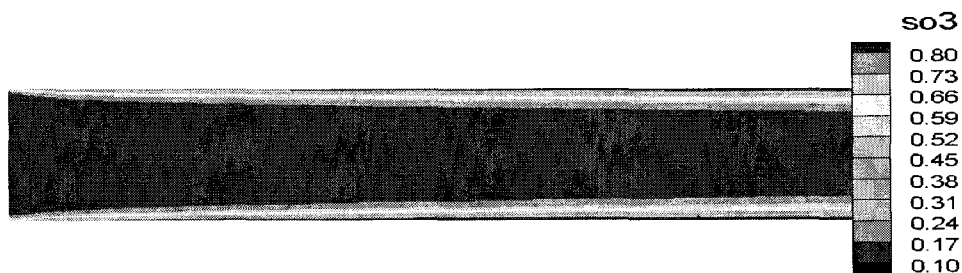


Figure 5.1. Contours of mass fraction of sulfur trioxide at the inlet of the reactor tube

From Figure 5.1, the variation of mass fraction of sulfur trioxide from walls to the center of the reactor tube at the inlet can be observed more clearly seen. Since the sulfur trioxide is decomposed at the walls because of the presence of catalyst ALFA-4, the mass fraction of sulfur trioxide close to the wall is zero. One can clearly see the dark blue color region close to the walls of the reactor tube indicates much lower mass fraction of sulfur trioxide. Similarly, the dark red color at the center of the reactor tube indicates high mass fraction of sulfur trioxide. The intermediate colors yellow and light green indicate the mass fractions of sulfur trioxide in between the maximum and minimum which occurred because of the species diffusion in the reacting mixture. Similarly the contours of mass fraction of SO_2 and O_2 are shown in Figures 5.2 and 5.3 where one can see a reversed pattern of the mass fraction, i.e., high mass fraction of sulfur dioxide and oxygen close to wall and very less mass fraction at the center of the reactor tube, because sulfur trioxide decomposes at the walls leaving the sulfur trioxide and oxygen as products of the reaction.



Figure 5.2. Contours of mass fraction of sulfur dioxide at inlet of the reactor tube

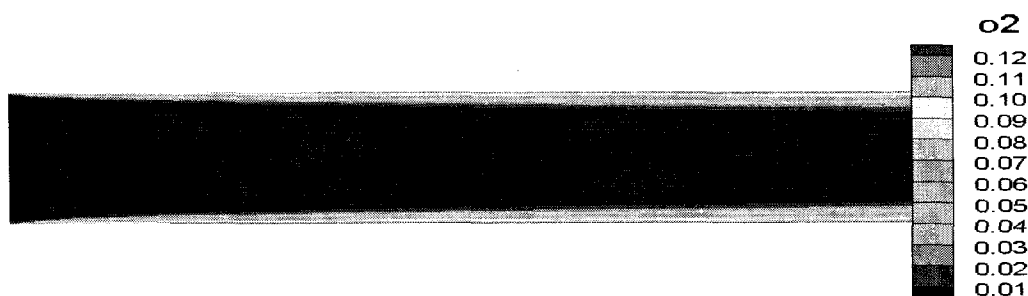


Figure 5.3. Contours of mass fraction of oxygen at the inlet of the reactor tube

But when it comes to the contours of mass fractions of H_2O , shown in Figure 5.4, there is no variation in the mass fraction from center to wall because water vapor is not participating in any chemical reaction unlike other species.

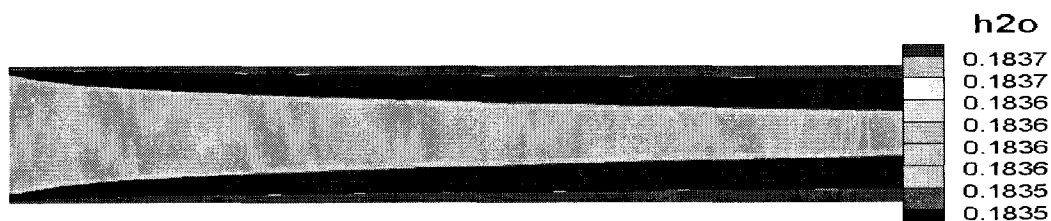


Figure 5.4. Contours of mass fraction of water vapor at inlet of the reactor tube

Mass fraction of sulfur trioxide along the length of the reactor tube at different radii, $y=0\text{mm}$ (wall), $y= 6.25\text{mm}$ (axi-symmetry), $y= 5\text{mm}$, $y=4\text{mm}$ and $y=2\text{mm}$ is shown in Figure 5.5.

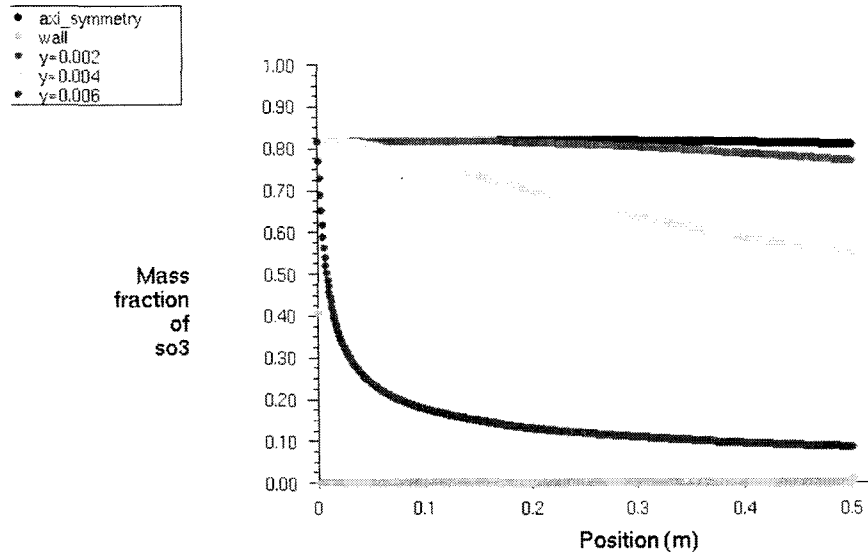


Figure 5.5. Mass fraction of SO_3 along the length of the reactor tube at different radii

The blue line in Figure 5.5 indicates that the mass fraction of sulfur trioxide at the wall is zero along the length of the reactor tube and at the same time the black line which is the center of the reactor tube indicating that there is no change in the mass fraction of sulfur trioxide from inlet to outlet of the reactor tube. Because of the diffusivity of the chemical species in the mixture there is an increase in the mass fraction of sulfur trioxide from the walls to the center of the reactor tube that is shown by the remaining lines in between the axi-symmetry and wall of the reactor tube. Variation in different parameters from inlet to outlet of the reactor is shown in Table 5.1.

Table 5.1. Variation in different parameters from inlet to outlet of the reactor tube of diameter 12.7 mm and length 500 mm at 7 atm.

Parameter	Inlet	Outlet
Number of moles of SO ₃ (mol/min)	0.8	0.548
Number of moles of H ₂ O(mol/min)	0.8	0.8
Number of moles of SO ₂ (mol/min)	0	0.251
Number of moles of O ₂ (mol/min)	0	0.125
Temperature (K)	873	1064
Pressure (Pa)	700,038	700,000
Velocity (m/s)	2.10	2.78
Density (kg/m ³)	4.68	3.78
Viscosity (kg/m-s)	0.0000584	0.0000625
Reynolds number	2137	2135

Since water vapor is not involved in any chemical reaction, the number of moles at the inlet is same as at the outlet. There is a pressure drop of 38 Pa from inlet to outlet of the reactor tube. There is a change in the velocity from inlet to outlet because of two different reasons. One is temperature of the reacting mixture is increasing from inlet to outlet which increases the volume of the reacting mixture. The other is the raise in the number of moles from inlet to outlet because of the chemical reaction. Viscosity of the mixture is increasing from inlet to outlet because the mixture is in a gaseous state. Percentage decomposition of sulfur trioxide is around 31. Reynolds number is in the

ballpark of 2150, so the flow is laminar. Reynolds number calculations are done using the following formula.

$$\text{Re}_D = \frac{\rho v D}{\mu} \quad (5.1)$$

From the numerical results it is more than clear that the wall surface reaction model is working properly as expected. It is important to find out conditions essential for better decomposition of sulfur trioxide. There are lots of parameters which actually affect the decomposition of sulfur trioxide. Among them the operating temperature, diameter of the reactor tubes, length of the reactor tubes and mole flow rate of the mixture are considered as dominant. Different simulation cases are carried out to find how the decomposition of sulfur trioxide is varying with the variation of the above mentioned parameters.

5.1 Investigation of Catalyst Performance at Different Temperatures

Performance of catalyst ALFA-4 is tested at different wall surface temperatures ranging from 600° C to 1000° C. The same computational geometry and grid as shown in Figure 2.1, diameter 12.7mm and length 500mm, are considered for this analysis. Applying the similar boundary conditions and keeping all other inputs constant except the wall surface temperature. Ten simulation cases are being carried out at different temperatures between 500° C and 1000° C and the results are postprocessed using Tecplot. The percentage decomposition of sulfur trioxide at the outlet of the reactor tube for different wall surface temperatures is shown in Figure 5.6.

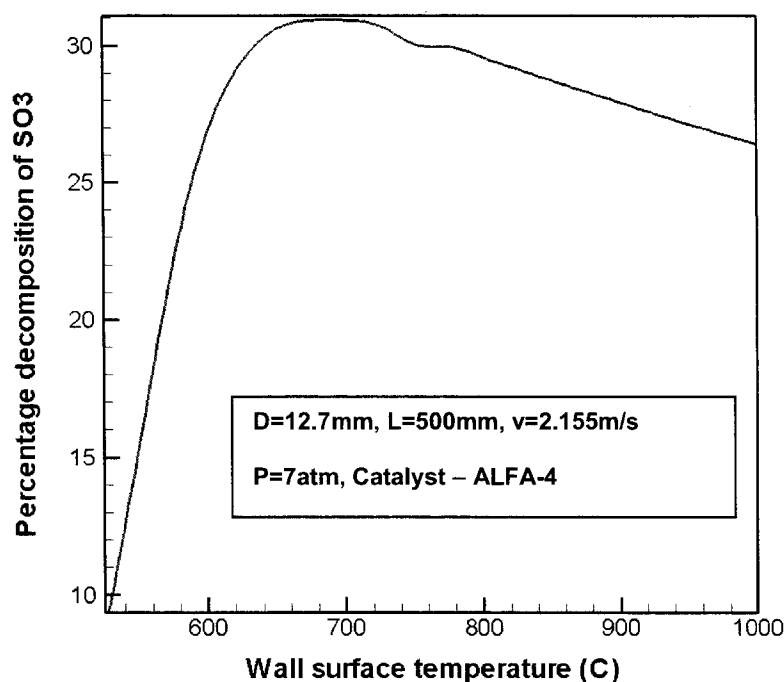


Figure 5.6. Percentage decomposition of SO_3 for different wall surface temperatures of the reactor tube using constant properties.

From Figure 5.6, percentage decomposition of sulfur trioxide increased with increasing wall surface temperature up to a temperature close to 700°C and later on it started dropping down, which is not a good sign of proper modeling because the percentage decomposition should increase with increase in temperature[1], [3]. There are a couple of reasons that explain the behavior of the SO_3 decomposition curve. The SO_3 decomposition was modeled as a wall surface reaction which means the sulfur trioxide molecules come in contact with the walls and decompose at the walls in the presence of catalyst. The decomposed products, SO_2 and O_2 , diffuse into the mixture allowing the SO_3 molecules in the mixture to come close to the wall. As the temperature of the mixture increases the diffusivity of the species increases allowing more and more sulfur trioxide to decompose which results in higher percentage decompositions. Diffusivity of

the species in the mixture plays a major role in reacting flows. In the present problem the constant binary mass diffusion coefficients at 700° C are incorporated which do not increase with increasing in the temperature of the mixture.

With the increase in the temperature the performance of the catalyst increases but at the same time the velocity of the mixture flowing through the tubes increases which does not provide enough time for species to diffuse in the mixture which results in less decomposition of sulfur trioxide. In the present problem the velocity increases with increasing temperature but the diffusivity of the species is kept constant at 700° C. The relationship between the velocity and the mass diffusion coefficients is very sensitive which effected the percentage decomposition of sulfur trioxide and resulted in lower decomposition rates even at higher temperatures. So it is very important to have variable mass diffusion coefficients for all the species involved in the mixture, especially when modeling reacting flows. Variable binary mass diffusion coefficients are incorporated in the model which allows the species to diffuse according to the temperature variations. Further investigations are carried out using the new variable mass diffusion coefficients for different wall surface temperatures of the reactor tubes and the percentage decomposition of sulfur trioxide values are shown in Figure 5.7 and the values are tabulated in Table 5.2.

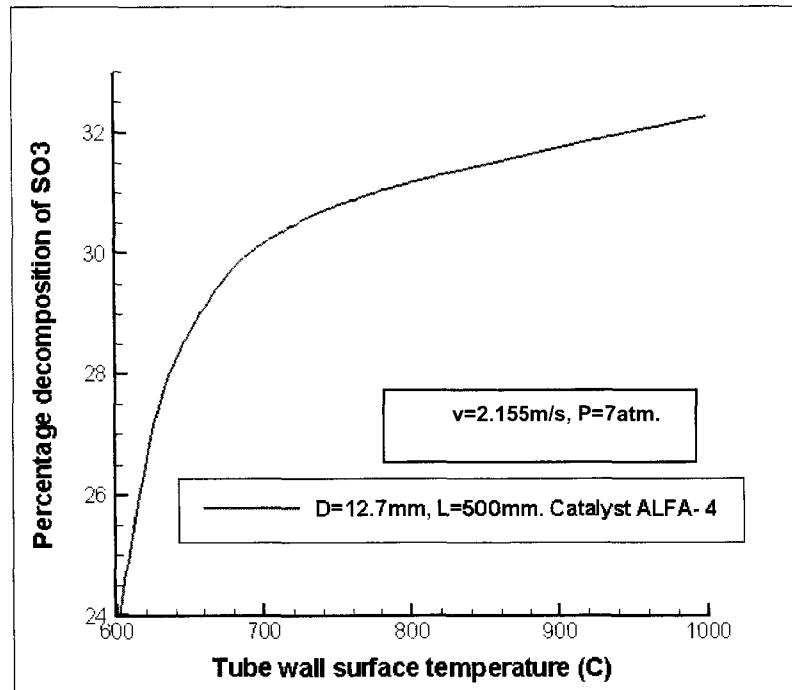


Figure 5.7. Percentage decomposition of SO_3 for different wall surface temperatures of the reactor tube using variable properties.

The percentage decomposition of SO_3 curve shown in Figure 5.7 indicates that the performance of the catalyst increases with increasing the operating temperature. There are two different reasons for having the high decomposition of sulfur trioxide at elevated temperatures. One is that when temperature increases the rate of reaction increases which is a direct analogy. The other is that the molecular diffusion increases with increasing temperature of the mixture because of the variable mass diffusion coefficients incorporated in the model. As the temperature increases the species at the wall, SO_2 and O_2 , diffuse more quickly allowing SO_3 molecules at the center to move towards the walls resulting in higher decompositions rates so variable properties play a major role in sulfur trioxide reduction reaction. The higher the operating temperature the higher the decomposition rates, however the operating temperatures really depend on the type of

material being used for the decomposer. If the material can withstand higher temperatures it is always advisable to operate the decomposer at elevated temperatures which provides higher decomposition of sulfur trioxide.

Table 5.2. Percentage decomposition of SO_3 for different wall surface temperatures of the reactor tube (D=12.7 mm, L= 500 mm, P=7 atm, $v= 2.155$ m/s and Catalyst- ALFA-4.).

Wall temperature(T_w)		Percentage decomposition of SO_3
K	C	
875	602	24.011
900	627	27.286
950	677	29.659
1000	727	30.549
1050	777	31.005
1100	827	31.331
1150	877	31.616
1200	927	31.886
1250	977	32.15
1275	1002	32.281

5.2 Effect of Variation of Diameter of the Reactor Tube on Decomposition of Sulfur Trioxide

The percentage decomposition of sulfur trioxide is around 31 for the reactor tube of diameter 12.7 mm and length of 500 mm. Figure 5.8 shows the contours of mass fractions of sulfur trioxide at the outlet of the reactor tube. Red color portion at the outlet

of the reactor tube represents the undecomposed sulfur trioxide. It is clear that there is a lot of undecomposed sulfur trioxide at the center of the reactor tube at the outlet.

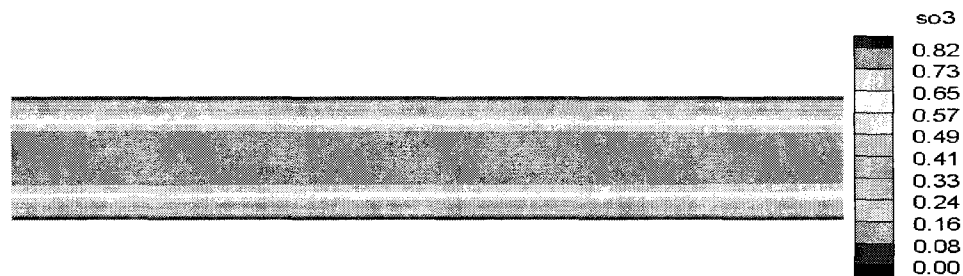


Figure 5.8. Contours of mass fraction of SO_3 at the outlet of the reactor tube of diameter 12.7 mm and length 500 mm.

There are many reasons which explain the presence of undecomposed sulfur trioxide at the center of the reactor tubes. Some of the reasons are performance of catalyst, diffusivity of the species when compared to the velocity of the mixture and surface area of the catalyst. Since the reaction of sulfur trioxide happens only at the wall of the reactor tube the diffusivity of the species and surface area of catalyst play major roles in getting higher decomposition. For a given temperature and pressure the diffusivity of species in the mixture and the performance of catalyst are constant and cannot be changed. Either velocity of the mixture entering the reactor tubes or surface area of the reactor tube should be changed in order to have higher decompositions. At first, a change in diameter of the reactor tubes is considered for analysis and at later stages a change in mass flow rate is also considered. A decrease in diameter allows having higher surface areas for the same mass flow rate by increasing the total number of tubes.

Different grids are generated for different reactor tube diameters starting from 12 mm to 1 mm keeping the length constant at 500 mm. Simulation cases are carried out on each of the reactor tubes at 1143 K constant wall surface temperature keeping the inlet velocity and other parameters constant for all the reactor tubes. Figure 5.9 shows the percentage decomposition of sulfur trioxide variation for all the reactor tubes of different diameters from 12 mm to 1 mm.

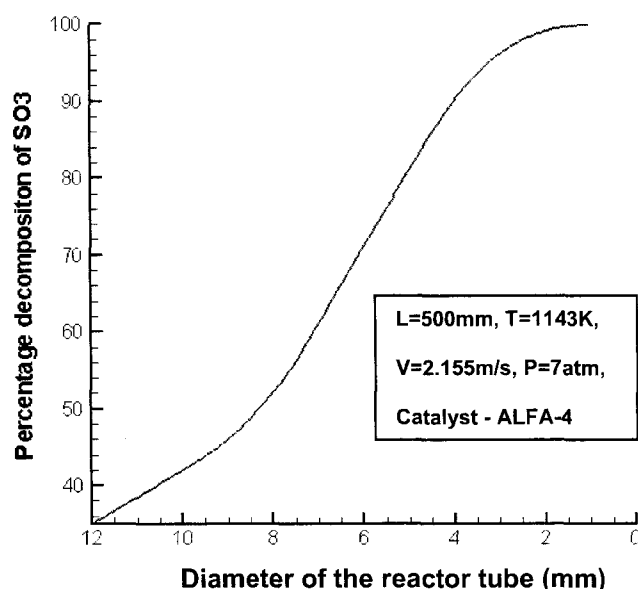


Figure 5.9. Percentage decomposition of SO₃ for different diameters of the reactor tube

From Figure 5.9 it can be seen that the decomposition of sulfur trioxide is increasing with decreasing diameter of the reactor tube and the decomposition is even close to 90% for diameters less than 4 mm. It would be interesting to find how the decomposition of sulfur trioxide varies with two different parameters at once such as, diameter of the reactor tube and wall surface temperatures. But this time only 4 diameters (4 mm, 3 mm, 2 mm and 1 mm) are considered for analyses. For each individual diameter

different simulation cases are carried out at different wall surface temperatures ranging from 600° C to 1000° C with an interval of 50° C. Results are shown in Figure 5.10 and values are tabulated in Table 5.3.

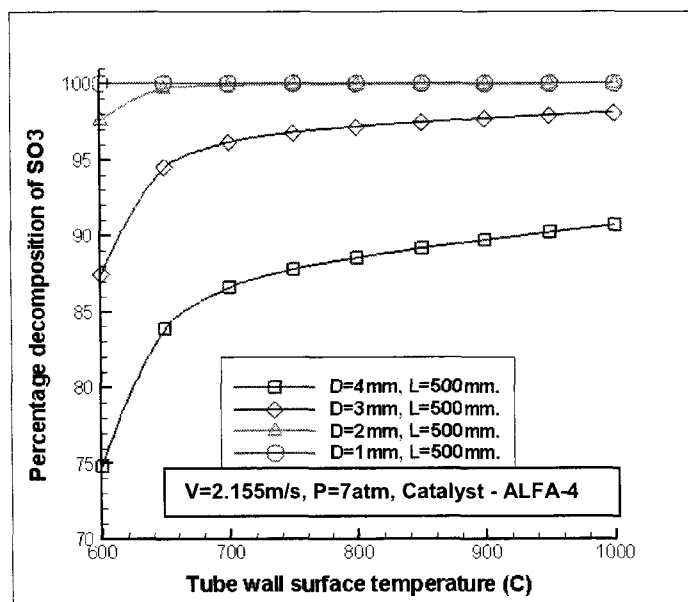


Figure 5.10. Percentage decomposition of SO₃ for different reactor tube diameters vs different wall surface temperatures.

Even though the decrease in diameter of the reactor tubes allows higher decompositions of sulfur trioxide we may not be able to go to lower diameters because the pressure drop across the reactor tubes will increase with decreasing the tube diameter. So pressure drop values from inlet to outlet of the reactor tube for different diameters are shown in Figure 5.11.

Table 5.3. Percentage decomposition of SO₃ for different diameters of the reactor tubes
vs different wall surface temperatures

Wall temperature		Percentage decomposition of SO ₃			
C	K	D=4mm	D=3mm	D=2mm	D=1mm
600	873	86.0	95.8	99.9	100.0
650	923	86.8	96.2	99.9	100.0
700	973	87.4	96.6	99.9	100.0
750	1023	88.1	96.9	99.9	100.0
800	1073	88.6	97.2	99.9	100.0
850	1123	89.2	97.5	100.0	100.0
900	1173	89.7	97.7	100.0	100.0
950	1223	90.2	97.9	100.0	100.0
1000	1273	90.7	98.1	100.0	100.0

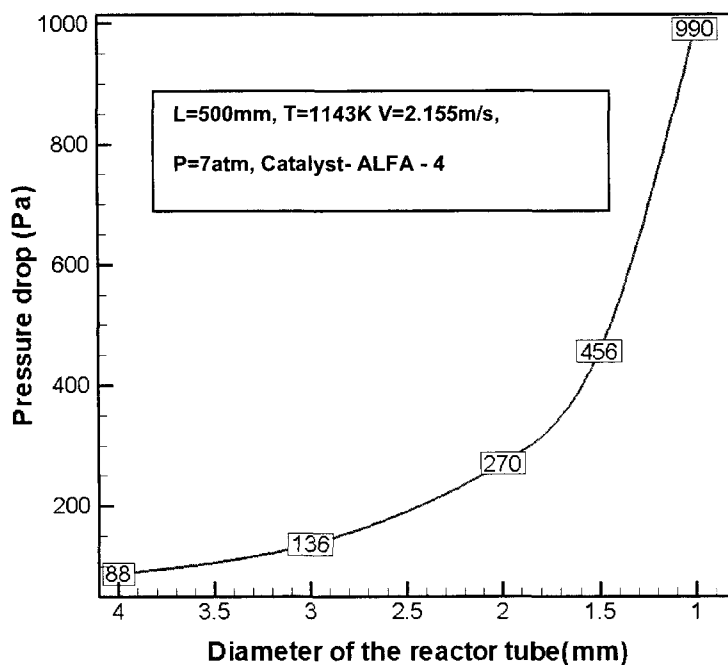


Figure 5.11. Pressure drop for different diameter reactor tubes.

Figure 5.10 shows that there is not much variation in the decomposition of sulfur trioxide for the reactor tubes of diameter 2 mm and 1 mm. From Figure 5.11 there is a drastic increase in the pressure drop values from 1.5 mm diameter reactor tube to 1 mm diameter reactor tube. So the reactor tubes of diameter less than 1.5 mm will increase a lot in pressure drop but with very little increase in the decomposition of sulfur trioxide. The pumping power calculations are also performed for all different reactor tube diameters using the following formula.

$$\text{Pumping Power} = \frac{\Delta P \times Q}{\eta_p} \quad (5.2)$$

Total volumetric flow rate of the reacting mixture for 24 kg/hr of sulfuric acid flow rate is equal to 4.91 m³/hr and pump efficiency is taken as 80%. The pumping power values for different reactor tube diameters are shown in Table 5.4.

Table 5.4. Pumping power calculations for different diameter reactor tubes.

Reactor tube diameter(mm)	4	3	2	1.5	1
Pumping power (W)	0.007	0.02	0.46	0.77	1.61

Apart from the high pressure drop values a couple of other factors may restrict use of smaller diameter reactor tubes (less than 1.5 mm) include difficulties in manufacturing small diameter tubes and the possibility of fouling in small diameter tubes.

5.3 Effect of Mole Flow Rate on Sulfur Trioxide Decomposition

The decomposition of sulfur trioxide is sensitive to the flow rate variations. To find the sensitivity of the sulfur trioxide decomposition for mole flow rate, reactor tube of diameter 4 mm and length of 500 mm are chosen. Three different mole flow rates, 4 mol/min, 5 mol/min and 7 mol/min are considered for investigation and the inlet velocities according to these mole flow rates are calculated using ideal gas relation. Different simulation cases are carried out for different wall surface temperatures from 600° C to 1000° C keeping all other input parameters constant except mole flow rate. Percentage decomposition of sulfur trioxide for different flow conditions different temperatures are shown in Figure 5.12 and Table 5.5.

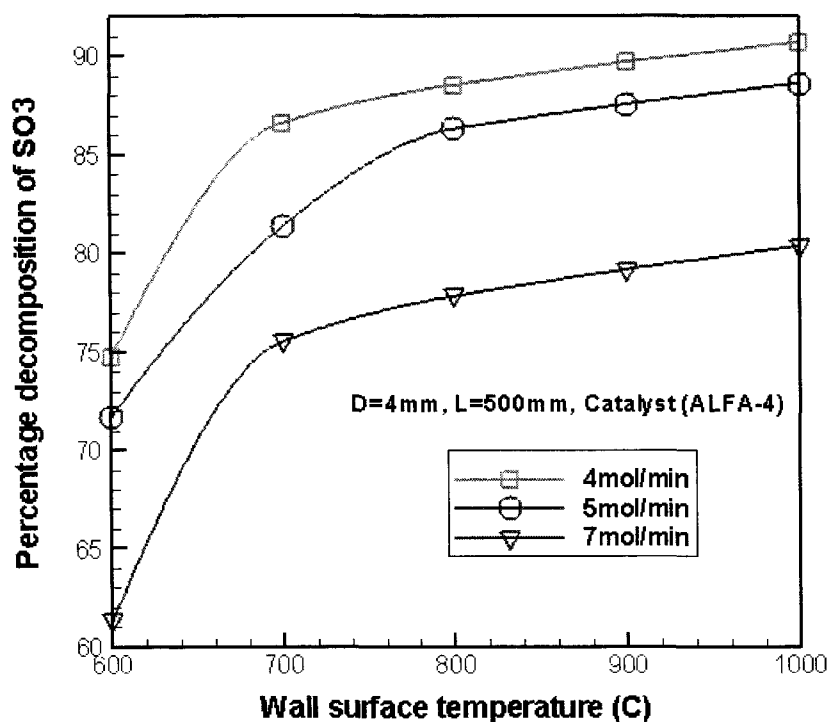


Figure 5.12. Percentage decomposition of SO_3 vs different wall surface temperatures for different flow conditions at 7 atm

From Figure 5.12 it can be found that the decomposition of sulfur trioxide is increasing with decreasing the mole flow rate. The more the mole flow rates the more the velocity of the mixture flowing through the tubes which does not allow sulfur trioxide to stay longer (i.e. resident time) in contact with catalyst at the walls that effects the decomposition of sulfur trioxide.

Table 5.5. Percentage decomposition of SO_3 for different flow conditions vs different wall surface temperatures.

Wall temperature		Percentage decomposition of SO_3 for different flow rates of sulfuric acid		
K	C	4 mol/min	5 mol/min	7 mol/min
873	600	74.755	71.702	61.340
973	700	86.599	81.342	75.511
1073	800	88.527	86.304	77.819
1173	900	89.690	87.542	79.164
1273	1000	90.694	88.615	80.359

5.4 Effect of Variation of Reactor Tube Length on Decomposition of Sulfur Trioxide

The length of the reactor tube is arbitrarily chosen as 500 mm and it is essential to find the appropriate length of the reactor for given operating conditions. Length of the reactor tube has an effect on the decomposition of sulfur trioxide. The more the length of the reactor tube the more the decomposition of sulfur trioxide, but the decomposition of sulfur trioxide need not necessarily be a linear function of length. In order to find how the

decomposition of sulfur trioxide varies with the variation in the length of the reactor tube, different diameter reactor tube grids are considered for post processing starting from 4 mm to 1 mm. The results are shown in Figure 5.13 and values are tabulated in Table 5.6.

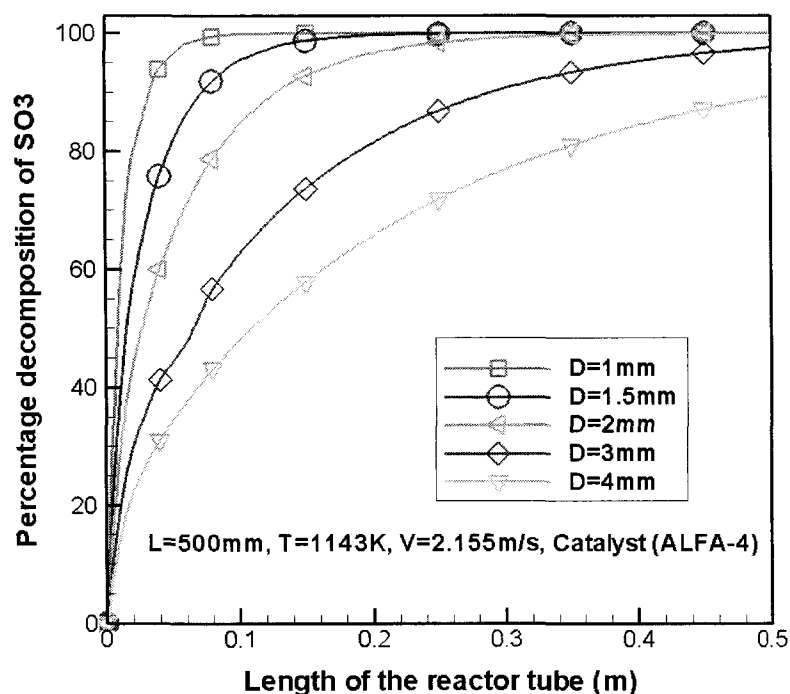


Figure 5.13. Percentage decomposition of sulfur trioxide for different reactor tubes diameters at different lengths

Figure 5.13 shows that for a diameter less than 2 mm, most of sulfur trioxide decomposition, close to 95%, occur within the first 150 mm of the reactor tube and remaining length of the reactor tube, 350 mm, is just supporting the extra 5% decomposition. So decrease in length of the reactor tubes to about 150 mm for diameters less than 2 mm would help in reducing the pressure drop values with a very little effect on sulfur trioxide decomposition. For the reactor tubes of diameter 3 mm and 4 mm the

length of reactor tube is sufficient to reach to 95% decomposition and for 100% decomposition the length of the tube should be longer than 500 mm.

Table 5.6. Percentage decomposition of SO_3 for different diameters of the reactor tube vs different lengths

Length of the reactor tube (mm)	Percentage decomposition of SO_3			
	D=4 mm	D=3 mm	D=2 mm	D=1 mm
0	0.0	0.0	0.0	0.0
20	22.1	29.7	43.8	57.3
40	30.9	41.2	59.9	75.7
60	37.6	47.7	70.9	86.0
80	43.2	56.7	78.7	91.9
100	48.0	62.6	84.4	95.2
150	57.9	73.7	92.7	98.7
200	65.6	81.4	96.6	99.7
250	71.8	86.8	98.4	99.9
300	76.9	90.6	99.2	100.0
350	81.0	93.3	99.6	100.0
400	84.4	95.2	99.8	100.0
450	87.1	96.6	99.9	100.0
500	89.4	97.6	100.0	100.0

CHAPTER 6

THREE-DIMENSIONAL NUMERICAL CALCULATIONS

A sulfur trioxide decomposer needs a design that enhances decomposition. A counter flow type heat exchanger with both hot and cold fluids flowing through the tubes is considered using the three-dimensional numerical analysis. A three dimensional model of the conceptual design of sulfur trioxide decomposer is shown in Figure 6.1. The decomposer is made up of layers of tubes where helium and reacting mixture flow in alternative layers. Such layers of tubes are piled into a cube of dimensions 0.5 m x 0.5 m x 0.5 m. The material of the heat exchanger at this point is considered as silicon carbide (SiC). This decomposer essentially is a counter flow type heat exchanger with hot fluid (helium) entering the decomposer from one end and allowing the cold fluid (reacting mixture) to enter at the other end. Since sulfur trioxide decomposition is an endothermic reaction helium supplies heat to the cold fluid which is a mixture of SO_3 , H_2O , SO_2 , and O_2 to perform the chemical decomposition.

From the two dimensional numerical modeling results it is evident that the reactor tube of diameter in between 1.5 mm and 2 mm is economical in terms of decomposition rates and also in pressure drops. So the diameter of the reactor tubes on both cold side and hot side is taken as 1.6 mm. Unlike two-dimensional modeling this decomposer uses platinum as a catalyst in decomposing the sulfur trioxide.

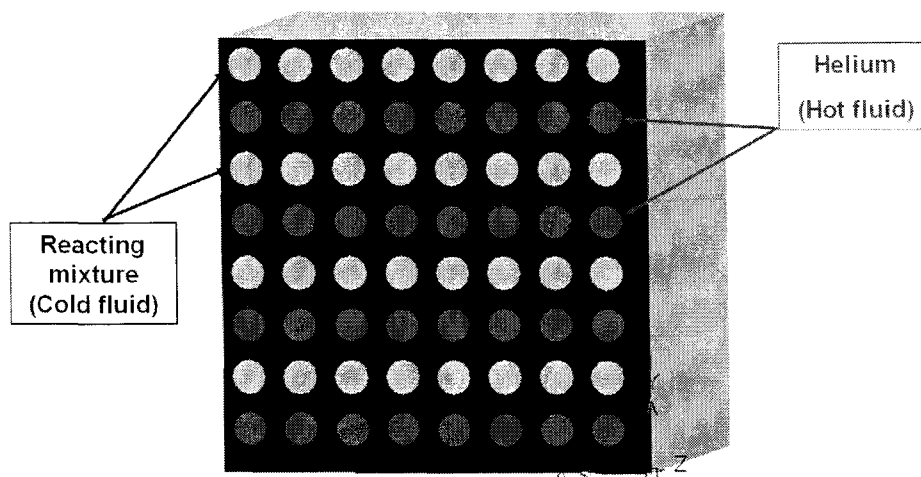


Figure 6.1. Conceptual design of sulfur trioxide decomposer

6.1 Three-Dimensional Single Fluid Analysis

Modeling and carrying out an investigation on the entire decomposer would take a lot of time, so just one reactor tube on the reacting mixture side is considered for initial investigations. The thermal energy required for the reaction can be obtained from a constant wall surface temperature boundary condition. The computational grid is generated using GAMBIT for one reactor tube with 50,000 nodes which is shown in Figure 6.2, where one can see the increase in the mesh density in radial direction from center to the walls.

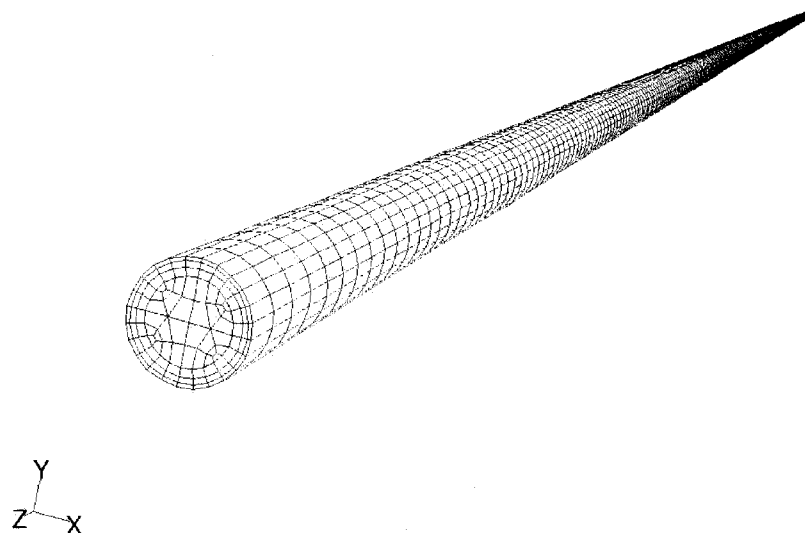


Figure 6.2. Three-dimensional grid for the reactor tube of diameter 1.6mm and length 500mm.

A simulation case is carried out using FLUENT at $T_w=1143$ K, $v=0.183$ m/s and $P=7$ atm, keeping every other input parameter similar to the two-dimensional analysis. Results of the analysis are shown in Figure 6.3. Since it is difficult to see the contours of different parameters throughout the length of the reactor tube, selected xy-planes at the inlet of the reactor tube are considered for viewing the results. To find how the wall surface reaction is working on three-dimensional numerical modeling, contours of Arrhenius reaction rate on some selected xy-planes are extracted using FLUENT post processor and are shown in Figure 6.3. From Figure 6.3 one can clearly see the reaction rates are high at the walls whereas there is not any reaction taking place at the center of the reactor tube, which is a good sign of proper modeling of wall surface reaction.

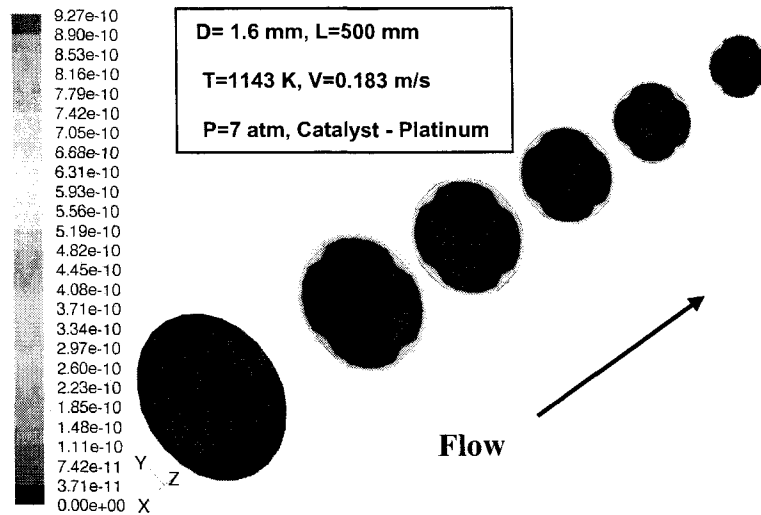


Figure 6.3. Contours of Arrhenius reaction rates ($\text{kg-mol/m}^3\text{-s}$) on different xy-planes along the length of the reactor tube

Similarly contours of mass fraction of sulfur trioxide, sulfur dioxide and oxygen are shown in Figures 6.4, 6.5 and 6.6 respectively.

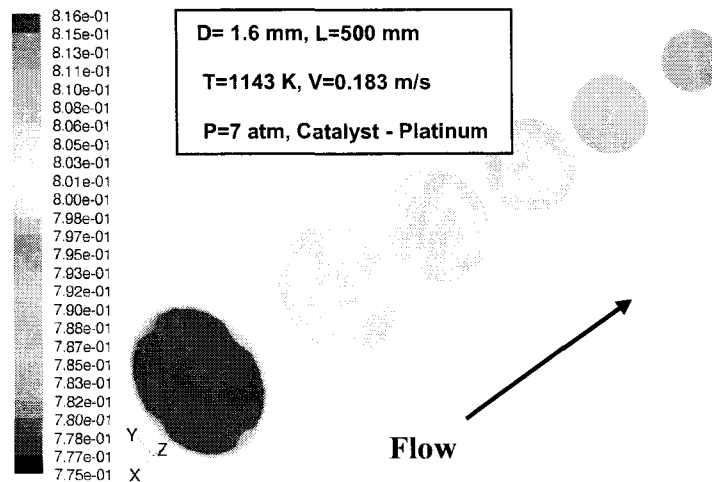


Figure 6.4. Contours of mass fraction of SO_3 on different xy-planes along the length of the reactor tube

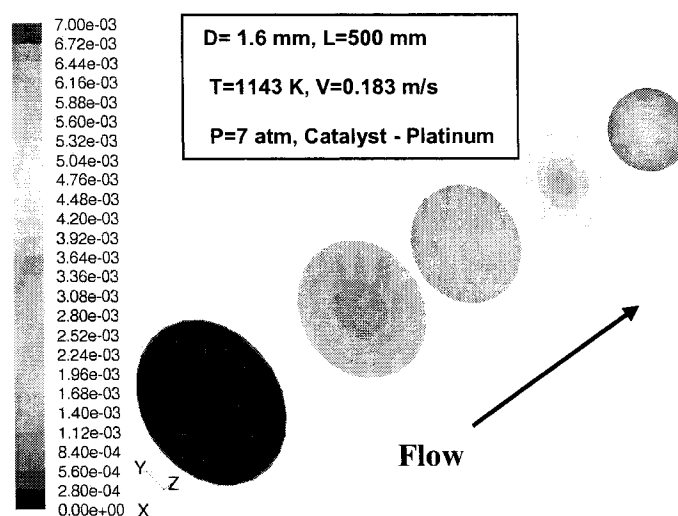


Figure 6.5. Contours on mass fraction of SO_2 on different xy-planes along the length of the reactor tube

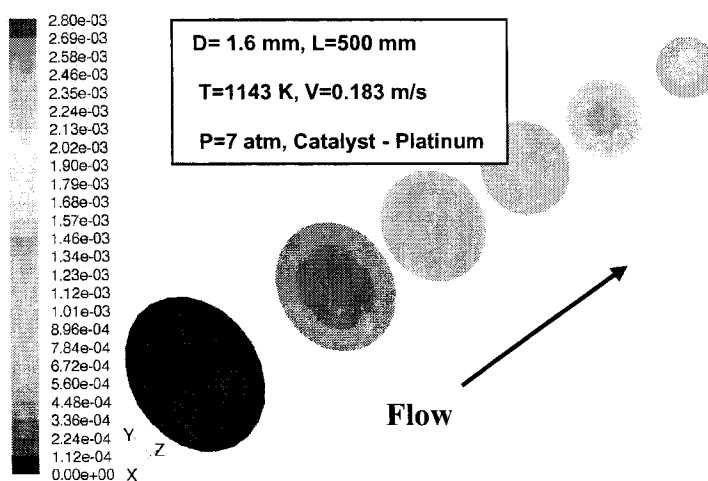


Figure 6.6. Contours of mass fraction of O_2 on different xy-planes along the length of the reactor tube

From Figures 6.4 to 6.6 one can clearly see the variation of mass fraction of different species from wall to the center of the reactor tube as a result of wall surface

decomposition of sulfur trioxide. The percentage decomposition of sulfur trioxide is close to 27% which is very less when compared with the ALFA-4 catalyst performance. SO_3 decomposition depends on the combination of activation energy (E_r) and the pre-exponential factor (A_r) values which vary with the type of catalyst. From the above figures it is clear that the three-dimensional numerical modeling of sulfur trioxide decomposition reaction is working properly and it will be interesting to find how the reaction works with the double fluid model where helium provides the thermal energy required for sulfur trioxide decomposition.

6.2 Three-Dimensional Double Fluid Analysis

The whole heat exchanger shown in Figure 6.1 can be represented using a simple unit cell model which is symmetric to all four sides, is shown in Figure 6.7.

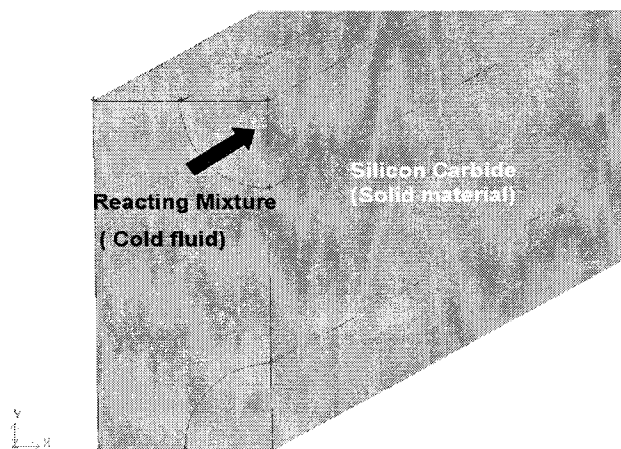


Figure 6.7. Unit cell that represents the whole heat exchanger

Since the unit cell can represent whole heat exchanger generating grid for the unit cell is enough to investigate the whole heat exchanger using the CFD techniques. The mesh generated using GAMBIT which contains 150,000 nodes is shown in Figure 6.8

where one can see dense mesh close to the walls on the cold fluid side and on the hot fluid side there is no variation in the mesh density in radial direction. Coarse mesh is used for the solid region, and there is no density variation in the mesh in the axial direction for both fluid sides as well as for the solid material.

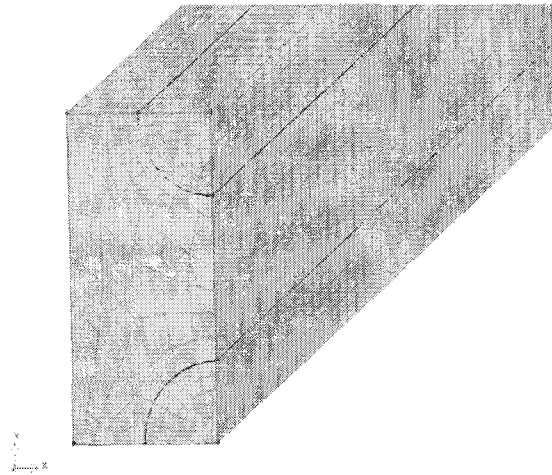


Figure 6.8. Mesh generated using GAMBIT for the unit cell

Helium enters the reacting mixture at a temperature of 1143 K and at a velocity of 16 m/s from one side of the decomposer. The reacting mixture at round 873 K enters the decomposer from the opposite side with a velocity of 0.183 m/s. Operating pressure of both helium and reacting mixture is 7 MPa and 0.7 MPa respectively. All other inputs remain constant and helium acts as a heat source for the endothermic reaction occurring on the cold fluid side. After investigating the sulfur trioxide decomposition on the three-dimensional numerical model the percentage decomposition of sulfur trioxide is around 4. The contours of mass fraction of sulfur trioxide at selected xy-planes are shown in Figure 6.9. One can clearly see the mass fraction values of the sulfur trioxide close to the

walls is less than the mass fraction at the center which is an indication of sulfur trioxide decomposition at the walls in the presence of catalyst platinum.

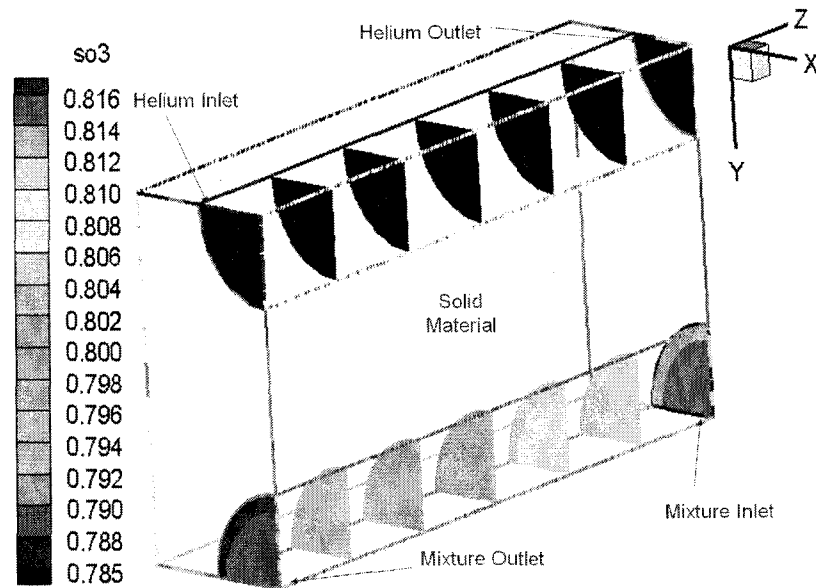


Figure 6.9. Contours of mass fraction of SO_3 at different xy-planes along the length of the decomposer

There is a 143 K drop in temperature on the helium side from inlet to outlet where as there is a 37 K raise in temperature on the reacting mixture side. The contours of temperature for hot fluid as well as cold fluid are shown in Figure 6.10.

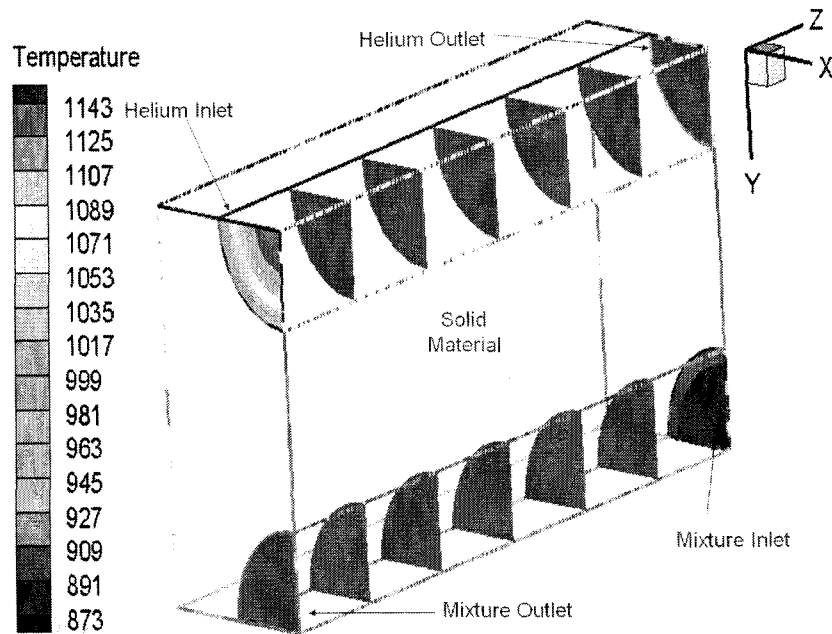


Figure 6.10. Contours of temperature (K) for both fluids at different xy-planes along the length of the decomposer

From the above temperature contours it is more than clear that the temperature drop on the helium side is very drastic at the inlet and thereafter there is not much variation in temperature along the length of the decomposer. It is evident that thermal energy supplied by the helium to the reacting mixture is not sufficient to raise the temperature of the reacting mixture and at the same time it could not provide the temperature required for better decomposition of sulfur trioxide. Increasing the thermal energy that is being supplied by the hot fluid to the cold fluid would result in better decomposition of sulfur trioxide.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The numerical methods are successful in predicting the decomposition of sulfur trioxide as a wall catalyzed reaction for different operating conditions and for different catalysts. Some of the conclusions on both two-dimensional and three-dimensional investigations are summarized below.

7.1.1. Conclusions Based on Two-Dimensional Results

- The percentage decomposition of SO_3 increases with increasing the operating temperature so elevated operating temperatures results in higher decomposition. But the operating temperatures really depend on the type of material that is used for the decomposer.
- The percentage decomposition of SO_3 depends on the type of catalyst. The iron oxide (ALFA-4) performance is good even at temperatures close to 700°C , where as there is not much decomposition observed for the catalyst platinum at those temperatures. The choice of catalyst will depend on whether or not the catalyst can be impregnated into the matrix of the base metal.
- The percentage decomposition of SO_3 increases with increasing the surface area for the same acid flow rate. The smaller the diameter of the reactor tube higher

the decomposition, but pressure drop in the reactor tube is the basic constraint in considering smaller diameter tubes for decomposer. From the two-dimensional investigations it is clear that although the pressure drop increases with decrease in diameter of the reactor tube there is a considerable increase in the decomposition of SO_3 . This type of pattern is observed only up to 1.5mm diameter. Going below 1.5mm diameter resulted in a drastic increase in the pressure drop values with much less increase in the decomposition of SO_3 . Apart from the high pressure drop values a couple of other factors which may restrict considering smaller diameter reactor tubes (less than 1.5 mm) include difficulties in manufacturing small diameter tubes and the possibility of fouling in small diameter tubes.

- The increase in the acid flow rate decreases the percentage decomposition of SO_3 . From two-dimensional investigations it is clear that the increase in the mole flow rate linearly affects the percentage decomposition, and there is no drastic variation in the percentage decomposition values. The flow rate that would provide better decomposition always depends on the operating temperatures and the type of catalyst. Since performance of the catalyst increases with the increase in the operating temperature, high decompositions can be obtained even at high mole flow rates.
- Length of the reactor tube has a major effect on the decomposition. Even though the increase in length of the reactor tube provides more surface area which helps in getting higher decompositions there is an increase in the pressure drop values also which results in higher pumping power. From the two-dimensional investigations it is clear that the reactor tube length can be reduced from 500 mm to 150 mm in case

that the smaller diameters less than 2 mm are used with ALFA-4 coating as a catalyst. The decrease in length of the reactor tubes decreases the pressure drop with less effect on the decomposition of SO_3 . As the diameter increases, the length of the reactor tube essential for higher decomposition increases. For the reactor tube of diameters more than 3mm the length of the reactor tube required to get close to 95% decomposition is more than 500 mm.

7.1.2 Conclusions Based on Three-Dimensional Results

- From the three-dimensional single fluid numerical results modeling it is clear that the percentage decomposition of sulfur trioxide in the presence of a catalyst platinum is 27%, which is considered as good for the platinum.
- From three-dimensional double fluid numerical results it is clear that the decomposition of sulfur trioxide is around 4% which is not as good compared with the single fluid model. The reason for variation in decomposition is because of the variation in the heat source. In single fluid model the thermal energy required for sulfur trioxide decomposition reaction is supplied by the constant wall surface temperature boundary condition which provides an unlimited heat source at the desired temperature. Whereas in the double fluid numerical model the heat energy required for sulfur trioxide decomposition reaction is supplied by the hot helium flowing through the decomposer. The thermal energy supplied by the helium is limited when compared with the constant temperature boundary condition. So the percentage decomposition values are less than the constant wall surface temperature. SO_3 decomposition can be increased by increasing the heat energy supplied to the mixture. Temperature of the helium coming from the high

temperature heat exchanger (HTHX) is constant at 1143 K, which cannot be changed. There are two different ways to increase the heat energy supplied to the mixture without varying the helium inlet temperature. One way is by increasing the mass flow rate on the helium side and the other is to increase the inlet temperature of the reacting mixture. The mass flow rate on helium side can be increased either by increasing the velocity of the helium or by increasing the diameter of the tubes on the helium side keeping the diameter of reactor tubes on the mixture side constant. Increasing the inlet temperature of the reacting mixture that is at 873 K, results in higher percentage decomposition of SO_3 .

7.2 Future Work

Numerical modeling of wall catalyzed sulfur trioxide decomposition reaction was modeled in both 2D and 3D. These models can be further used for investigating the other candidate catalysts for sulfur trioxide decomposition and also for improving the decomposer performance. However there are some modifications in the numerical models which would help in predicting the SO_3 decomposition with better accuracy. Some of them are discussed below

- Sulfur trioxide decomposition reaction is modeled assuming that the mixture of sulfur trioxide and water vapor enters the reactor tubes but in reality there is a probability that some undecomposed sulfuric acid (H_2SO_4) may enter the decomposer. So sulfuric acid decomposition reaction that results in sulfur trioxide and water vapor should also be included in the model along with the SO_3 decomposition reaction.

- Effect of different parameters on the decomposition of sulfur trioxide such as wall surface temperature of the reactor tube, diameter of the reactor tube, length of the reactor tube and mass flow rate at the inlet of the reactor tube are investigated using two-dimensional numerical model. Operating pressure and inlet temperature of the reacting mixture are two more parameters that have considerable effect on the decomposition of sulfur trioxide. So using the same two-dimensional numerical model, investigation is to be carried out on both the parameters to find out how SO_3 decomposition can be affected.
- From the three-dimensional numerical modeling it is clear that the percentage decomposition of sulfur trioxide is less because of insufficient supply of heat energy to the reacting mixture. So analytical calculations need to be carried out to find out exactly how much thermal energy is required to decompose at least 50% of the sulfur trioxide. Modifications either on the helium side or on the mixture side are needed according to the thermal energy requirements. The possible modifications can be
 1. Increasing the velocity on the helium side which allows higher mass flow rates of helium.
 2. Increasing the diameter of the tubes carrying the helium keeping the velocity constant at 16 m/s.
 3. Increasing the inlet temperature of the reacting mixture entering the decomposer up to 1143 K.

- Since double fluid three-dimensional numerical modeling of the decomposer needs many hours of computing time, there is a need for double fluid two-dimensional numerical models where the simulation cases can be carried out at a faster rate.
- There is chance that decomposer may receive structural damage at the time of starting and stopping because of very high pressure gradients between the two layers of the tubes. So there is a need to carry out both thermal stress analysis as well as mechanical stress analysis on the decomposer.

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2. Kiran K. Muramalla, Yitung Chen, Anthony E. Hechanova, Simulation of Decomposition of Sulfur Trioxide Gas on Self-Catalytic Metallic Material, Proceedings of the AIChE Annual Meeting 2005, Cincinnati Convention Center, Cincinnati, Ohio, USA, October 2005.
3. Kiran K. Muramalla, Simulation of Homogeneous Decomposition of Sulfur Trioxide Gas in a Wall Catalyzed Reactor Tube, ANS Students Conference 2005, Columbus, Ohio, USA, April 2005

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