

Chapter 2: Literature Survey

2.1 Introduction

A survey was conducted to review relevant studies reported in the literature. A further aim was to identify shortcomings of studies of the sulphur trioxide decomposition reaction, which forms part of the HyS cycle. A brief overview was given with regard to the emerging hydrogen economy, as well as the complete Hybrid Sulphur cycle. The sulphur trioxide decomposition reaction was investigated from literature with specific focus on the overall process evaluation. The catalysts utilized in literature for the sulphur trioxide decomposition reaction are discussed, with attention to activity and stability under operating conditions. The kinetics evaluated in literature for the decomposition reaction is reviewed. Packed bed reactors are investigated, including reactor work completed on the sulphur trioxide decomposition reaction, fundamental reactor modelling concepts, heat transfer mechanisms in a packed bed as well as numerical modelling conducted on packed beds. Based on results reported in literature the solubility of sulphur trioxide in water is investigated.

2.2 Hydrogen Economy

The properties of hydrogen enable it to serve as an energy carrier as it can be stored to be used as required. Despite this advantage, hydrogen has a lower Higher Heating Value than other fuels currently available (Bossel, 2006). The Higher Heating Value of hydrogen at 800 bar pressure is 10 GJ/m^3 , while methane at 800 bar delivers approximately 32 GJ/m^3 , which is much higher, but the available sources are limited (Bossel, 2006). The global hydrogen economy can be summarized in three sections, namely hydrogen production, hydrogen economy and hydrogen usage. Hydrogen production includes methods such as electrolysis, reforming and potential thermochemical cycles (Dincer, 2012). Hydrogen economy includes various sections to be considered, and can be classified under the following headings (Bossel, 2006)(Andrews, 2012):

- Packaging
- Distribution
- Storage
- Transfer

All of the above-mentioned areas still require research and development to aid the progression of the hydrogen economy. Andrews and Shabani (2012) propose that the above-mentioned areas should be addressed as follows: investigate the most suitable methods for hydrogen production from biomass, hydrogen storage capacity on a level suitable for incorporation into a national electricity grid, technical feasibility of hydrogen storage in natural or artificial storage forms and hydrogen storage and fuel cell systems suitable for extensive operation. Although some of these areas have been developed to an advanced stage, further work is required for commercialization.

With the above-mentioned issues concerning a sustainable hydrogen economy in mind, the Department of Science and Technology (DST), South Africa, initiated the Hydrogen South Africa (HySA) program aimed to establish Competence Centers where intellectual property, knowledge, prototypes, products and components can be developed, with specialization in fuel cell technology (Pollet, 2013). With three HySA national competency centers addressing catalysis research (PGM) and infrastructure, South Africa is joining the world-wide venture to obtain a sustainable hydrogen economy from production to utilization (Pollet, 2013).

The cost of hydrogen production, based in 2012 for commercially available electrolysis systems, was between \$2,5 (US) to \$3.5 (US) per kg, while for ideal electrolyzers without any losses the cost amounted to \$1.95/kg, the issue being the desalination and demineralization of water prior to electrolysis (Dincer, 2012). Although the idea of a hydrogen economy to produce electricity as needed is exciting, the cost of hydrogen is currently about four times higher than electricity from the grid (Bossel, 2006). Although hydrogen holds promise as a truly sustainable global energy future, the future is uncertain. Hydrogen systems have to break through to a new level with regard to technology and cost, and even if this were to happen in the near future, transition into a sustainable hydrogen economy would still take decades (Morgan, 2006). For now fossil fuels remain the backbone of the global energy economy, while hydrogen has the potential to play a dominant role in the distant future.

2.3 Hybrid Sulphur Cycle (HyS)

The Hybrid Sulphur cycle investigated in this study was intended to be coupled to a High Temperature Gas Nuclear Reactor (PBMR) that had been under investigation. The Hybrid Sulphur Cycle, also known as the Westinghouse Sulphur Cycle or the Ispra Mark 11, is a two-step thermo-chemical cycle for decomposing water into hydrogen and oxygen (Brecher, 1977), (Summers, 2005). Two chemical reactions are responsible for the production of hydrogen and oxygen, the first being:



(Thermo-chemical, 800-900°C)

And the second:



(Electro-chemical, 80-120°C)

The simplified representation of the HyS cycle can be seen in Figure 2-1 where pure water, thermal and electrical energy are required to drive the system.

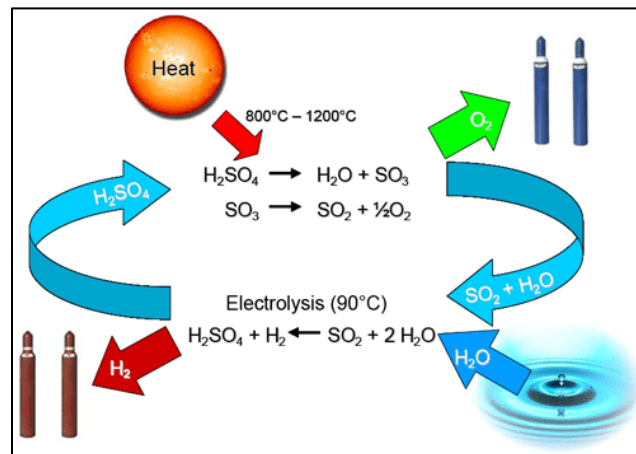


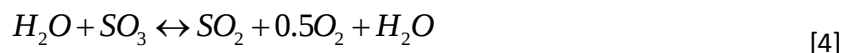
Figure 2-1: Hybrid Sulphur Cycle (PREC, 2014)

A concentrated sulphuric acid stream is sent to the decomposer section, which consists of 2 decomposition sections, where firstly the sulphuric acid is completely decomposed at a high temperature. The reaction takes place in Section 1:



$$(\Delta H = +97.54 \text{ kJ/mol})$$

The product is fed to section 2 where the following reaction takes place:



$$(\Delta H = +98.92 \text{ kJ/mol})$$

Section 2 is said to be the dominant unit of the cycle, because the efficiency of the sulphur trioxide decomposition has a major impact on the economy of the process. These two reactions are highly endothermic and therefore favoured by high temperatures. There is also an increase in volume with reaction which means that the process is favoured by operating at low pressures. Section 2, which is the sulphur trioxide decomposer, is the section under investigation. The product stream coming from section 2 is sent through various heat exchangers to recover the heat and lower the temperature so that phase separation is possible. A series of flash evaporators are used to separate oxygen from the rest of the liquid species. The product of the last evaporator is almost pure oxygen. The rest of the mixture consisting of mainly SO_2 , sulphuric acid and water is sent back to the electrolyser section (Summers, 2005). The various off-streams from different sections are mixed together at an anolyte preparation tank to form a feed stream to the electrolyser (Summers, 2005). The electrolyser is where the hydrogen is produced. According to theory the main advantage that the electrolyser of the thermo-chemical process has over the regular water splitting cycles, is that the power requirements are less than 15% of that required for the conventional electrolysis (Brecher, 1977). Hydrogen with a very high purity is collected at the cathode while the remainder of the mixture is concentrated. The off-stream from the electrolyser is passed through a series of heat exchangers and flash evaporators to obtain the required sulphuric acid concentration, in order to recycle it back to the reactor section (Summers, 2005). The sulphur oxides in the system are used only as recycling intermediates (Brecher, 1977). The Sulphur-Iodine cycle also requires a sulphuric acid decomposition unit, but will not be discussed or compared to the HyS cycle.

2.4 Sulphur Trioxide Decomposition

The decomposition of sulphur trioxide into sulphur dioxide and oxygen has been investigated by various authors in literature and ranges from conceptual designs to experimental work. The work reported in

literature was evaluated mainly for the HyS and SI cycles. Extensive research has gone into the development and improvement of these cycles: Oztruk et al. 1995 presented a new design with thermodynamic and engineering analysis of the H_2SO_4 decomposition section in the SI cycle, Rodriguez et al. (2006) presented a development methodology for the sulphur trioxide decomposition step in the SI cycle, Summers et al. (2005) specifically studied the development of the electrolyser unit, Huang et al. (2005) indicated that the kinetics and thermodynamics could be improved at higher temperatures only obtainable from solar energy and did a complete mass and energy balance over the system using Aspen HYSYS process simulation software. Although these cycles have been investigated since the 1970s not many experimental results have been published. The work reported in literature on the decomposition reaction includes the following:

- Catalytic activity and stability tests (Section 2.4.1)
- Kinetics analysis (Section 2.4.2)
- Conceptual designs of the sulphur trioxide decomposer (Section 2.5.1)
- Experimental work on various decomposers (Section 2.5.1)
- Elementary as well as CFD modelling of the reactor systems (Section 2.5.5.1)

The above-mentioned work reported in literature is given in the appropriate section together with the relevant fundamentals to investigate the system.

2.5 Catalyst and Kinetics

2.5.1 Activity and Stability

The catalyst of a heterogeneous reactor system is crucial as it influences the operating and capital cost of that system. One of the difficulties in the HyS process is to identify a catalyst that is highly active and will be stable for extensive times under the harsh operating conditions. In literature it has been reported that 30 odd catalysts have been tried and tested for the decomposition of sulphur trioxide into sulphur dioxide and oxygen. Some of the more promising options are the metal oxide combinations and Platinum Group Metal combinations. Idaho National Laboratories have done novel work with PGM catalyst combinations: In some of their earlier work (Ginosar, 2007) they compared three platinum combinations; 0.1-1 wt% metal loading of $\text{Pt}/\text{Al}_2\text{O}_3$, Pt/TiO_2 and Pt/ZrO_2 . Reaction times varied between 24 hours and 240 hours on stream. They found that the Pt/TiO_2 which had lower surface area, had a lower initial activity but had the best stability for the duration of the experiments.

In further work Ginosar et al. (2009) determined the activity and stability of FeTiO_3 , MnTiO_3 , NiFe_2O_4 , CuFe_2O_4 , NiCr_2O_4 , $2\text{CuO} \cdot \text{Cr}_2\text{O}_3$, CuO and Fe_2O_3 . Activity was determined in the temperature range between 725 and 900°C while stability tests were conducted at 850°C for 1 week during continuous operation. All the metal oxides showed a reduction in surface area after exposure to reaction conditions and seemed to lose much of its initial activity. There were some good candidates but all seem to lose too much activity due to material sintering, phase changes, low activity at moderate temperatures as a result of sulphate formation and decomposition into their original oxides. Rashkeev et al. (2009) performed density functional theory based on first principles calculations to obtain a better understanding of the factor responsible for catalyst activity. He found that Pt and Pd were “softer” (binding energy) PGMs and they had larger initial activity than the “harder” PGMs but also deactivated much more rapidly than the harder metals. Rashkeev et al. (2009) and Ginosar (2009) combined the harder and softer PGMs. They tested combinations of 1 wt% Pt, 0.3 wt% Ir/ TiO_2 and 1 wt% Pt, 0.3 wt% Ru/ TiO_2 which showed better stability than just the plain 1 wt% Pt/ TiO_2 basis.

Banerjee et al. (2008) investigated the activity and stability of Cr substituted Fe oxide catalysts, $\text{Fe}_{2(1-x)}\text{Cr}_{2x}\text{O}_3$. Although this catalyst combination has not been tested for long periods the $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ showed to be an active and stable catalyst for the decomposition process. Another variation of Pt catalyst was evaluated by Nagaraja et al. (2009) who prepared 1 wt% Pt/ BaSO_4 by using three different methods and determining which method gave the highest activity. Good activity was found, but unfortunately no stability tests were performed for this catalyst. In the work done by Kim et al. (2006) they determined the activity of Fe/Al and Fe/Ti catalysts, as well as proposed a mechanism for sulphur trioxide decomposition. The increase in Fe loading caused an increase in activity for these two catalysts, indicating that the Fe component should be active. Other innovative catalyst combinations were evaluated by Barbarossa et al. (2006) who used an Ag-Pd intermetallic compound and Fe_2O_3 supported on SiO_2 with temperatures in the range of 773 to 1 373 K. They found that, for the catalysts mentioned, a large onset temperature a decrease in activation for this reaction was achieved. Abimanyu et al. (2008) evaluated the activities of $\text{Cu}/\text{Al}_2\text{O}_3$, $\text{Fe}/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{Fe}/\text{Al}_2\text{O}_3$ composite granule catalysts in an attempt to find a suitable catalyst for the SO_3 decomposition reaction. In the temperature range of 750-950°C the catalyst with the best activity was found to be $\text{Cu}/\text{Fe}/\text{Al}_2\text{O}_3$ composite with an optimum ratio of $[\text{Cu}]/[\text{Fe}]=1/2$. With Pt having such a high activity, Zhang et al. (1998) determined not only the activities of CuCr_2O_4 and CuFeO_4 at various space velocities but they also tested Pt/SiC to increase

stability. They found that CuCr_2O_4 had the highest activity of the three while Pt/SiC had better stability. Zhang et al. (1998) also proposed reasons why these catalysts deactivated which include formation of sulphate, agglomeration and decreasing specific area.

In an attempt to evaluate the catalytic activity of three different ferro-spinels, Banerjee et al. (2011) found the following order in terms of most reactivity for the decomposition process: $\text{CuFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4$. They also proposed a plausible mechanism for sulphuric acid decomposition over spinel ferrites. The mechanism entails metal sulphate formation and decomposition, followed by an oxygen evolution step, with the sulphate decomposition step as the rate determining step. The catalytic activities of various metal oxides were evaluated by Brittain & Hildebrand (1983) and Dokiya et al. (1977). The metal oxide catalyst combinations show great initial activity, however lack in stability, while the platinum group metal catalyst shows good activity and better stability. With the work done by Ginosar (2009) the probable way forward is to have a combination of platinum group metals on a TiO_2 basis that will reduce the loss of platinum metal from the catalyst pellet.

2.5.2 Kinetics and Literature

The kinetics evaluated in literature for the sulphur trioxide decomposition reaction, although not many, gave some insight into the system, specifically the setup and operating conditions. A thorough review was completed by Brown & Revankar (2012) summarizing the catalytic work reported in literature for the sulphur trioxide decomposition reaction. Below the work of the authors cited in the review will be treated. These include the work done by Karasawa et al. (2005) who determined the activation energy and pre-exponential factor with and without Fe_2O_3 catalyst; Giaconia et al. (2010) who evaluated the activation energy and pre-exponential factor for Fe_2O_3 pellets and Fe_2O_3 coated on a honeycomb structure; Kondamudi & Upadhyayula (2010) used a Fe_2O_3 supported on alumina catalyst and evaluated the activation energy and pre-exponential factor. Although the method of Lin & Flaherty (1983) is not known, they also published a pre-exponential factor and activation energy for ALFA4 (Fe_2O_3); Spewock et al. (1976) evaluated the kinetics for two proprietary catalysts named WX-1 & WX-2. Based on comparison with recent work WX-2 is suggested to be platinum-based (Brown, 2012); The first PGM-based catalyst kinetics were evaluated by Ishikawa et al. (1982) for 1 wt% Pt/ Al_2O_3 .

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The pre-exponential factor and the activation energy are reported for this catalyst; Ivanova et al. (1991) studied chromium phosphate as a catalyst and evaluated the kinetic parameters for the catalyst; a more advanced kinetic model was evaluated by Petropavlovskii et al. (1989) and will be discussed later. Almost all the authors mentioned above used the first order approximation to evaluate the activation energy and pre-exponential factors. It is difficult to compare the data of the work mentioned because none used the same process conditions, WHSV, catalyst shape and form. Thus Table 2-1 will summarize the work of the above-mentioned authors who investigated a 1st order kinetic approach rather than compare them.

Table 2-1: Kinetic parameters for sulphur trioxide decomposition reaction (1st order)

Author	Catalyst Material	Catalyst State/Form	Activation Energy (kJ/mol)	Pre-Exponential factor (s ⁻¹)
Karasawa et al. (2005)	Fe ₂ O ₃	Unknown	301.78	1.31x10 ¹⁵
Kondamudi et al. (2010)	Fe ₂ O ₃	Alumina supported pellet	138.6	
Giaconia et al. (2011)	Fe ₂ O ₃	Pellet	162.6-165.6	2.3-3x10 ⁸
	Fe ₂ O ₃	Honeycomb structure	223.0-224.6	1.3-3.1x10 ¹¹
Lin & Flaherty (1983)		Unknown	196	1.04x10 ¹⁰
Spewock et al. (1976)	WX-1	Powder	228	2.13x10 ¹⁰
	WX-2	Powder	73.05	6.81x10 ⁴
Ishikawa et al. (1982)	Pt/Al ₂ O ₃	Powder	70.7	4.2x10 ⁷
Ivanova et al. (1991)	CrPh	Unknown	178.6	3.96x10 ¹⁰

Kondamudi et al. (2010) stated that they were operating in the kinetic controlled regime because of the straight line obtained in the data plot. There is not much information available on the PGM-doped catalysts with regard to operating procedures and specific forms of deactivation incorporated into the kinetic model. The only values found for activation energy for PGM-doped catalysts will be used as a guide for experimental values obtained. An advanced Langmuir-Hinshelwood reaction rate was utilized by Petropavlovskii et al. (1989) on a Pa/Al catalyst and they found the forward reaction rate activation

energy to be 154 kJ/mol. Adsorption energies are also provided, but not much is further known about that investigation (Brown, 2012). Three main mechanisms may be the controlling mechanism and include surface reaction controlling, adsorption of species and desorption of species. Due to the effect of deactivation on the performance of a catalyst it must be accounted for in kinetic evaluation and reactor modelling. Sintering has been identified as a main source of catalyst deactivation in PGM-based catalysts at elevated temperatures (Forzatti, 1999). The effect of loss of active surface area will not be investigated in this study, but has been done by various authors (Boskovic, 2004), (Lif, 2002), (Monzon, 2003), (Forzatti, 1999). Since global particle kinetics was investigated in this study, together with steady state conditions, the effect of deactivation could be ignored, thereby eliminating the need for a transient model.

2.5.3 Equipment used for Kinetics Evaluation

Various methods are available to evaluate kinetic parameters for a reaction under investigation and the equipment associated with these methods have to be investigated to make the correct choice for the system under investigation. Equipment for this evaluation can include micro differential-, packed bed- and spinning basket type reactors using pellets. The spinning basket type reactor has been used with great success by many investigators for many other catalysts with high conversions suitable for many reactions (Berty, 1999). However, the construction of such a reactor with a large number of moving parts and seals to handle very corrosive gases can be problematic. The use of a laboratory-scale packed bed with many pellets would require consideration of the packing effects (pressure drop and porosity), which would be similar to the pilot plant reactor. However, a differential bed with a small number of separate pellets (one level) would eliminate the complex packing effect, but would require modelling of the flow and chemical effects around separate single pellets.

2.6 Fixed Bed Reactors

2.6.1 Reactor Systems in Literature

The most important unit in the HyS cycle is the sulphur trioxide decomposition unit as the amount of sulphur dioxide produced is proportional to amount of hydrogen that can be produced. It is the most energy-intensive operation and it dictates the efficiency of the process. Significant work involving concept designs of sulphur trioxide reactors, mostly assuming one-dimensional homogenous reactor

systems, are the following: Shin et al. (2009) simulated the dynamic start-up procedures for a packed bed reactor considering the influence of temperature variation in the system, Brecher et al. (1977) were of the first researchers involved in the Westinghouse cycle (or HyS as it is known). They gave some insight into the research done at that stage as well as discussed the potential for Hydrogen in 1977; Lee et al. (2010) developed a point model to use as a guideline for SO_3 decomposer designers to achieve a target decomposition ratio with the aid of economic considerations; Lin & Flaherty (1983) investigated the possibility of using solar concentrators as power sources, together with the design of a SO_3 decomposer including thermodynamics, reaction kinetics, heat transfer, mechanical considerations and a brief description of the test unit.

In other work, Choi et al. (2009) performed some CFD analysis with CFX11 on a shell-and-tube type configuration using the Finite Rate Chemistry model on a design containing RA 330 Alloy construction material. They found good performance in tests of SO_3 decomposition for the design parameters; Kim et al. (2008) evaluated another heat exchanger type for the decomposer configuration, i.e. a hybrid compact heat exchanger with printed circuit of the hot gas side and fin type heat exchanger on the colder process gas side. Two of the most influential parameters in the system were found to be the reaction rate constant and retention time. Kuchi et al. (2009) also investigated the possibility of a shell-and-tube heat exchanger chemical decomposer with porous media in Fluent 6.2.16. Their model consisted of steady state approximation, laminar flow, 2D axisymmetric shell-and-tube configuration with counter current flow.

Some of the more important parameters were found to be the Reynolds number, surface to volume ratio and the activation energy; Connolly et al. (2009) discussed the design of a multi-tube composite reactor that included pre-heating, concentrating and decomposing sulphuric acid; Kim et al. (2008) developed a dynamic model to evaluate the SO_3 decomposition process by considering heat and material balances in PDE form. After sizing the decomposer they simulated the responses corresponding to changes in operating conditions. Gelbard et al. (2005) at SNL were some of the few investigators who built a SO_3 decomposer setup i.e. a packed bed. They performed a series of pressurized acid tests with the following objectives in mind; obtain data on the fraction of SO_3 decomposed into SO_2 and O_2 ; demonstrate real-time measurements of the converted acid for the use of process control; obtain

measurements of conversion as a function of time; and assess rapid quenching of acid to minimize corrosion of metallic components (Gelbard, 2005).

In more recent research Park et al. (2013) developed an Aspen model to compare against experimental data from a bayonet type reactor. The Equation of State was varied to satisfy data from Perry's Handbook to find the best model. The evaporation, acid dissociation and SO_3 decomposition showed promising results specifically the SO_3 decomposition section. Thomey et al. (2012) developed a solar concentrator reactor for the SO_3 decomposition reaction. Acid flow rates were between 2-6 ml/min with a temperature range of 650 to 950°C. Two catalysts, Fe_2O_3 and CuFe_2O_3 , were evaluated on honeycomb structures and while good conversion was achieved it was found that a variation in results could not be obtained for low WHSVs.

2.6.2 Fundamental Concepts

The modelling of fixed bed reactors have been widely investigated and formulated in literature (Froment, 1979) and to establish models applicable to this investigation a thorough review was done. Applicable models started at the most basic homogenous plug flow, advancing to the most complicated 2/3D heterogeneous model. The methodology and progression to the more advanced heterogeneous model combined with Computational Fluid Dynamic capabilities was ultimately the goal and are thus discussed in that order.

2.6.2.1 *One-Dimensional Pseudo-Homogeneous Model*

The one-dimensional pseudo-homogeneous model is a basic/ideal model where temperature and concentration gradients are assumed to be only in the axial direction. This model is commonly referred to as a plug flow model as it only takes the overall flow rate into consideration. The conservation of mass and energy in steady state for a single reaction in a tube are given by Froment & Bischoff (1979):

$$-u_s \frac{dC_A}{dz} = \rho_B r_A \quad [5]$$

$$u_s \rho_B c_p \frac{dT}{dz} = (-\Delta H) \rho_B r_A - 4 \frac{U}{d_t} (T - T_R) \quad [6]$$

The respective initial boundary conditions: $z = 0; C_A = C_{A0}; T = T_0$

The one-dimensional homogeneous model involves many assumptions and has shortcomings in the sense of oversimplification. To rectify these flaws, various other parameters will be gradually introduced, ensuring advancing reactor models. Some of the concerns of the ideal model are that the flow in a packed bed reactor deviates from the ideal pattern because of radial variations in flow velocity and mixing effects due to the presence of packing and the assumption that temperature is uniform in the cross section of a tube. The catalyst packing inside the reactor tube causes advanced turbulent flow patterns and in turn causes dispersion in the axial and/or radial direction. The steady state mass and energy equations accounting for axial dispersion are given as (Froment, 1979):

$$\varepsilon D_{ea} \frac{d^2 C_A}{dz^2} - u_s \frac{dC_A}{dz} - r_A \rho_B = 0 \quad [7]$$

And

$$\lambda_{ea} \frac{d^2 T}{dz^2} - \rho_g u_s c_p \frac{dT}{dz} + (-\Delta H) r_A \rho_B - \frac{4U}{d_t} (T - T_R) = 0 \quad [8]$$

The equations above are second order partial differential equations with the following boundary conditions:

$$u_s (C_{A0} - C_A) = -\varepsilon D_{ea} \frac{dC_A}{dz} \quad \text{for } Z=0 \quad [9]$$

$$\rho_g u_s c_p (T_0 - T) = \lambda_{ea} \frac{dT}{dz} \quad \text{for } Z=0 \quad [10]$$

$$\frac{dC_A}{dz} = \frac{dT}{dz} = 0 \quad \text{for } Z=L$$

Care must be taken when utilizing this set of equations because the introduction of axial mixing into the basic equations leads to the possibility of more than one steady state. It is therefore necessary to ensure that initial values of the problem are quite accurate i.e. the initial values will determine where steady state will be. To ease the process of reactor modelling, criteria have been developed for which certain assumptions are found to be valid. This makes it possible to choose a highly accurate model for the specific reactor system without going through the trouble of solving all available models. The following criteria that can be used to determine if axial dispersion has an impact on the reactor system are proposed by Mears (1976). Axial dispersion in the reactor system can be neglected if the following criteria are met:

$$\left| \frac{n.Da_I}{Pe_{a,m}} - \frac{Ar.Da_{III}}{Pe_{a,h}} \right| < 0.05 \quad [11]$$

2.6.2.2 *Two-Dimensional Homogeneous Model Accounting for Radial Mixing*

The concept of radial mixing is introduced because the addition and removal of heat in a packed bed reactor is of crucial importance in endothermic and exothermic reactions most of the time. The heat transfer parameters that are necessary to solve 2D models will be explained in greater detail in Section 2.6.3. This section will only focus on the reactor models. The mass and energy equations for a single reaction at steady state are given as (Froment, 1979):

$$\varepsilon D_{er} \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) - u_s \frac{\partial C}{\partial z} - \rho_B r_A = 0 \quad [12]$$

And

$$\lambda_{er} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - u_s \rho_g c_p \frac{\partial T}{\partial z} + \rho_B (-\Delta H) r_A = 0 \quad [13]$$

With the boundary conditions given as:

$$C = C_0 \text{ at } z=0 \quad 0 \leq r \leq R_t \quad \text{and} \quad T = T_0 \quad \text{at } r=0 \quad r=R_t$$

$$\frac{\partial C}{\partial r} = 0 \quad ; \quad \frac{\partial T}{\partial r} = 0 \quad \text{at } r=0 \quad \text{with} \quad \frac{\partial T}{\partial r} = -\frac{\alpha_w}{\lambda_{er}}(T_R - T_w) \quad \text{at } r=R_t$$

The term for effective transport in the axial direction has been neglected in this model. Mears (1971) also introduced criteria to determine whether radial dispersion might be superimposed. The following criteria must be met in order to use a one dimensional model and neglect radial dispersion:

$$\left| \frac{-\Delta H_r \cdot r_{eff}^* d_t^2}{\lambda_r T_w} \right| \cdot Ar < \frac{1.6}{1 + \frac{8}{Bi_w}} \quad [14]$$

2.6.2.3 One-Dimensional Heterogeneous Model Accounting for Interfacial Gradients

Up until now the homogeneous models have made no distinction between the fluid phase and the solid catalyst pellet. For rapid reactions where heat effects are considered important, it is necessary to distinguish between the conditions of the fluid and at the catalyst particle surface. The steady-state equations for energy and mass for both the fluid and the solid state are given as (Froment, 1979):

Fluid:

$$-u_s \rho_g c_p \frac{dC}{dz} = k_m a_v (C - C_s^s) \quad [15]$$

And

$$u_s \rho_g c_p \frac{dT}{dz} = h_{fs} a_v (T_s^s - T) - 4 \frac{U}{d_t} (T - T_r) \quad [16]$$

Solid:

$$\rho_B r_A = k_m a_v (C - C_s^s) \quad [17]$$

$$(-\Delta H) \rho_B r_A = h_{fs} a_v (T_s^s - T) \quad [18]$$

With the necessary boundary conditions:

$$C = C_0 \quad \text{and} \quad T = T_0 \quad \text{at } z=0$$

Mears (1971) proposed a criterion for detecting the onset of inter-phase temperature and concentration gradients. The criteria are as follows:

$$\text{Interfacial temperature} \left| \frac{(-\Delta H_r) \rho_B r_{eff} d_p}{2h_s T_0} \right| Ar < 0.15 \quad [19]$$

$$\text{Interfacial concentration} \left| \frac{r_{eff} d_p}{2C_{A0} k_s} \right| < \frac{0.15}{n} \quad [20]$$

2.6.2.4 One-Dimensional Heterogeneous Model Accounting for Intra-Particle Gradients

The reaction rate will not be uniform throughout the catalyst particle when the resistance to mass transfer and heat transfer in the catalyst particle is important. The model equations at steady-state accounting for the resistance to heat and mass transfer through the particle for cylindrical dimensions are given as (Froment, 1979):

Fluid:

$$-u_s \frac{dC}{dz} = k_m a_v (C - C_s^s) \quad [21]$$

$$u_s \rho_g c_p \frac{dT}{dz} = h_s a_v (T_s^s - T) - 4 \frac{U}{d_t} (T - T_r) \quad [22]$$

Solid:

$$\frac{D_{eff,m}}{\zeta'^2} \frac{d}{d\zeta'} \left(\zeta'^2 \frac{dC_s}{d\zeta'} \right) - \rho_s r_A(C_s, T_s) = 0 \quad [23]$$

$$\frac{\lambda_{e,s}}{\zeta'^2} \frac{d}{d\zeta'} \left(\zeta'^2 \frac{dT_s}{d\zeta'} \right) + \rho_s (-\Delta H) r_A(C_s, T_s) = 0 \quad [24]$$

Boundary conditions

$$C = C_0 \text{ and } T = T_0 \quad \text{at } z=0$$

$$\frac{dC_s}{d\zeta'} = \frac{dT_s}{d\zeta'} = 0 \quad \text{at } \zeta' = 0$$

$$-D_{eff,m} \frac{dC_s}{d\zeta'} = k_m (C_s^s - C) \quad \text{at} \quad \zeta' = \frac{d_p}{2} \quad \text{together with} \quad -\lambda_{e,s} \frac{dT_s}{d\zeta'} = h_{fs} (T_s^s - T) \quad \text{at} \quad \zeta' = \frac{d_p}{2}$$

In order to take the gradients inside of the catalyst into consideration, Mears (1971) proposed a criterion to establish if this model is applicable. The criterion is as follows:

$$Da_{II} |n - Ar.P_t| < 1 \quad [25]$$

2.6.2.5 Modelling Approach

The homogeneous, together with heterogeneous reactor models, may become confusing, especially when using the criteria to determine the applicability of the specific model. Jakobsen (2011) compiled a summary of all the tests with their specific models. The following figure shows a summary of the tests to determine the applicability of the respective reactor models.

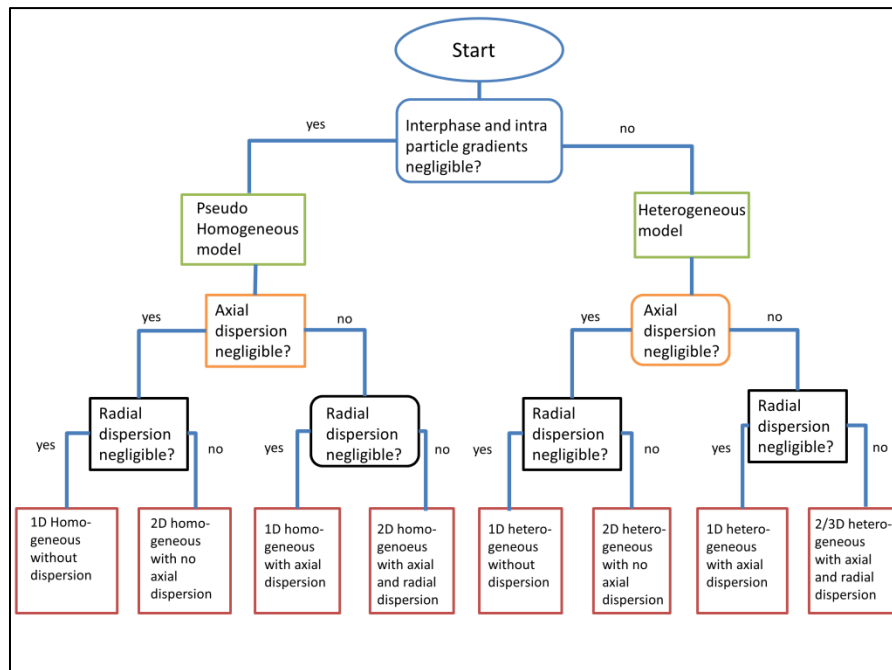


Figure 2-2: Proposed flowchart to choose an appropriate reactor model

The difference between homogenous and heterogeneous models is determined by the influence of inter-phase and intra-particle transport. If none of this transport is applicable, the system can be described as a homogeneous system. The specific system under consideration can be refined by determining whether axial and/or radial dispersion is evident in the system. The criteria of Mears, as

described in reactor models of Froment & Bischoff (1979), are used to answer these questions. The appropriate reactor model can be sufficiently chosen by using this method.

2.6.3 Heat Transfer

2.6.3.1 *Effective Radial Thermal Conductivity*

The effective thermal conductivity in a packed bed can be seen as a lumped parameter consisting of mainly three components (Bauer, 1990):

$$k_{bed} = k_{eff} + k_{f,eff} + k_{s,eff} \quad [26]$$

The first component is the effective thermal conductivity in the wall, near wall and bulk region. This component is a combination of various mechanisms:

- Conduction through solid
- Conduction through contact area between adjacent spheres accounting for sphere roughness
- Conduction through the stagnant fluid/gas phase
- Thermal radiation between touching and non-touching solid surfaces
- Conduction between spheres and wall interface
- Conduction through the gas phase in the wall region
- Thermal radiation between spheres touching and not touching the wall interface

These effects are applicable to spheres as well as cylindrical particles. The second component in Equation 26 is the enhanced fluid effective thermal conductivity, $k_{f,eff}$, due to turbulent mixing of fluid in the void spaces between stationary particles. The third component, $k_{s,eff}$, is when the gas-fluid phase is in motion due to vibrations, etc. For this study the third component is not applicable. When using non-spherical particles the effective particle diameter can be calculated as the diameter of a sphere that has the same surface area or volume. The volume particle diameter is given in Appendix A.

Chapter 2: Literature Survey

The effective thermal conductivity is usually presented in a dimensionless form, and as stated earlier in this study, the movement of particles will not influence the thermal conductivity, as the packed bed is stagnant. When representing the effective thermal conductivity in dimensionless form (Appendix A) the initial Peclet number divided by the infinite Peclet number represents the thermal conductivity due to fluid convection and dispersion (Koning, 2002), (Agnew, 1970), (Olbrich, 1972). The Peclet number for radial mass transfer in packings of spherical particles was derived by Fahien & Smith (1955) and further refined for spheres, cylinders and Raschigh rings by Spechia et al. 1980 (Appendix A).

Van Antwerpen (2009) distinguished and explained the various models available in literature to predict the effective thermal conductivity and tabulated these models for simplification. A simplified table of these various models including solid and fluid effective thermal conductivity, is given in Appendix A. Most of the models in Appendix A do not take radiation into account nor contact area and/or roughness. Hsu et al. (1994:2751) and Bahrami et al. (2006:3691) showed semi-empirical correlations for two and three dimensional structures, respectively. Kaviany (1991:127) presented a two-dimensional model which was only applicable in certain porosity ranges. The models by Hsu et al. (1994:2751), Bahrami et al. (2006:3691) and Kaviany (1991:127) accounted for contact area and Bahrami et al. (2006:3691) included surface roughness. These models, however, do not account for radiation effect in between the particles. The model of Bauer & Schlünder (1978:189) will be utilized in the bulk region as it is a two-dimensional semi empirical correlation accounting for radiation between particles. The radiation effective thermal conductivity is of great importance especially in Packed Bed Reactors (PBRs) to effectively describe the mechanism of decay heat removal. In high temperature packed bed applications radiation effective thermal conductivity will have an influence on the system, but not so detrimental that separate models are needed. The model of Bauer & Schlünder (1978:189) which includes radiation will be sufficient. Van Antwerpen (2009) gives a thorough literature review on effective radiation thermal conductivity.

Because of the variation in porosity, especially in the wall region of a packed bed, different correlations must be derived to describe that region. The velocity at the wall region is lower than in the bulk because of the larger void volumes and in turn causes a lower Reynolds number and lower heat transfer. Yagi & Kunii (1961:760), Robold (1982:1) and Tsotsas (2002) proposed semi-empirical correlations for

the wall region which include radiation effects. In addition to the models mentioned Yagi & Kunii (1959) proposed a model that lumped together conduction through the solid and fluid as well as radiation. The last model worth mentioning is from Dixon & Cresswell (1979) in which the overall effective radial thermal conductivity is used specifically in pseudo-homogeneous models (Appendix A). All of these models include some kind of discrepancy because of the difficulty in predicting the porosity at the wall. Although various correlations exist to predict the effective thermal conductivity for a packed bed the heat transfer parameters depend on the experimental procedure, as well as the calculation method, as they are developed for specific particle size, geometry, packing structure, etc. Rather than to compare various correlations care must be taken to select a correlation which has the most characteristics applicable to the setup under investigation.

2.6.3.2 *Effective Axial Thermal Conductivity*

Effective axial thermal conductivity usually does not play a significant role in the overall heat transport mechanism in a packed bed. Criteria established by Mears (1971) will determine whether axial dispersion is important to be included in the reactor models. Votruba et al. (1972) proposed an empirical correlation for the Peclet number for heat dispersion in the axial direction for packings of spheres and rings. Dixon & Cresswell (1979) derived a model similar to the effective radial thermal conductivity for the axial direction (Appendix A). If the axial dispersion is important in the reactor modelling the model predicted by Dixon & Cresswell (1979) will be implemented.

2.6.3.3 *Wall Thermal Conductivity*

The effective thermal conductivity in the wall region is one of the most difficult parameters to estimate because of the variation in porosity, and in turn variation of fluid velocity. Empirical correlations that are commonly referred to in literature include the work by Li & Finlayson (1977), Dixon & Paterson (1978) and Martin & Niles (1993). In the following works, authors attempted to provide some theoretical background for the experimental correlations for wall heat transfer coefficient: Specchia et al. (1979), Hennecke and Shlunder (1973), Dixon and Cresswell (1979). Koning (2002) did not use correlations in literature but assumed that α_w increased with fluid flow rate according to a power function. The correlations from the above-mentioned authors will be presented in Appendix A.

2.6.3.4 *Fluid to Particle Heat and Mass Transfer*

There are many variables that may influence the modelling of a packed bed system, especially when solving the heterogeneous reactor models. Some of the most important parameters when doing reactor modelling are the fluid-to-particle heat and mass transfer. Heat and mass transfer may be a rate limiting factor in heterogeneous catalytic reactions. Koning (2002) states that the literature data on fluid-to-particle heat and mass transfer is quite consistent for Re larger than 500, but at lower Re numbers large differences can be observed due to flow maldistribution, axial dispersion or incorrect prediction of the radial concentration profile (Rexwinkel, 1997). In many cases the mechanisms of heat and mass transfer are similar and the Chilton-Colburn analogy is often used (Westerterp, 1984). Mass transfer coefficients in packed beds of spheres with flowing liquid and gas were determined by Theones and Kramers (1958). In the work done by Koning (2002) he utilized the correlations from Gnielinski (1982), which was derived using the most extensive set of experimental data. Gnielinski (1982) made a thorough investigation of available literature data on gas and liquid heat and mass transfer in packed beds of spheres, cylinders and Raschig rings. Iordanidis (2002) summarized some empirical correlations for heat and mass transfer in a packed bed. The correlations of Gnielinski (1982) and Martin & Niles (1978), as well as Bird et al. (1960) for fluid-particle heat transfer can be utilized. These correlations also hold for mass transfer when Pr and Nu are replaced by Sc and Sh numbers. Empirical correlations for heat and mass transfer by the authors mentioned above can be found in Appendix A.

2.6.3.5 *Axial and Radial Mass Dispersion*

The effects of radial and axial dispersion of heat and mass can have a significant effect on the performance of a packed bed reactor, especially where concentration and temperature gradients become large (Mears, 1971). In gases the molecular diffusivity is several orders larger than molecular diffusion and thus the effective diffusivity is determined by convective mixing as well as molecular diffusion. The dispersion of mass is similar to the dispersion of heat if transport through the solid phase is negligible and in literature these effects, especially at low Reynolds number, have been investigated to a large extent. It has been found that for tubular reactors with large aspect ratios and Reynolds number between 300 and 400 empirical correlations for axial dispersion agree quite well (Koning, 2002). Axial dispersion of heat and mass is usually not a significant factor when compared to radial dispersion of heat and mass. The most recommended value for axial dispersion is a value of $Pe_{m,ax} = 2$ (Koning,

2002). Another good approximation for the flow-dependent part of radial mass dispersion is to take the Peclet number for the radial mass dispersion as equal to that for radial heat dispersion.

2.6.4 Advanced Reaction Modelling

The reaction modelling approaches followed in literature (Froment, 1979) to describe a chemical packed bed ranging from a basic homogenous to a more advanced heterogeneous model was the basis for the modelling approach followed in this study. The heat transfer in a packed bed was described and is equally as important to solve the reaction equations. However in this study a more advanced approach was followed where a heterogeneous reactor model was solved by incorporating the capabilities of Computational Fluid Dynamics to account for advanced fluid flow (Discard plug flow assumption), heat and mass transfer effects without the necessity of using empirical correlations. The two dimensional heterogeneous reactor model was applied in this study where axial and radial transport mechanisms was incorporated. The next section provides a discussion on CFD modelling and the capabilities from literature with regards the reaction modelling.

2.6.5 Modelling

2.6.5.1 Computational Fluid Dynamics

Computational Fluid Dynamics simulations are increasing in the field of reaction engineering and have been recognized and developed as a robust tool for obtaining detailed flow and scalar transport information in packed beds or segments thereof (Dixon, 2008). With the capabilities of CFD it is possible to gain detailed information on flow processes and heat-and-mass transfer processes (Taskin, 2007). CFD involves the numerical solution of conservation equations for mass, momentum and energy in the flow geometry of interest, with capability of additional equations describing the specific problem (Taskin, 2007). Typical CFD codes use one of three discretization methods namely the finite difference method (FDM), the finite volume method (FVM) and the finite element method (FEM). In these methods the geometry is divided into a large number of cells (control volumes or elements) in which a discrete representation of the relevant conservation equations is made, after which an iterative solution procedure is invoked to obtain the solution of the non-linear equations. Figure 2-3 gives an illustration of the mesh or elements generated for a typical catalyst particle in this project.

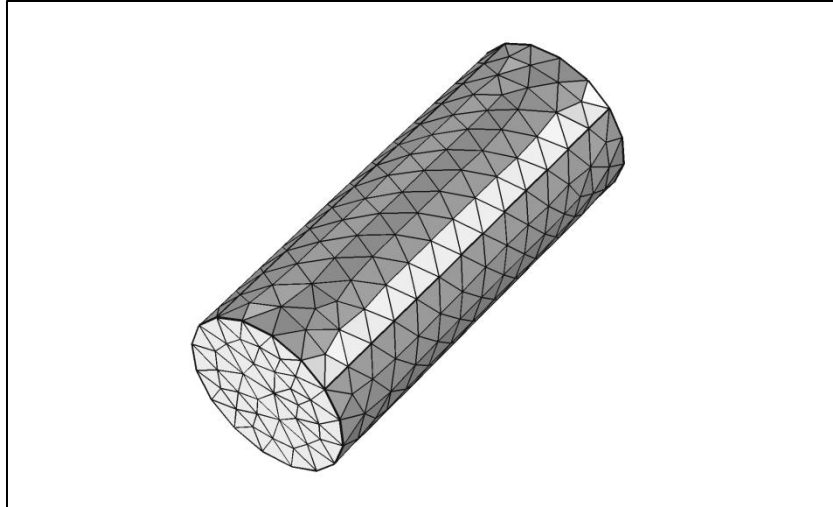


Figure 2-3: Discretization of geometry in COMSOL MultiPhysics® 4.3b

One of the earliest CFD simulations was done by Dalman et al. (1986) who used a two-dimensional model to investigate the flow behaviour in an axisymmetric radial plane. During this limited study the difference in flow patterns with their respective eddies forming between particles cause problems with heat transfer as Reynolds numbers change. In the work of Stewart et al. (1991) the fluid phase of a packed bed was investigated for laminar and turbulent flow with the assumption that the mass and energy conservation equations were linear. Parsons and Porter (1992) described a numerical technique for modelling a three-dimensional single phase gas flow with specific reference to implement a vectorial form of the Ergun equation. A 3-sphere model was evaluated in 3D CFD to obtain modelling parameters such as Nu_w by Dixon & Derkx (1996). The three sphere model was improved by an 8-sphere model with an aspect ratio of $N=2.43$ (Logtenberg and Dixon, 1998a). The results from the 8-sphere model matched data from literature reasonably well. Improving on the 8 sphere model, Logtenberg et al. (1999) evaluated a 10-sphere model including contact points between particles and wall.

Simulating a 3D packed bed system in CFD the true nature of a system can be replicated and specifically in the wall region, which varies drastically because of the variation on void fraction (compact at centre with large open spaces at the wall). Further improvement to the CFD simulations were made by Dixon & Nijemeisland (2001) who developed a model consisting of 44-spheres with $N=2$. The CFD results were validated with experimental data by comparing radial temperature profiles. All the simulations did by Dixon and co-authors were conducted in ANSYS (Fluent) with mesh generating software GAMBIT. With

these simulations they showed that with the necessary limitations and considerations taken into account that quantitative and qualitative agreement between experiments and CFD were obtained. Comparing experimental results with CFD simulations on CFX-5.3 Callis et al. (2001) found that the pressure drop from the CFD simulations was within 10% error. Romkes et al. (2003) developed a CFD modelling technique with the aim of finding mass and heat transfer characteristics for a composite catalytic reactor packing and determined whether CFD could be used to develop simple engineering correlations for this type of reactor. Three different turbulent models were evaluated and they found that the RNG k-e model gave better heat transfer predictions of experimental data. Certain heat transfer correlations gave results within 10% of experimental data and mass transfer correlations were found to be within 15%.

In further work Dixon et al. (2003) completed a study on a 120° wall segment for a steam reforming process. Fluent was utilized as CFD package for evaluation of cylindrical and spherical particles. The kinetics of steam reforming was modelled with consideration of thermal effects of reaction which were represented by inclusion of temperature dependent heat sinks in solid particles. As was the case with previous studies the results seemed physically reasonable to the authors. To investigate the influence of the turbulence model in CFD modelling of wall to fluid heat transfer in packed beds, Guardo et al. (2005) used Fluent 6.0 with a variety of turbulence models. They found that all the models showed good agreement with the Ergun equation with the Spalart-Allmaras being slightly superior. Using a unit cell approach Gunjal et al. (2005) studied different packing arrangements of spheres using GAMBIT 2.0 mesh generating software and FLUENT 6.1.18 CFD software. Overall results were satisfactory against experimental data except for low Reynolds numbers. Taskin (2007) did simulations for steam reforming where intra-particle reaction and gradients were resolved for the wall section with porous packing. The physics inside of the particle which included conduction, species diffusion and reaction were coupled to realistic 3D flow and temperature patterns. In the study by Taskin (2007) a thorough layout of progress that CFD has made up to the present, can be observed with only some of the work mentioned in the paragraphs above. CFD simulations have been validated against experimental work in terms of heat transfer.

The commercial CFD software code FEMLAB from MATLAB was used to do some heat transfer validations at Iran University of Science and Technology. Ahmadi Motlagh and Hashemabadi (2008a) investigated two and three-dimensional CFD modelling of heat transfer from cylindrical particles in different orientations. Experimental data from literature papers and experimental correlations showed good quantitative and qualitative agreement between the two. The same authors also investigated the heat transfer in a bed of cylinders with an aspect ratio of 2. The k-e turbulent model was used to describe the system in which naphthalene sublimation mass transfer experiments were carried out (Ahmadi Motlagh, 2008). Nusselt numbers were obtained for each particle inside the bed and it was shown that CFD simulations could predict heat transfer characteristics with an acceptable average error compared to experimental results. Mirhashemi and Hashemabadi (2012) did similar naphthalene sublimation experiments with different aspect ratios for a single cylindrical catalyst particle. A CFD-based correlation was proposed to consider the wall effects on the particle, which gave an average error of 2.19%. Mirhashemi and Hashemabadi (2012) evaluated the flow and heat transfer characteristics of regularly arranged cylindrical particles. The k-e turbulent model used in FEMLAB (MATLAB) gave a good quantitative and qualitative agreement between the CFD model and experimental results from naphthalene experiments. From the above-mentioned authors it can be concluded that FEM can be successfully used for CFD simulations and more precisely to investigate and predict the heat transfer effects inside the reactor system. For the purposes of CFD simulations the Navier Stokes (momentum) equation is utilized:

$$\rho_f ((u \cdot \nabla) u) = \nabla \cdot \left[-PI + \mu_f (\nabla u + (\nabla u)^T) - \frac{2}{3} \mu_f (\nabla \cdot u) I \right] \quad [27]$$

To conduct a more thorough investigation and compare heat transfer in the packed bed the turbulent flow patterns may also be investigated. This requires an advanced turbulence model to be implemented in the simulation to describe eddies in high turbulent flow. Turbulence can be considered as high frequency fluctuations of transport quantities and can be considered to be computationally very expensive. Therefore, a separate model consisting of several equations must be implemented to meet this challenge. To transform the Navier Stokes equation two methods have been developed, which are known as the Reynolds averaging (RANS) and Large-Eddy simulation (LES) models (Taskin, 2007). For practical engineering calculations the RANS approach is often used with one of the following models; Spalart-Allmaras; κ - ϵ and its variants: κ - ω and its variants; and Reynolds Stress Model (RSM). The

Renormalization Group based κ - ϵ turbulence model is usually applied to more complex flow but not available in COMSOL Multiphysics.

2.6.5.2 Randomly Packed Bed Generation

With the progress in computational abilities the effects of heat and mass transfer in a packed bed can be simulated with great accuracy, as discussed in the sections above. A great obstacle in simulations with CFD is the geometry of the bed under consideration. Various authors have used a section of a packed bed or used only a certain number of particles to reduce computational effort as well as geometrical constraint. Various authors reported algorithms which were utilized to generate randomly packed beds of particles of mostly spheres and cylinders; Nolan & Kavanagh (1995) reported an algorithm to model random close and loose packings comprised of cylindrical, bean and nail shaped particles. The computer simulated and experimental values of the packing density for random close packing compared excellently with each other; Nandakumar et al. (1999) developed an algorithm using computational geometry and collision-detection algorithms to analyse and predict the geometrical properties of a randomly packed structure using packing objects of arbitrary structure; Freund et al. (2003) implemented a Monte-Carlo process imitating the physical process of filling a tube with particles based on an algorithm from literature. In the study they found that the packing structure has a significant effect on the global fluid dynamics of the system and emphasized the necessity of CFD when comparing local flow velocities to averaged values.

Another algorithm was proposed by Salvat et al. (2005) to simulate a packed bed of mono-sized spheres in a cylindrical container. The algorithm employed a soft sphere algorithm with gravity and contact force between particles included. This algorithm also provided detailed information about the packing structure so that it could be used to evaluate local and global properties. Simulations compared satisfactorily with data. Meuller et al. (2005) developed an approach to pack spheres in cylinders using a numerical algorithm. The results obtained from the algorithm are highly accurate for mean and radial porosity compared against experimental data. The algorithms mentioned above are the few available in literature, but as the outcomes of this study do not include development or implementation of such algorithms, other means of generating a packed bed were investigated. Others means of getting

accurate packed bed geometry includes Magnetic resonance imaging coupled with image-based meshing, rapid prototyping and Monte-Carlo and CAD-based approaches.

In the study by Bai et al. (2009) the discrete element method (DEM) was coupled with CFD to model a fixed bed reactor with low aspect ratio. Laboratory experiments included particle packings of up to 150, while plant scale experiment packing structures were increased to 1 500 particles to do CFD simulations. The commercial DEM software PFC^{3D} was utilized to generate the randomly packed bed while CFD simulations were conducted in Fluent. Predicted pressure drops correlated to within 10% with data from industrial reactors. Baker (2010) used the code Macropac, which utilizes a Monte Carlo approach, to generate geometry of 160 spherical particles in a column with aspect an ratio of 7.14. CFD simulations were carried out for air flow over this geometry to verify theoretical predictions versus experimental data. The pressure drop over the column generated in CFD correlated very well with experimental data and equation reported in literature.

In the first study by Caulkin et al. (2006) the software code DigiPac™ was used to simulate and evaluate the packing structure of mono, binary and ternary mixtures of spherical particles. Although results compared well with experimental data, the study by Caulkin et al. (2009) on cylindrical particles is of more importance. In the study mentioned above they showed that the code DigiPac™ could be used to predict beds of random cylindrical particles with the capability of predicting bulk and local voidage with a reasonable degree of accuracy. The computer codes discussed above are all quite accurate in predicting voidage of randomly packed beds of spheres and/or cylinders. The digital algorithm DigiPac™ was utilized in this study to generate a randomly packed bed of cylindrical particles varying in size.

2.6.5.3 COMSOL Multiphysics® 4.3b

The software code COMSOL Multiphysics® 4.3b was utilized in this study due to capabilities of solving PDE on 1 to 3D geometries numerically. Although other software codes like ANSYS Fluent, Open Foam and Star CCM+ may be used to serve the same function, COMSOL Multiphysics was chosen due to flow conditions being laminar without the need to solve turbulent flow. COMSOL Multiphysics® 4.3b uses the FEM analysis together with adaptive meshing and error control using a series of numerical solvers.

COMSOL provides the ability to solve 2nd order, 2D and 3D partial differential equations numerically without the need to write script. The program has the option of defining your own partial differential equations in three ways, namely coefficient form, general form and weak form. COMSOL also has the option of different physics modules which can be added and include pre-defined equations in that field of study. The governing Partial Differential equations are solved in integral form. The following procedure can be implemented in COMSOL:

- Create geometry in the specified dimensions or import geometry from SolidWorks® (2 or 3D)
- Define PDEs on the geometry with the necessary boundary conditions
- Divide domain into discrete control elements i.e. generate a mesh over the domains
- Ensure the governing equations are fully coupled
- Choose the solver method i.e. Direct or segregated
- Solve system

COMSOL has the same capabilities as the more general code, ANSYS Fluent, with the advantage that an additional code, i.e. Gambit, is not required to generate a mesh and that there is no need to write script to evaluate the reaction with regard to heat and mass transfer between fluid and solid phase. The main difference between COMSOL (FEM) and Fluent (FVM) is that Fluent is mainly implemented for purely fluid dynamics whereas COMSOL covers a wider range of applicability. The author did not compare these two software programs with computational time in mind. When comparing ANSYS Fluent to COMSOL Multiphysics the main purpose of each code is as follows: ANSYS Fluent was developed mainly for fluid dynamic purposes, therefore a variety of turbulent models can be found to solve a system. COMSOL, on the other hand, was developed as a numerical tool to solve PDEs in chemical reactor theory, with the initial code called FEMLAB. By changing the name to COMSOL Multiphysics and including more physics, turbulent models for fluid dynamics were included, but with limitations. The PARDISO solver, mostly utilized in this study, is based on a Level-3 BLAS update where a combination of left-looking and right-looking techniques are utilized. PARDISO is multithreaded on platforms that support multithreading (COMSOL, 2013). For further details surrounding the solver algorithms as utilised the reader is referred to the COMSOL MultiPhysics (2013) reference manual.

2.7 Chemistry of SO₂ in H₂O/H₂SO₄

The analysis of the sulphur trioxide decomposition reaction is of significant importance since the component to be measured may influence the results. Investigations into the solubility of SO₂ in H₂O and, furthermore, H₂SO₄/H₂O solution started early in the 20th century. Some of the earliest work was done by Miles & Fenton (1919) when they evaluated the amount of SO₂ that dissolved at 20°C for an acid concentration range between 55 and 100 wt%. Sherwood (1925) investigated the solubility of SO₂ in water for the temperature range of 0-50°C and various partial pressures of SO₂. Beushlein and Simenson (1940) extended the work done by Sherwood by increasing the partial pressure and temperature range. Another variation in this study field was by Miles and Carson (1946) who investigated the solubility of SO₂ at 20°C for various concentrations of SO₃ in H₂SO₄, to form oleum. In more recent work Hayduk et al. (1988) investigated the solubility of SO₂ in 97 wt% sulphuric acid, at temperatures of 298 and 323 K with variations in partial pressure. Govindarao & Gopalakrishna (1993) presented a simplified model to predict the solubility of SO₂ at low concentration in diluted sulphuric acid. Experimental work at high concentration enabled evaluation of Henry's constant for different temperatures. The study from Zhang et al. (1998) investigated acid concentration in the range of 60-96 wt%, temperatures of 298; 383; 393 K at different partial pressures for SO₂. They determined Henry's constants with the dependence on temperature. A correlation was presented that was able to accurately predict the solubility of SO₂. It was also reported that sulphuric acid solutions contain molecular and ionic forms as follows:



Due to the fact that H₂SO₃ or sulphurous acid has not been verified to exist under earth conditions (Townsend, 2012) it is most likely that the SO₂.H₂O combination will take on an ionic form.