Chapter 1: Introduction

1.1 Background and Motivation

The world energy crisis, together with climate change issues, is driving the population towards using more renewable, sustainable clean fuels. The International Energy Administration predicts an increase in energy consumption of more than 53% from 2008 until 2035 (Geagla, 2013). Figure 1-1 shows that developed countries, or countries that fall under the umbrella of the so-called Organization for Economic Corporation and Development (OECD), do not show such a large predicted increase in energy consumption. On the other hand, developing countries (shown in red) are responsible for the largest projected increase. The fossil fuels that must sustain this increase in demand are projected to be depleted in approximately 200 years’ time. It is also these fossil fuels that are responsible for emitting most of the CO$_2$ into the environment, and have been identified as the chief cause of noticeable climate changes. These CO$_2$ emissions are projected to increase by a staggering 42% from 2008 to 2035.

![Figure 1-1: Projected world energy consumption (quadrillion Btu) (Geagla, 2013)](image-url)
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The major sources of energy (eventually causing CO$_2$ pollution) are coal, oil and natural gas. Figure 1-2 shows the predicted increase in consumption of these energy sources from 1990 until 2035.

![Figure 1-2: World energy consumption by source produced (Geagla, 2013)](image)

It is clear that the ever increasing demand for energy and the reliance on fossil fuels are unsustainable (Geagla, 2013). This has led researchers in the energy sector to focus their efforts on finding renewable and sustainable energy sources. Some sources that have generated interest include solar panels, wind turbines, hydro-electricity and the most sustainable source of them all, nuclear. An energy vector that has long been touted as being a viable energy option is hydrogen. Hydrogen is produced at a rate of 70 million tons per annum (2009) using various non-sustainable techniques with a increase in demand at a rate of 7% per annum (Association, 2010). The different fossil sources utilized to produce electricity and in turn hydrogen include natural gas, oil, coal and water electrolysis (Association, 2007). The two main processes consuming hydrogen are the upgrading of heavy crude oils and tar sands together with the production of ammonia fertilizer (Dincer, 2012). The processes used to produce hydrogen include steam reforming of natural gas, gasification or partial oxidation of coal or heavy hydrocarbons, biomass gasification, water splitting and smaller scale applications. These small scale applications consist of water electrolysis with wind/solar, photo-electrochemical and photo-biological generation (Summers, 2012) (Dincer, 2012). These processes however are not free of CO$_2$ emissions and are highly energy...
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intensive (Geagla, 2013). Figure 1-3 gives a representation of the relative production of hydrogen per industrial process, as well as the world wide hydrogen consumption and applications (Summers, 2012).

![Figure 1-3: A: Energy sources of hydrogen; B: Worldwide hydrogen usage and application](image)

Figure 1-3 shows that the current sources used to produce hydrogen, as well as the application of the hydrogen in the current economy, do not include hydrogen being introduced as source for fuel application. Therefore, it is necessary to develop the hydrogen infrastructure to accommodate this demand. The main advantage that H₂ has, is that it can be used effectively as an energy carrier (Dincer, 2012). Unlike electrical power, hydrogen produced can be stored and utilized when needed. Sectors in the economy that will be influenced by a hydrogen economy are electricity generation (fuel cells), cogeneration, industry and transportation (fuel cells). Figure 1-4 is a graphical illustration of the H₂ economy influencing the sectors mentioned above.

![Figure 1-4: Integrated renewable energy grid incorporated with a hydrogen economy](image)
While there are challenges in constructing a safe and effective hydrogen infrastructure, it is interesting to note that there are already 70 hydrogen filling stations operating in the USA (Summers, 2012). A promising way forward seems to be the implementation of electrolysers (Alkaline, Proton Exchange Membrane (PEM) and SO₂) to produce hydrogen instantaneously, to be converted in fuel cells to generate electricity when needed. A review by Dincer (2012) provides a comprehensive layout of the various paths for the generation of “green” hydrogen, as well as the sources required by the different methods. Various methods are being investigated for water electrolysis (Summers, 2012) (Dincer, 2012). This study focuses on a section of a thermochemical cycle involving sulphur dioxide electrolysis.

During the 1980s over 200 distinct thermo-chemical cycles were considered by the Gas Research Institute (Carty, 1981). The most promising of these cycles were identified as the Hybrid Sulphur (HyS) and Sulphur Iodine (SI) cycles. The HyS cycle investigated in this study requires a high temperature heat source to drive the decomposition reaction, as well as an electrical source to drive the sulphur dioxide electrolyser unit. Typical heat sources identified include High Temperature Gas cooled nuclear Reactors or to use solar energy as a heat source (Dincer, 2012). Several groups, such as General Atomics, have investigated the thermal decomposition of sulphuric acid using solar reactors. A concept process, known as CRISTINA, to use air as an energy vector was introduced in 1980 by Joint Research Centre, Ispra (Thomey, 2012). Corrosion to the reactor was highly reduced but this required additional effort to separate air from products. A concept to use sand, heated from solar concentrators, was introduced by Kolb et al. (2007) as heating media for the decomposition reactor. Other investigations by Japan Atomic Energy Agency proposed using the heat generated by a High Temperature Gas cooled Reactor (Nakajima, 1999). Various investigations by countries like Germany, USA (SNL, INL), Japan and other European Union countries have contributed largely to the development of thermochemical cycles but due to difficulty in obtaining detail in literature on these developments, only mention is made to them.

The two cycles mentioned have one step in common, namely the decomposition of sulphur trioxide. The efficiency of the unit with regard to hydrogen production is directly proportional to the amount of sulphur dioxide produced in the sulphur trioxide decomposer. Various authors have different ideas of how the sulphur trioxide decomposer should be conceptualized and operated. Some of the typical geometries include a shell-and-tube type reactor (fixed bed) (Lin, 1983) (Gelbard, 2005), a compact heat
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exchanger type (Kim, 2008), a plate type heat exchanger and a bayonet type heat exchanger (Nagarajan, 2009). Although various authors suggested conceptual designs, limited experimental data is available in literature. The H$_2$SO$_4$/SO$_3$ decomposition section still requires in-depth research in order to reach pilot plant operation scale.

Up to date the kinetics for the sulphur trioxide decomposition process has been evaluated for a 1 wt% Pt/Al$_2$O$_3$, proprietary catalysts from Westinghouse and Fe$_2$O$_3$ (Spewock, 1976; Ishikawa, 1982). Although various catalysts and combinations of catalysts have been evaluated, none have been identified as a suitable candidate that is highly active and stable for an extensive time. The PGMs on TiO$_2$ support catalyst have been identified as being an active catalyst for the reaction; however, a stable PGM combination should be obtained that does not deactivate during operation (Ginosar, 2007). Up to date no study has evaluated the kinetics of the catalyst for the specific reaction, obtained reactor data or modelled the system with the obtained kinetics. Some 1-D reactor models were reported in the literature to describe such a system, the most advanced being a CFD model from which accurate results were obtained (Nagarajan, 2009). Investigation of the sulphur trioxide decomposition reaction with regard to experimental work and modelling will provide insight for further large scale development of this unit.

1.2 Motivation

The increase in energy demand and supply worldwide has necessitated the implementation of alternative energy sources to reduce the load on fossil fuels. The utilization of hydrogen is an acceptable option; however, with the vast increase in demand in future more efficient production techniques needs to be developed. Various processes have been identified as being viable options for the production of hydrogen, which include the Hybrid Sulphur cycle and Sulphur Iodine cycle, both involving a sulphur trioxide decomposition reactor. This endothermic reaction can be carried out with a catalyst in a packed bed with different modes of heating, following the homogeneous decomposition of sulphuric acid. For an acceptable conversion this reaction needs to operate at high temperatures and in reactors consisting of special materials capable of handling the corrosive gases. Under these conditions it is also essential to use a thermally stable and active catalyst with suitable heating of the catalytic reactor and to use special materials of construction, to ensure prolonged operation. The evaluation of a suitable catalyst
for operation in an experimental fixed bed with special attention afforded to stable operation and modelling of the momentum, heat and mass transfer, including chemical reaction, was considered to be important and was consequently investigated.

1.3 Problem Statement

The evaluation of a non-isothermal fixed bed (laboratory scale) reactor with electrical heating for the decomposition of sulphur trioxide involving a detailed reaction kinetic study of a synthesised platinum group metal on titania catalyst, and the construction and commissioning of the reactor together with validation of an advanced reactor model constituted the problem to be studied. The modelling equations included momentum, and heat and mass transfer with chemical reaction to provide accurate predictions and understanding of the performance of the sulphur trioxide decomposition.

1.4 Objectives of the Investigation

The overall objective of the project undertaken was to evaluate the operation of a catalytic fixed bed for the decomposition of sulphur trioxide with emphasis on the catalyst properties and the modelling of the transport and chemical processes in the reactor. This study was envisaged to contribute to the development of the HyS process considered by other investigators especially with respect to detailed description and understanding of the sulphur decomposition reactor. In order to achieve this overall objective the following tasks were formulated:

(I) Identify a suitable Platinum Group Metal-based catalyst that could be used for the decomposition reaction. Use various characterization techniques to determine the properties of fresh, sintered and spent catalyst samples.

(II) Conduct experiments in a laboratory reactor under various process conditions using the chosen catalyst. Construct and operate a suitable reactor and determine the kinetics for the catalyst using appropriate procedures.

(III) Design and construct an electrically heated fixed bed reactor system for the decomposition reaction using the chosen catalyst. Conduct experiments with suitable analytical techniques to evaluate the performance of the reactor and catalyst with variations in process conditions.
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(IV) Develop a fixed bed reactor model that will be able to provide accurate predictions of the experimental results obtained from the fixed bed reactor. Propose an advanced heterogeneous model with experimental validation for the fixed bed reactor.

1.5 Scope of Study

The objectives were defined in the previous section and a specific scope was constructed to address these objectives. The study consists of seven chapters (including this one) in total to address the goals set. An illustration of the scope can be seen in Figure 1-5 as a simplified layout. The contents, issues and layout to be addressed in this study are briefly described for the various chapters as can also be seen in Figure 1-5.

Chapter 2

The study was undertaken by doing a thorough literature review of the sulphur trioxide decomposition reaction and all facets thereof. The literature survey included catalytic work, reactor work and modelling of the system. Kinetic parameters reported in literature are reported, as well as reaction rate equations. The investigation required knowledge about the heat and mass transfer effects between solid and fluid phase and thus a thorough investigation was undertaken of these mechanisms, as well as their applicability in the current system. The progress of CFD modelling in reaction engineering was discussed with mention of its applicability in the current system. The solubility of sulphur dioxide in H₂O/H₂SO₄ is of great importance in the system since the measurement of this component in experimental work may be misleading.

Chapter 3

A suitable catalyst was identified to be used in the study. In this chapter the various analysis techniques used are described, as well as the results obtained for fresh and spent samples. The following are techniques used to describe and characterize the catalyst in this chapter:

➤ Surface area and porosity
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- Metal composition
- Metal dispersion
- Dominant support phase present

Chapter 4

The following topics are discussed and investigated in this chapter to obtain the global kinetics needed in Chapter 6 for reactor modelling:

- Experiments in a micro pellet laboratory reactor to evaluate average conversion achieved for the catalyst mentioned
- Model development to obtain a CFD model that gives an accurate representation of the system and includes inter-and intra-particle effects
- Evaluate the CFD model and evaluate important physics present
- Use the finalized model together with Least Squares Objective regression to obtain pre-exponential factor and activation energy simultaneously
- Determine the accuracy of the model and kinetic parameters obtained

Chapter 5

The fixed bed reactor system for the sulphur trioxide decomposition reaction was developed and investigated by conducting a range of experimental runs under different process conditions. To successfully perform this investigation a certain approach was followed, including:

- Design and construction of fixed bed reactor system
- Investigate different sections in bed; Acid vaporizer, sulphur trioxide decomposer and condensation/analysis section
- Commission system with nitrogen and acid combinations
- Examine the effect of process variables on the performance of the catalyst bed
- Conduct mass balance and product analysis
Figure 1-5: Scope of study
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Chapter 6

The fixed bed reactor modelling linked all the different chapters. Kinetics obtained in Chapter 4, properties of catalyst in Chapter 3 and fixed bed experimental data in Chapter 5 were used to construct and validate the fixed bed reactor models. The following topics are discussed and investigated in this chapter to comply with the objectives:

- Obtain a representative geometry of fixed bed packing for heterogeneous model
- Develop advance heterogeneous model (effects of heat and mass transfer) and validate model
- Compare models as well as accuracy

Chapter 7

The results obtained in the previous chapters are summarized with the highlights of each chapter. The objectives that were initially set are evaluated and determined whether satisfactory results have been obtained. The conclusions made from the study are discussed and suggestions for further studies are made.