Chapter 7: Conclusions & Recommendations

7.1 General Conclusions
The general conclusions reached in accordance with the objectives given in Chapter 1 are as follows:

(1) A catalyst consisting of platinum and palladium supported on rutile (titania) was selected for this investigation and was characterized using standard catalytic methods, reactivity involving the determination of a reaction rate equation and performance in a fixed bed reactor. This catalyst was chosen following an extensive literature search on the evaluation of the different catalysts examined for sulphur trioxide decomposition. Since the investigation was confined to the evaluation of a fixed bed reactor it was necessary to use a catalysts in the form of a pellet.

(2) The catalyst used was prepared from a supported catalyst consisting mainly of anatase as the support followed by sintering to produce a stable rutile support. This transformation was accompanied by a 25% decrease in overall volume, decreasing metal dispersion and total surface area and an increasing metal particle size as expected. The catalyst properties after sintering were found to be suitable for the reaction as evident from the results obtained from experiments with a micro pellet reactor and a fixed bed reactor.

(3) A laboratory scale reactor (micro pellet reactor) was constructed and used to evaluate the performance and the overall reaction kinetics of cylindrical catalyst pellets. An advanced model using computational flow dynamics (CFD) was successfully developed to describe the behaviour of the reactor and for the evaluation of the reaction rate equation and associated parameters.
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(4) The activity of the sintered catalyst after reduction with hydrogen was found to be stable after six hours of operation with an acceptable activity for reactions within the temperature range of 923 to 1073 K. This temperature range was very similar to that used by other investigators for powdered catalysts which did not display the stability observed in this investigation. This result result can be attributed to the sintering at high temperatures of the prepared catalyst which generated a relatively stable structure before reduction and reaction.

(5) A reversible reaction rate was found to describe the reaction rate and an activation energy for the first order forward reaction was larger than published results for supported platinum/palladium catalysts characterized by a first order reaction. A detailed analysis of the behaviour of the reactor showed velocity, temperature and concentration profiles which were considered important for the determination of the reaction rate equation and the associated transport mechanisms.

(6) A fixed bed reactor consisting of a sulphuric acid vaporizer, a single reactor tube with the catalyst and heated with a surrounding electrical furnace was constructed and operated successfully. The condensable products were collected in a series of chilled containers and analysed using standard analytical techniques. Three process variables were investigated which included the inlet temperature, the weight hourly velocity and the residence time in order to assess the performance of the reactor and generate results for developing a model. The results obtained included the wall and reactor centreline temperature profiles and average sulphur trioxide conversion.

(7) As a result of the complexity of the chemistry and the phases present containing the products from the reactor a detailed calculation was done using vapour/liquid equilibrium with the accompanying mass balance (Aspen-Plus®) to determine the distribution of sulphur trioxide, sulphur dioxide, oxygen and steam. A mass balance was successfully completed with analysis including SO$_2$, O$_2$ and H$_2$SO$_4$.

(8) The results obtained from the fixed bed showed that a steady state (constant conversion) was obtained after approximately six hours and that it was possible to obtain sulphur trioxide conversion on the order of 76% which was within 80% of the equilibrium value for bed lengths of 400 mms with low weight hourly space velocities. The results obtained demonstrated the feasibility of the fixed bed with the catalyst synthesized for the decomposition of sulphur trioxide and provided information for further experimentation for detailed modelling suitable for optimisation. This was accordingly achieved with
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shorter beds equivalent to 100 mms with conversions up the 56% suitable for the validation of the reaction rate over the full length of the reactor.

(9) A heterogeneous model was successfully developed and solved using a commercial CFD package COMSOL Multiphysics® 4.3b with parameters obtained from theory, literature and experimentation. The experimentation included the determination of the reaction rate equation and parameters with a micro pellet reactor developed in this investigation. The modeling and solution included detailed characterization of the packing using the software code DigiPac™ and optimization of the mesh structure.

(10) The modeling was confined to a two dimensional axi-symmetrical model (cylindrical co-ordinates with radial and axial variations) with inclusion of radiation in combination with the convective term. The results obtained was found to agree with experimental results consisting of average conversions and temperature profiles for different temperatures and weight hourly space velocities.

7.2 Contributions to the Knowledge of Sulphur Trioxide Decomposition Technology

The following results are considered to be a contribution to the scientific and engineering knowledge base concerning of the development of the sulphur trioxide decomposition reactor for inclusion in the Hybrid Sulphur cycle for hydrogen production:

(1) The examination of a catalyst suitable for industrial application with particular reference to pelletized catalysts for fixed bed reactors. The composition of the catalyst (platinum and palladium on rutile) was similar to powdered catalysts evaluated previously with the exception that the support was initially mainly anatase. The catalyst was sintered at temperatures slightly above reaction conditions to ensure a stable physical structure. The evaluation of the pelletized catalyst was achieved with a micro pellets reactor with a detailed evaluation procedure involving CFD modelling.
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(2) A laboratory scale fixed bed reactor with electrical heating was designed, constructed and operated successfully which attained a steady state operation after a reasonable time after start-up with conversion close to equilibrium. The design and operating conditions were suitable for effective heat transport from the electrical furnace to the catalyst pellets to ensure stable conditions.

(3) A comprehensive CFD model was developed and validated which can be used for optimization studies involving design of pilot and industrial reactors for further development. This model included various heat transfer mechanisms inside the reactor which is also applicable to other reactors with other different types of heating.

7.3 Recommendations for Further Investigations
The following areas of research are recommended in order to supplement results obtained in this investigation and other results.

(1) The understanding of the structural and catalytic properties of the pelletized catalyst examined in this investigation in order to explain the stability and reactivity observed. The durability over very long periods of time also needs to be established on pellet scale as well as on larger fixed bed scale. Investigate other procedures to deposit PGM metal to improve effectiveness of catalyst.

(2) The development and evaluation of a fundamentally-based reaction rate equation such as the Langmuir-Hinshelwood type equations in order to improve the accuracy of modelling and evaluate in the absence of mass-transfer limiting effects.

(3) The accuracy of the CFD modelling can be improved by using a more accurate code for determination of the fixed bed structure with experimental validation and the use of a three dimensional model.

(4) The design, construction and evaluate a fixed bed pilot plant with special reference to the following:
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(4.1) Utilization of heating sources such as energy from nuclear reactors (integrated process).

(4.2) Optimization of the process using CFD with three dimensional models.

(4.3) Using operating conditions compatible with conditions proposed for the HyS process, such as feed composition, temperatures and pressures. Integration with sulphuric acid decomposition reactor.

(4.4) The materials of construction for handling the very corrosive substances present.

(5) The use of the catalyst examined in this investigation in solar reactors and others currently under investigation.