

Evaluation of a catalytic fixed bed reactor for sulphur trioxide decomposition

Barend Frederik Stander

B.Eng (Chemical Eng) (NWU), M.Eng (Nuclear Eng) (NWU)

13029355

Thesis submitted for the degree *Doctor Philosophiae* in Chemical Engineering at the Potchefstroom Campus of the North-West University

Promoter: Prof RC Everson

Co promotor: Prof HWJP Neomagus

June 2014

Declaration

Declaration

I, Barend Frederik Stander, hereby declare that the thesis entitled: “**Evaluation of a catalytic fixed bed reactor sulphur trioxide decomposition**”, submitted in fulfilment of the requirements for the degree Ph.D in chemical engineering is my own work, except where acknowledged in the text, and has not been submitted to any other tertiary institution in whole or in part.

Signed at Potchefstroom

Barend Frederik Stander

Date

Acknowledgements

Acknowledgements

There are various people who contributed to this study into being a success and the author would like to acknowledge the impact that these people made:

Project Orientated:

- Prof Ray Everson for guidance, motivation and mentorship for the duration of the study
- Prof Hein Neomagus for guidance and Fridays braai
- Prof SW Vorster for language editing of the thesis
- Stephen Roberts at UCT for assistance in catalyst manufacturing and characterization
- Christiaan Hattingh for assistance with COMSOL Multiphysics
- Dr Mike Dry for assistance with the Aspen Plus model
- Hestelle Stoppel for administration help and support when ever needed and always available for a quick chat
- Max Tietz who has been of invaluable help in the whole project
- Frikkie van der Merwe for help in changing projects, financial support and help in the project
- Jan Kroeze and Adrian Brock for assistance in the workshop and the social interaction at the Friday afternoon braai
- Ted Paarlberg for building of apparatus and dedication in helping to fix the system at any time necessary, your assistance was invaluable
- Hans Ulco de Boer for assistance with the experimental apparatus
- Eleanor de Koker and Sanet Botes for diverse reasons
- Prof. Diane Hildebrandt with help regarding interpretation of experimental results
- Louis le Grange for help and guidance with regards to CFD modelling

Personally Orientated:

- Nicolene Louw who always encouraged me and supported me through the tough times and good times. She always helped where ever possible and provided me love and attention through the difficult times. You will never realise how much it meant to me. All my love.
- My father Hennie, mother Christel, stepmother Sandra and sisters Lizel and Jolene for motivation and support and always being there for me.

Acknowledgements

- A special thanks to a great friend I made along the way, Burgert Hatttingh, we had some good times through very difficult times.
- All other family and friends for support, especially Robert and Engela Reid.
- For my friends a special thanks; Max Tietz, Altus van Zyl and Daniel Beneke.

Finally and most importantly I would like give all the glory and praise to our heavenly Father, God Almighty, for blessing me with the talents to pursue this career, as well as carrying me through the tough times and blessing me with wonderful family and friends. Without the presence and influence of our heavenly Father I would not have been able to accomplish anything.

Abstract

The world energy supply and demand, together with limited available resources have resulted in the need to develop alternative energy sources to ensure sustainable and expanding economies. Hydrogen is being considered a viable option with particular application to fuel cells. The Hybrid Sulphur cycle has been identified as a process to produce clean hydrogen (carbon free process) and can have economic benefits when coupled to nuclear reactors (High Temperature Gas Reactor) or solar heaters for the supply of the required process energy. The sulphur trioxide decomposition reactor producing sulphur dioxide for the electrolytic cells in a closed loop system has been examined, but it is clear that development with respect to a more durable active catalyst in a reactor operating under severe conditions needs to be investigated. A suitable sulphur trioxide reactor needs to operate at a high temperature with efficient heating in view of the endothermic reaction, and has to consist of special materials of construction to handle the very corrosive reactants and products. This investigation was undertaken to address (1) the synthesis, characterisation, reactivity and stability of a suitable catalyst (2), determination the reaction rate of the chosen catalyst with a suitable micro reactor (3) construction and evaluation of a packed bed reactor for the required reaction, and (4) the development and validation of a reactor model using computational fluid dynamics with associated chemical reactions.

A supported catalyst consisting of 0.5 wt% platinum and 0.5 wt% palladium on rutile (TiO_2 , titania) was prepared by the sintering of an anatase/rutile supported catalyst with the same noble metal composition, synthesized according to an incipient impregnation procedure using cylindrical porous pellets (± 1.7 mm diameter and ± 5 mm long). Characterization involving: surface area, porosity, metal composition, - dispersion, - particle size, support phase and sulphur content was carried out and it was found from reactivity determinations that the sintered catalyst, which was very different from the synthesized catalyst, had an acceptable activity and stability which was suitable for further evaluation.

A micro pellet reactor was constructed and operated and consisted of a small number of pellets (five) placed apart from each other in a two-stage quartz reactor with sulphur trioxide generated from sulphuric acid in the first stage and the conversion of sulphur trioxide in the second stage, respectively. Attention was only confined to the second stage involving the conversion of sulphur trioxide with the supported catalyst. The overall reaction kinetics of the pellets involving momentum, heat and mass transfer and chemical reaction was evaluated and validated with constants obtained from literature and with an unknown reaction rate equation for which constants were obtained by regression. As result of

Abstract

the complexity of the flow, mass and heat transfer fields in the micro pellet reactor it was necessary to use a CFD model with chemical reactions which was accomplished with a commercial code COMSOL MultiPhysics[®] 4.3b. A reversible reaction rate equation was used and a least squares regression procedure was used to evaluate the activation energy and pre-exponential factor. The activation energy obtained for the first order forward reaction was higher than values obtained from literature for a first order reaction rate (irreversible reaction) for the platinum group metals on titania catalysts. Detailed analyses of the velocity, temperature and concentration profile revealed the importance of using a complex model for determination of the reaction parameters.

A fixed bed reactor system consisting of a sulphuric acid vaporizer, a single reactor tube (1 m length, 25 mm OD) heated with a surrounding electrical furnace followed, by a series of condensers for the analysis of the products was constructed and operated. 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 together with average conversion. 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 analyses including SO₂ with a GC, O₂ with a paramagnetic cell analyser, acid/base titrations with sodium hydroxide, SO₂ titrations with iodine and measurement of condensables (mass and volume). The results obtained showed that a steady state (constant conversion) was obtained after approximately six hours and that it was possible to obtain sulphur trioxide conversion approaching equilibrium conditions for bed lengths of 100 mm with very low weight hourly space velocities.

A heterogeneous 2D model consisting of the relevant continuity, momentum, heat transfer and mass transfer and the reaction rate equation determined in this investigation was developed and solved with the use of the commercial code COMSOL MultiPhysics[®] 4.3b with an appropriate mesh structure. The geometry of the packed bed (geometry) was accomplished by generating a randomly packed bed with a commercial package DigiPac[™]. The model predicted results that agreed with experimental results with conversions up to 56%, obtained over the following ranges: weight hourly space velocity equal to 15 h⁻¹, temperatures between 903 K and 1053 K and residence times between 0.1 and 0.07 seconds. The post-

Abstract

processing results were most useful for assessing the effect of the controlling mechanisms and associated parameters.

Keywords: Sulphur Trioxide Decomposition, Supported Platinum Group Metal Catalyst, Kinetics, Packed Bed Reactor, CFD model.

Uittreksel

Uittreksel

Die wêreld-energiesituasie met betrekking tot vraag en verskaffing het 'n punt bereik waar dit nodig is om alternatiewe energiebronne te ondersoek om 'n volhoubare en groeiende ekonomie te stimuleer. Waterstof is geïdentifiseer as 'n geskikte opsie met betrekking tot waterstofselle om elektrisiteit op te wek. Die Swael-Hibriedproses is as 'n moontlike opsie geïdentifiseer om skoon waterstof (in 'n koolstof-vrye proses) te produseer en het ekonomiese voordele as dit gekoppel sou word met 'n kernreaktor (Hoëtemperatuur Gasreaktor) of sonenergie om die vereiste prosesenergie te verskaf. Die swaeltrioksiedreaktor wat swaeldioksied vir die elektrochemiese selle in 'n geslote sisteem produseer, is evalueer en dit is duidelik dat daar nog ondersoek ingestel moet word na die ontwikkeling van 'n stabiele en aktiewe katalisor en 'n reaktor wat onder uiterste prosesondisies kan funksioneer. 'n Geskikte swaeltrioksiedreaktor wat by hoë temperatuur kan funksioneer met geskikte verhitting (gegewe 'n endotermiese reaksie) moet van spesiale material gebou word wat bestand is teen die hoë korrosietempo in die reagense en produkte. Die studie is onderneem om die volgende te ondersoek: (1) die sintese, karakterisering, reaktiwiteit en stabiliteit van 'n geskikte katalisor, (2) bepaling van die reaksietempo van die gekose katalisor met behulp van 'n geskikte mikroreaktor, (3) konstruksie en evaluering van 'n gepakte bedreaktor vir die spesifieke reaksie en (4) die ontwikkeling en validasie van 'n reaktormodel met behulp van berekeningsvloei dinamiese (CFD) metodes met geassosieerde chemiese reaksies.

'n Ondersteunde katalisor wat bestaan uit 0.5 massa% platinum 0.5 massa% palladium op 'n rutiel-titania-basis is voorberei deur sintering van die spesifieke katalisor pastille wat gesintetiseer is deur uitwendige impregnering van 'n silindriese poreuse pastille (± 1.7 mm diameter en ± 5 mm lengte) met 'n edelmetaal-oplossing. Karakterisering is van die pastille gedoen, en sluit in: oppervlakarea, porositeit, metal-samestelling, -dispersie, -partikel grootte, ondersteuningsfase en swael inhoud en dit was uit reaktiwiteitseksperimente duidelik dat die gesinterde katalisor en vars katalisor baie verskil, maar eersgenoemde het aanvaarbare aktiwiteit en stabiliteit getoon, wat verdere ondersoek regverdig het.

'n Mikro-pastilreaktor is gebou, wat beperk was tot vyf katalisor pastille wat verspreid geplaas is in 'n tweestadium kwartsreaktor waar swaeltrioksied in die eerste stadium gegenereer word en saam met stikstof, wat as draergas dien, ontbind tot swaeldioksied in die tweede stadium. Alle aandag was

gefokus op die tweede stadium vir die ontbinding van swaeltrioksied met behulp van die katalisor. Die algehele reaksiekinetika van die katalisor pastille wat hitte-en-massa oordrag insluit, gepaard met chemiese reaksie, is geëvalueer en gevalideer met konstantes wat uit literatuur verkry is met 'n onbekende reaksievergelyking waarvoor parameters bepaal is met behulp van regressie. As gevolg van die gekompliseerde vloeipatrone vir snelheid, massa en hitte was dit nodig om 'n gevorderde CFD-tipe-model te gebruik met behulp van die kommersiële sagteware COMSOL MultiPhysics® 4.3b. 'n Omkeerbare reaksietempovergelyking is gebruik waarmee die aktiveringsenergie en voor-eksponensiële faktor met behulp van 'n kwadraat-regressie-metode bepaal is. Die aktiveringsenergie wat vir die platinum-groep-metale verkry is, was veel hoër as in literatuur gerapporteer, maar was van dieselfde orde as die van ysteroksied-katalisatore wat in die literatuur gerapporteer is. 'n Volledige analise is gedoen met betrekking tot snelheid-, temperatuur- en konsentrasieprofile en het die belangrikheid van die gebruik van 'n komplekse model vir die bepaling van reaksieparameters aangedui.

'n Gepakte bedreaktorsisteem wat bestaan uit 'n swaelsuurontbinder, 'n enkelbuisreaktor (1 m lengte, 25 mm buitenediameter), verhit deur 'n omliggende elektriese oond, wat gevolg is deur 'n reeks kondenseer flesses vir produkanalise, is gebou en bedryf. Drie prosesse veranderlikes is ondersoek, wat insluit: die inlaattemperatuur tot katalisor-bed, die gewig-uur-ruimte-snelheid (WHSV) en die residensityd om die vermoëns van die katalisor en sisteem te toets, sowel as om resultate te lewer vir modelleringsdoeleindes. Die resultate gegenereer sluit in buiswand-temperatuur, middelbuis-temperatuur en algehele omsetting. As gevolg van die kompleksiteit van die chemie en fases teenwoordig wat reaksieprodukte van die reaktor bevat het, is 'n Aspen Plus®-model ontwikkel om die verspreiding van swaeltrioksied, swaeldioksied, suurstof en stoom te beskryf. 'n Massabalans is suksesvol oor die sisteem gedoen met analises wat insluit: beplaings van swaeldioksied op 'n GC, suurstof op paramagnetiese sel-analiseerder, suur/basis-titrasie met natriumhidroksied, swaeldioksiedtitrasie met jodium en meting van gekondenseerde produk (massa en volume). Die resultate het getoon dat omsetting 'n van 56% by 1053 K met 'n WHSV van 15 h⁻¹ moontlik was en dat temperatuur die grootse invloed op resultate gehad het. Die resultate het aangedui dat die sisteem onder gestadigde toestande was, wat soortgelyk was aan resultate wat gevind is met die mikro-pastilreaktor sisteem.

Uitreksel

Tweefase-model wat saamgestel is uit kontinuïteit, momentum, hitte-oordrag en massa-oordrag met reaksietempovergelyking is gedurende die studie ontwikkel en opgelos met die numeriese sagtewareprogram COMSOL MultiPhysics® 4.3b, wat 'n geskikte maas insluit. Die geometrie was 'n ewekansige gepakte bed wat deur die kommersiële kode DigiPac™ gegeneer is. Die model het data voorspel vir 'n bedlengte van 100 mm en is vergelyk met die volgende prosestoestand: $WHSV = 15 \text{ h}^{-1}$, $T = 903\text{-}1053 \text{ K}$, $\tau=0.1\text{-}0.076 \text{ s}$. Die voordeel van die gebruik van 'n gevorderde heterogene reaktormodel is dat realistiese vloeipatrone en hitte-en massa-oordrag in ag geneem word.

Slutelwoorde: Swaeltrioksied-ontbinding; Platinum Groep Metaal Katalisor; Kinetika; Gepakte Bedreaktor; CFD-Model

Table of Contents

Table of Contents

Declaration.....	i
Acknowledgements.....	ii
Abstract.....	iv
Uittreksel.....	vii
Table of Contents.....	x
List of Figures	xvi
List of Tables	xxii
List of Symbols	xxiv
Glossary.....	xxx
Publications.....	xxxii
1. Chapter 1: Introduction	1
1.1 Background and Motivation	1
1.2 Motivation.....	5
1.3 Problem Statement.....	6
1.4 Objectives of the Investigation	6
1.5 Scope of Study.....	7
2. Chapter 2: Literature Survey.....	11
2.1 Introduction	11
2.2 Hydrogen Economy.....	11
2.3 Hybrid Sulphur Cycle (Hys)	13
2.4 Sulphur Trioxide Decomposition.....	14
2.5 Catalyst and Kinetics	15
2.5.1 Activity and Stability	15
2.5.2 Kinetics and Literature	17
2.5.3 Equipment used for Kinetics Evaluation	19
2.6 Fixed Bed Reactors.....	19
2.6.1 Reactor Systems in Literature	19
2.6.2 Fundamental Concepts	21

Table of Contents

2.6.2.1	One-Dimensional Pseudo-Homogeneous Model	21
2.6.2.2	Two-Dimensional Homogeneous Model Accounting for Radial Mixing	23
2.6.2.3	One-Dimensional Heterogeneous Model Accounting for Interfacial Gradients.....	24
2.6.2.4	One-Dimensional Heterogeneous Model Accounting for Intra-Particle Gradients.....	25
2.6.2.5	Modelling Approach.....	26
2.6.3	Heat Transfer	27
2.6.3.1	Effective Radial Thermal Conductivity	27
2.6.3.2	Effective Axial Thermal Conductivity	29
2.6.3.3	Wall Thermal Conductivity.....	29
2.6.3.4	Fluid to Particle Heat and Mass Transfer	30
2.6.3.5	Axial and Radial Mass Dispersion.....	30
2.6.4	Advanced Reaction Modelling	31
2.6.5	Modelling	31
2.6.5.1	Computational Fluid Dynamics	31
2.6.5.2	Randomly Packed Bed Generation	35
2.6.5.3	COMSOL Multiphysics® 4.3b.....	36
2.7	Chemistry of SO ₂ in H ₂ O/H ₂ SO ₄	38
3	Chapter 3: Catalyst Properties	39
3.1	Introduction	39
3.2	Experimental	39
3.2.1	Preparation of Catalyst	39
3.2.1.1	Fresh Catalyst.....	39
3.2.1.2	Sintered Catalyst	40
3.2.2	Analytical Methods for Characterization	41
3.2.3	Sintering of Pellets	43
3.3	Results and Discussion	44
3.3.1	Fresh Catalyst.....	44
3.3.1.1	Catalyst Support (Anatase/Rutile)	44

Table of Contents

3.3.1.2	Platinum/Palladium Loading on Anatase/Rutile Support	45
3.3.2	Sintered Catalyst	51
3.3.2.1	Sintering of Pellets	51
3.3.2.2	Platinum/Palladium Loading on Rutile Support.....	54
3.3.3	Spent Catalyst	55
3.4	Summary	59
4	Chapter 4: Catalyst Kinetics and Pellet Modelling	61
4.1	Introduction	61
4.2	Review and Motivation	61
4.3	Experimental Apparatus and Procedure	62
4.3.1	Catalyst and Properties	62
4.3.2	Laboratory Reactor and Experimental Configuration	63
4.3.3	Experimental Planning and Procedure.....	66
4.4	Reaction Rate Modelling.....	68
4.4.1	Description	68
4.4.2	Governing Equations.....	71
4.4.3	Numerical Solution and Procedure	73
4.5	Results and Discussion	74
4.5.1	Experimental Results.....	74
4.5.2	Model Evaluation	77
4.5.2.1	Mesh Independence Study	77
4.5.2.2	Pellet Model Experimental Validation	80
4.5.2.3	Numerical Solution and Kinetic Parameter Evaluation.....	82
4.5.2.4	Model Results.....	83
4.6	Sensitivity Analysis	88
4.7	Summary	90
5	Chapter 5: Fixed Bed Reactor Design, Construction and Performance	92
5.1	Introduction	92
5.2	Experimental.....	93

Table of Contents

5.2.1	Design and Layout.....	93
5.2.1.1	Acid Vaporizer	95
5.2.1.2	Sulphur Trioxide Decomposer.....	96
5.2.1.3	Condensers and Scrubbers.....	98
5.2.2	Procedure and Planning.....	100
5.2.2.1	Procedure for Start-up and Reduction.....	102
5.2.2.2	Procedure for Reaction	103
5.2.2.3	Procedure for Shut-Down	103
5.2.3	Analysis of Products	103
5.2.4	Analytical Methods	106
5.2.4.1	GC/Paramagnetic Cell	106
5.2.4.2	Acid/Base Titration.....	106
5.2.4.3	Iodine Titration	107
5.3	Results and Discussion	108
5.3.1	Process Mass Balance	108
5.3.1.1	Product Analysis Section	108
5.3.1.2	Overall Process Mass Balance.....	111
5.3.2	Analysis of Pre-Heat Section	114
5.3.3	Packed Bed with Reaction.....	118
5.3.3.1	Effect of Inlet Temperature	118
5.3.3.2	Effect of Weight Hour Space Velocity	124
5.3.3.3	Effect of Residence Time.....	130
5.3.3.4	Inlet Pressure	132
5.4	Summary	134
6	Chapter 6: Fixed Bed Reactor Modelling	136
6.1	Introduction	136
6.2	Description of Reactor Structure	136
6.3	Structure of Packing.....	137

Table of Contents

6.4	Reactor Modelling.....	142
6.4.1	Governing Equations.....	142
6.4.2	Numerical Solution and Procedure.....	146
6.5	Results and Discussion.....	147
6.5.1	Geometry Mesh.....	147
6.5.2	Packed Bed Model Results.....	147
6.6	Summary.....	158
7	Chapter 7: Conclusions & Recommendations.....	160
7.1	General Conclusions.....	160
7.2	Contributions to the Knowledge of Sulphur Trioxide Decomposition Technology.....	162
7.3	Recommendations for Further Investigations.....	163
	References.....	165
A.	Appendix A: Transport Properties Correlations.....	180
	A1: Pressure Drop.....	180
	A2: Heat Transfer Correlations.....	181
	A3: Thermal Properties.....	189
	A4: GC calibration Standard Gases.....	193
B.	Appendix B: Micro Pellet Reactor Model.....	194
	B1: Physical Properties.....	194
	B2: Particle Sizes.....	195
	B3: Supplementary CFD Results.....	198
C.	Appendix C: Porosity and Void Fraction Calculations.....	201
D.	Appendix D: Heat and Mass Transfer Criteria.....	203
	D1: Overall Particle Model.....	203
	D2: Packed Bed Model.....	206
E.	Appendix E: Thermodynamic Equilibrium Conversion.....	210
	E1: Kinetic Setup Equilibrium Conversion.....	210
	E2: Packed Bed Setup Equilibrium Conversion.....	215
F.	Appendix F: Reactor Equations.....	217
	F1: 3D Particle Model.....	217

Table of Contents

G.	Appendix G: Fixed Bed Reactor Data	219
	G1: Fixed Bed Experimental Data	219
	G2: Heterogeneous Model Data	220
H.	Appendix H: Catalyst Characteristics	222
	H1: H ₂ Chemisorption:	222
	H2: N ₂ Physisorption (BET)	226
	H3: TPR Analysis	230
	H4: TEM Images	233
	H5: XRD Results	236

List of Figures

Figure 1-1: Projected world energy consumption (quadrillion Btu) (Geagla, 2013).....	1
Figure 1-2: World energy consumption by source produced (Geagla, 2013).....	2
Figure 1-3: A: Energy sources of hydrogen; B: Worldwide hydrogen usage and application.....	3
Figure 1-4: Integrated renewable energy grid incorporated with a hydrogen economy.....	3
Figure 1-5: Scope of study.....	9
Figure 2-1: Hybrid Sulphur Cycle (PREC, 2014).....	13
Figure 2-2: Proposed flowchart to choose an appropriate reactor model.....	26
Figure 2-3: Discretization of geometry in COMSOL MultiPhysics® 4.3b.....	32
Figure 3-1: TEM images for fresh catalyst support; A: Scale of 0.2 µm; B: Scale of 100 nm.....	44
Figure 3-2: Pt-Pd/TiO ₂ (nominally 0.5 wt% each) in catalyst pellets extrusions. The colour variation is due to non-homogeneity of metal distribution.....	45
Figure 3-3: Volume of hydrogen adsorbed as a function of pressure to determine metal dispersion on TiO ₂ catalyst support material.....	46
Figure 3-4 Results from BET analysis for the determination of surface area.....	47
Figure 3-5: TEM images for fresh catalyst support with metal loading where the bar scales are: A: 20nm; B: 10 nm; C: 20 nm; D: 50nm.....	49
Figure 3-6: Metal particle frequency distribution.....	50
Figure 3-7: TPR results to obtain reduction temperature of PGM compounds.....	50
Figure 3-8: Reduction in average pellet diameter as a function of time (1 103 K).....	51
Figure 3-9: Pellet length distribution for TiO ₂ catalyst support.....	52
Figure 3-10: Pure TiO ₂ support before and after sintering.....	53
Figure 3-11: SEM micrographs of TiO ₂ support pellets displaying different colours after sintering; A: White; B: Yellow; C: Grey; D: Orange; E: White; F: White (20 000x).....	53
Figure 3-12: TEM images for sintered catalyst sample; A: Scale of 1 µm; B: Scale of 0.2 µm.....	55
Figure 3-13: Total surface area at three different sample times.....	57
Figure 3-14: TEM images for spent samples with metal loading: A: Sample 1; B: Sample 1; C: Sample 4; D: Sample 4.....	58
Figure 3-15:TEM images for spent samples with metal loading of sample 5.....	58
Figure 4-1: Representation of the micro pellet reactor used for pellet kinetics analysis.....	63
Figure 4-2: Sketch of catalyst packing.....	64

List of Figures

Figure 4-3: Process flow diagram of sulphur trioxide kinetic experimental setup	65
Figure 4-4: Complete micro-pellet experimental apparatus	66
Figure 4-5: Experimental catalyst loading without bottom end quartz wool plug; A: Top view; B: Side view	67
Figure 4-6: Average reaction rate as a function of time at different temperatures for various temperatures	74
Figure 4-7: Conversion as a function of time at different temperatures for two concentrations.....	75
Figure 4-8: Averaged reaction rate at different operating temperatures for various inlet concentrations	76
Figure 4-9: Averaged conversion at different operating temperatures for various theoretical inlet concentrations	77
Figure 4-10: Geometry of pellet representative model.....	78
Figure 4-11: Average outlet concentration versus amount of elements.....	79
Figure 4-12: Mesh generated on the fluid-solid interface.....	80
Figure 4-13: Individual pellet model experimental validation results; A: Concentration distribution of SO ₃ (mol/m ³); B: Temperature distribution (K); C: Velocity distribution (m/s); D: Average conversion predicted by model versus experimental results (F indicates fluid phase and S solid phase).....	81
Figure 4-14: Model prediction of average conversion fraction versus experimental data	82
Figure 4-15: Velocity profiles across tube diameter (m/s) [Inlet velocity=0.86 m/s; Inlet Temperature = 1073 K; Inlet Concentration=0.84 mol/m ³ ; Average Conversion=24%]	84
Figure 4-16: Velocity vectors in gas-fibre region across catalyst pellets (m/s) [Inlet velocity=0.86 m/s; Inlet Temperature = 1073 K; Inlet Concentration=0.84 mol/m ³ ; Average Conversion=24%]	84
Figure 4-17: Temperature profile near tube wall including nearest pellet [Inlet velocity=0.86 m/s; Inlet Temperature = 1073 K; Inlet Concentration=0.84 mol/m ³ ; Model Outlet Temperature=1070 K; Average Conversion=24%]	85
Figure 4-18: Temperature of gas-fibre region only (K) [Inlet velocity=0.86 m/s; Inlet Temperature = 1073 K; Inlet Concentration=0.84 mol/m ³ ; Average Conversion=24%]	86
Figure 4-19: Sulphur trioxide concentration distribution in both regions (mol/m ³) [Inlet velocity=0.86 m/s; Inlet Temperature = 1073 K; Inlet Concentration=0.84 mol/m ³ ; Average Conversion=24%]	87
Figure 4-20: Concentration profiles near wall including one pellet [Inlet velocity=0.86 m/s; Inlet Temperature = 1073 K; Inlet Concentration=0.84 mol/m ³ ; Average Conversion=24%]	87

List of Figures

Figure 4-21: Concentration of sulphur trioxide in both regions (mol/m^3) [Inlet velocity=0.86 m/s; Inlet Temperature = 1073 K; Inlet Concentration=0.84 mol/m^3 ; Average Conversion=24%]	88
Figure 4-22: Sensitivity analysis results for inlet velocity, porosity, effective diffusivity and molecular diffusion	89
Figure 4-23: Sensitivity analysis for thermal conductivity of glass wool	90
Figure 5-1: Physical layout of the packed bed reactor system	93
Figure 5-2: Process flow diagram of Packed Bed Reactor system	94
Figure 5-3: Configuration of vaporizer coil and box furnace	95
Figure 5-4: Thermocouple placement in reactor tube for long (A) and short bed (B)	97
Figure 5-5: Sulphur trioxide decomposition reactor system	99
Figure 5-6: Aspen Plus® model to account for solubility of sulphur dioxide in system	104
Figure 5-7: Variation in sulphur dioxide fraction readable as a function of condenser temperature at various reactor conversions	111
Figure 5-8: Centreline and wall temperature profiles for inert-heating region in fixed bed reactor	115
Figure 5-9: Conversion of sulphur trioxide in absence of catalyst	116
Figure 5-10: Average pre-catalyst conversion achieved for three flow variations at inlet temperature of 953 K	117
Figure 5-11: Average conversion achieved as a function of time ($\text{WHSV} = 1.2 \text{ h}^{-1}$)	119
Figure 5-12: Average conversion at steady state for different catalyst bed inlet temperatures ($\text{WHSV} = 1.2 \text{ h}^{-1}$)	120
Figure 5-13: Centreline temperature profiles over time	121
Figure 5-14: Centreline temperature profiles along the length of reactor tube for various catalyst bed inlet temperatures at constant $\text{WHSV} (1.2 \text{ h}^{-1})$	122
Figure 5-15: Wall temperature profiles along the length of reactor tube for various catalyst bed inlet temperatures at constant $\text{WHSV} (1.2 \text{ h}^{-1})$	123
Figure 5-16: Centreline and wall temperature for inlet conditions of 1103 K and constant $\text{WHSV} (1.2 \text{ h}^{-1})$	124
Figure 5-17: Centreline temperature profiles for the three different acid flow rates at temperature 1103 K	126
Figure 5-18: Wall temperature profiles for three different acid flow rates at inlet temperature of 1103 K	126
Figure 5-19: Conversion at various WHSV s for inlet temperature of 1103 K	128

List of Figures

Figure 5-20: Conversion at three WHSVs for inlet temperature of 953 K	129
Figure 5-21: Conversion achieved at various operating temperatures and flow	131
Figure 5-22: Centre and wall temperature profiles of flow 1	132
Figure 5-23: Absolute pressure before and after total reactor bed	133
Figure 6-1: Reactor (100 mm bed section) with thermocouple placements.....	137
Figure 6-2: Geometry of packed bed of pellets created from polygons.....	138
Figure 6-3: Pellet size distribution of cylindrical catalyst pellets as evaluated experimentally (length in mm).....	139
Figure 6-4: Geometry by DigiPac™; A: 3D rendering of cylinder filled with pellets; B: Geometry rendering at top of cylinder; C: Cross section of packing in a plane	139
Figure 6-5: Cross sectional illustrations of packed bed geometry at various sections in the radial direction	140
Figure 6-6: Void fraction distribution along axial (z) direction for 100 and 400 mm beds.....	141
Figure 6-7: Void fraction distribution in radial (X) tube direction	142
Figure 6-8: Representative 2D cross sectional geometry of packed bed with boundary conditions	143
Figure 6-9: Final mesh (partial) generated on the geometry.....	147
Figure 6-10: Velocity distribution along the length of catalyst bed (m/s).....	148
Figure 6-11: Temperature distribution in both fluid and catalyst phase (K)	149
Figure 6-12: Temperature distribution in model (K); A: Radial temperature distribution at x = 0.05 m; B: Temperature distribution between pellet and fluid (K).....	150
Figure 6-13: Concentration distribution of sulphur trioxide in both fluid and catalyst phase (mol/m ³)..	152
Figure 6-14: Centreline concentration distribution	153
Figure 6-15: Concentration distribution (mol/m ³); A: Radial concentration variation at x = 0.05 m; B: Concentration distribution between pellet and fluid	154
Figure 6-16: Average conversion by model versus experimental for flow: 1 m/s.....	154
Figure 6-17: Average conversion by model versus experimental for flow: 1.23 m/s.....	155
Figure 6-18: Average conversion by model versus experimental for flow: 1.32 m/s.....	155
Figure 6-19: Pressure drop comparison between numerical model and Ergun equation	157
Figure 6-20: Effective radial thermal conductivity from empirical correlation	158
Figure B-1: Model Results; A: Cross sectional (axial & radial) velocity distribution (m/s); B: Streamline velocity distribution through the porous media (m/s); C: Cross sectional (radial) velocity distribution (m/s); D: Centreline velocity profile (m/s)	198

List of Figures

Figure B-2: 2D Cross sectional results for concentration 1 at temperature 1 073 K inlet; A: Concentration distribution of SO ₃ (mol/m ³); B: Concentration distribution of SO ₂ (mol/m ³); C: Concentration distribution of O ₂ (mol/m ³); D: Centreline concentration profile through fluid and one particle (F indicates fluid phase and S solid phase)	199
Figure B-3: Distribution on surface of particles; A: Concentration of SO ₃ (mol/m ³); B: Concentration of SO ₂ (mol/m ³); C: Concentration of O ₂ (mol/m ³); D: Temperature distribution on surface of particles as well as fluid (K) (F indicates fluid phase and S solid phase)	200
Figure E-1: Equilibrium conversion for pure SO ₃ at different pressure as a function of temperature.....	211
Figure E-2: Equilibrium conversion for pure H ₂ SO ₄ at different pressure as a function of temperature .	212
Figure E-3: Equilibrium conversion of H ₂ SO ₄ with inert nitrogen	213
Figure E-4: Equilibrium conversion of feed composition to differential bed at different pressure as a function of temperature	214
Figure E-5: Equilibrium conversion of particle kinetics for different inlet concentrations as a function of temperature and constant inlet pressure.....	215
Figure E-6: Equilibrium conversion for variable WHSV process conditions as a function of pressure (Acid=3 ml/min)	216
Figure E-7: Equilibrium conversion for variable WHSV process conditions as a function of pressure (Acid=4 ml/min)	216
Figure G-1: Metal content in sulphuric acid solution	219
Figure H-1: H ₂ Chemisorption – Sample 1.....	222
Figure H-2: H ₂ Chemisorption – Sample 2.....	222
Figure H-3: H ₂ Chemisorption – Sample 3.....	223
Figure H-4: H ₂ Chemisorption – Sample 4.....	223
Figure H-5: H ₂ Chemisorption – Sample 5.....	224
Figure H-6: H ₂ Chemisorption – Sample 6.....	224
Figure H-7: BET Analysis – Sample 1	227
Figure H-8: BET Analysis – Sample 2	227
Figure H-9: BET Analysis – Sample 3	228
Figure H-10: BET Analysis – Sample 4	228
Figure H-11: BET Analysis – Sample 5	229
Figure H-12: BET Analysis – Sample 6	229
Figure H-13: TPR Analysis – Sample 1	230

List of Figures

Figure H-14: TPR Analysis – Sample 2	230
Figure H-15: TPR Analysis – Sample 3	231
Figure H-16: TPR Analysis – Sample 4	231
Figure H-17: TPR Analysis – Sample 5	232
Figure H-18: TPR Analysis – Sample 6	232
Figure H-19: TEM Images of Sample 1; A: 0.2 μm ; B: 100 nm; C: 50 nm	233
Figure H-20: TEM Images of Sample 2; A: 100 nm; B: 50 nm; C: 50 nm; D: 0.2 μm	233
Figure H-21: TEM Images of Sample 3; A: 1 μm ; B: 0.2 μm ; C: 0.2 μm ; D: 100 nm	234
Figure H-22: TEM Images of Sample 4; A: 0.2 μm ; B: 0.2 μm	234
Figure H-23: TEM Images of Sample 5; A: 0.2 μm ; B: 100 nm; C: 100 nm	235
Figure H-24: TEM Images of Sample 6; A: 0.2 μm ; B: 0.2 μm ; C: 0.2 μm	235
Figure H-25: X-Ray Diffraction Spectrum Sample 1	236
Figure H-26: X-Ray Diffraction Spectrum Sample 2	236
Figure H-27: X-Ray Diffraction Spectrum Sample 3	237
Figure H-28: X-Ray Diffraction Spectrum Sample 4	237
Figure H-29: X-Ray Diffraction Spectrum Sample 5	238
Figure H-30: X-Ray Diffraction Spectrum Sample 6	238

List of Tables

Table 2-1: Kinetic parameters for sulphur trioxide decomposition reaction (1 st order)	18
Table 3-1: Void fraction and pellet density of fresh catalyst support with metal loading	48
Table 3-2: Thermal conductivity of gas species	51
Table 3-3: Process conditions to which samples were exposed	56
Table 3-4: Metal loading on catalyst samples.....	56
Table 3-5: Comparison of properties: Fresh catalyst, Sintered catalyst and Spent catalyst	60
Table 4-1: Operating conditions of catalyst pellet experimentation.....	67
Table 4-2: Parameters for solution of model.....	70
Table 4-3: Applicability of terms in gas-quartz fluid and catalyst phase respectively.....	73
Table 4-4: Representative pellet geometry detail	78
Table 4-5: Sensitivity parameter values.....	88
Table 5-1: Experimental planning	101
Table 5-2: Experimental conditions used in Aspen Plus [®] model.....	105
Table 5-3: Experimental results comparison against Aspen Plus [®] model.....	108
Table 5-4: Mass balance for Calculation 1	109
Table 5-5: Mass and mole balance over whole system part 1 (values x10 ⁻³)	112
Table 5-6: Mass and mole balance over whole system part 2 (values x10 ⁻³)	113
Table 5-7: Process conditions for pre-heat packing investigation.....	114
Table 5-8: Inlet conditions for catalytic bed obtained from pre-heating bed section.....	117
Table 5-9: Process conditions for variable inlet temperature experiments	118
Table 5-10: Process conditions for variable WHSV (low).....	124
Table 5-11: Results obtained from acid flow rate (WHSV) variation.....	125
Table 5-12: Process conditions for WHSV variation (catalyst mass).....	127
Table 5-13: Process conditions for variation in residence time.....	130
Table 5-14: Results for variable inlet temperature.....	134
Table 6-1: Applicability of parameters to conservation equations.....	145
Table 6-2: Centreline temperature absolute error (%) between model and experimental value	151
Table A-1: Thermal conductivity coefficients	189
Table A-2: Dynamic viscosity coefficients	190
Table A-3: Heat capacity coefficients.....	191

List of Tables

Table A-4: GC calibration standard gases	193
Table B-1: Catalyst pellet CFD model parameter values.....	194
Table B-2: Catalyst pellet sizes used in experiments and model	195
Table C-1: Void fraction and particle density.....	201
Table D-1: Interfacial gradients for particles (Concentration 1).....	203
Table D-2: Intra-particle gradients for particles (Concentration 1)	204
Table D-3: W-W-W criteria for pore diffusion	205
Table D-4: Interfacial gradients for packed bed	207
Table D-5: Intra-particle gradients for packed bed.....	207
Table D-6: Axial dispersion criteria for packed bed	208
Table D-7: Radial dispersion criteria for packed bed	209
Table G-1: Model properties of 2D homo and heterogeneous models.....	220
Table G-2: Error percentages for average conversion by model versus experimental	221
Table H-1: H ₂ Chemisorption analysis results	225

List of Symbols

Symbol	Description	Unit
Ar	Ratio of activation energy to temperature and universal gas constant	-
Bi_w	Thermal Wall Biot number	-
C_A	Concentration of SO ₃ in fluid phase	mol/m ³
C_s	Concentration of SO ₃ in solid phase	mol/m ³
$c_{p,f}$	Heat capacity at constant pressure of fluid phase	J/mol.K
Da_I	Damköhler group 1 number – ratio between chemical reaction rate and bulk mass flow	-
Da_{II}	Damköhler group 2 number – ratio between chemical reaction and molecular diffusion	-
Da_{III}	Damköhler group 3 number –ratio between heat liberated and bulk transport of heat	-
D_{AB}	Binary diffusion coefficient	m ² /s
D_{kn}	Knudsen diffusion coefficient	m ² /s
$D_{e,a}$	Axial dispersion coefficient	m ² /s
$D_{e,r}$	Radial dispersion coefficient	m ² /s
$D_{ef,m}$	Effective diffusion in pellets	m ² /s
D_{H_2}	Dispersion of active metal	%
d_{pore}	Average catalyst pore diameter	m
d_p	Pellet diameter	m
$d_{p,c}$	Average metal particle size	nm
d_t	Tube diameter	m
E_a	Activation energy	kJ/mol

List of Symbols

H	Henry constant	mol/kg.bar
h_{fs}	Heat transfer coefficient between fluid and solid phase	W/m.K
h_w	Wall heat transfer coefficient	W/m.K
I	Unit Matrix	-
J	Regression objective function	-
k_0	Pre-exponential factor	s^{-1}
k_{bed}	Effective thermal conductivity of bed	W/m.K
k_{eff}	Effective thermal conductivity	W/m.K
$k_{f,eff}$	Effective thermal conductivity of fluid	W/m.K
$k_{s,eff}$	Effective thermal conductivity of solid	W/m.K
k_m	Mass transfer coefficient between fluid and solid phase	m/s
k_{fr}	Forward rate constant	s^{-1}
K_{br}	Permeability	m^2
K_{eq}	Equilibrium constant for reaction	$mol^{0.5}/m^{1.5}$
K_{SO_3}	Adsorption constant for SO_3	m^3/mol
L	Length of reactor tube	m
\dot{m}_{SO_3}	Mass flow rate of SO_3 in the system	g/min
n	Reaction order	-
p	Pressure in system	Pa
$Pe_{a,h}$	Axial heat Peclet number	-
$Pe_{a,m}$	Axial mass Peclet number	-
P_t	Prater number	-

List of Symbols

Q	Heat sink/source	W/m^3
r_A	Reaction rate	$mol/m^3.s$
R	Universal gas constant	$J/mol.K$
R_t	Radius of tube	m
S	Surface area	m^2
T_R	Reference temperature, 298 K	K
T_s	Temperature of catalyst pellet	K
T_f	Temperature of fluid	K
T_w	Wall temperature	K
U	Overall heat transfer coefficient	$W/m^2.K$
u_s	Velocity of fluid	m/s
v_i	Diffusion volume of atoms	cm^3/g
\dot{V}_{gas}	Volumetric flow of process gas	l/min
$\dot{V}_{H_2SO_4}$	Volumetric flow rate acid	l/min
\dot{V}_{N_2}	Volumetric flow rate nitrogen	l/min
V_{open}	Open space in catalyst bed	m^3
W_{cat}	Catalyst mass	g
$X_{exp,i}$	Average experimental conversion	-
$X_{mod,i}$	Average conversion achieved in model	-
y_i	Molar fraction of specie	-
Greek Symbols		
α_v	Surface to volume ratio	m^{-1}
α_w	Wall heat transfer coefficient	$W/m^2.K$

List of Symbols

ε_{gw}	Porosity of quartz wool packing	-
ε_p	Porosity of catalyst pellet	-
δ	Diffusive layer thickness	m
λ_{er}	Thermal conductivity of solid/fluid	W/m.K
$\lambda_{e,a}$	Thermal dispersion in axial direction	W/m.K
μ	Dynamic viscosity of fluid	Pa.s
ρ_b	Density of bulk catalyst pellets	kg/m ³
ρ_f	Density of fluid phase	kg/m ³
ρ_s	Density of catalyst pellets	kg/m ³
τ	Tortuosity	-
τ_{res}	Residence time of process gas in system	s
ζ	Radius of catalyst particle	m
σ_f	Density of glass wool	lb/in ³
σ_P	Packing fraction	-

Abbreviations

Abbreviation	Meaning
BET	Brunauer Emmet Teller
CAD	Computer Aided Design
CFD	Computational Fluid Dynamics
DST	Department of Science and Technology
GC	Gas Chromatograph
HyS	Hybrid Sulphur
HySA	Hydrogen South Africa
ICP-AES	Inductive Coupled Plasma Atomic Emission Spectrometry
IEA	International Energy Administration
INL	Idaho National Laboratories
IR	Infra-Red
OECD	Organization for Economic Corporation and Development
PBMR	Pebble Bed Modular Reactor
PDE	Partial Differential Equations
PEM	Proton Exchange Membrane
PGM	Platinum Group Metals
PTFE	Polytetrafluoroethylene
SEM	Scanning Electron Microscopy
SI	Sulphur Iodine
SNL	Sandia National Laboratories
TCD	Thermal Conductivity Detector
TEM	Transition Electron Microscopy
TPR	Temperature Programmable Reduction
UCT	University of Cape Town

Abbreviations

WHSV	Weight Hour Space Velocity
WPI	Worcester Polytechnic Institute
WWW	Wagner-Weisz-Wheeler
XRD	X-ray Diffraction

Glossary

“Fresh Catalyst” – Refers to the 0.5 wt% platinum 0.5 wt% palladium on TiO₂ support, consisting of 75 wt% anatase and 25 wt% rutile phase, with metal loading just after manufacturing.

“Heterogeneous Model” – Heterogeneous model refers to a model where distinction is made between the fluid and solid domain and as a result of that incorporates inter-particle limitations of heat and mass.

“Long Bed” – Refers to the catalyst bed in the packed bed reactor loaded with a bed length of 400 mm catalyst.

“Overall Kinetics” – The reaction rate observed from the catalyst which includes limitations of heat and mass transfer (diffusion and conduction).

“Particles: - Refers to the active metal particles deposited on the titania support.

“Pellets” – Refers to the combined titania support with metal loading (cylinders).

“Short Bed” – Refers to the catalyst bed in the packed bed reactor loaded with a bed length of 100 mm catalyst.

“Sintered Catalyst” – Refers to 0.5 wt% platinum 0.5 wt% palladium on TiO₂ support with metal loading, consisting mainly of rutile phase with little to none anatase phase, that has been sintered for 12 hours and is taken as the catalyst for reaction section.

Glossary

“Spent Catalyst” – Refers to 0.5 wt% platinum 0.5 wt% palladium on TiO₂ support with metal loading, consisting mainly of rutile phase with little to no anatase phase, that has been exposed to process conditions for 6 hours on stream (Packed Bed).

Publications

PhD in Chemical Engineering

June 2014

Thesis title: Evaluation of a catalytic fixed bed reactor for sulphur trioxide decomposition

MEng in Nuclear Engineering (Cum Laude)

November 2009

Dissertation title: Concept design of a combined chemical/heat-exchanger reactor for the decomposition of sulphur trioxide

BEng in Chemical Engineering

November 2007

National Conferences:

- Stander, B.F., Everson, R.C., Neomagus, H.J.W.P. 2012. Evaluation of a advanced fixed bed reactor model for sulphur trioxide conversion to sulphur dioxide with supported platinum catalyst. CATALYSIS SOCIETY OF SOUTH AFRICA (CATSA), Club Mykonos, Langebaan, South Africa, 11-14 November 2012
- Stander, B.F., Everson, R.C., Neomagus, H.J.W.P., van der Merwe, A.F. 2013. Global kinetic evaluation for SO₃ decomposition using PtPd/TiO₂ catalyst pellets. CATALYSIS SOCIETY OF SOUTH AFRICA (CATSA), Wild Coast Sun, Port Edward, South Africa, 17-20 November 2013
- Everson, R.C., Stander, B.F., Neomagus, H.W.J.P., van der Merwe, A.F., le Grange, L., Tietz, M.R. 2014. Evaluation of a catalytic fixed bed reactor for sulphur trioxide decomposition: Hys process for hydrogen production. ICCT SAICHe Conference, Durban, South Africa, 27 July -1 August 2014.

Articles Submitted:

- Stander, B.F., Everson, R.C., Neomagus, H.W.J.P., van der Merwe, A.F., le Grange, L., Tietz, M.R. 2014. Sulphur trioxide decomposition with supported platinum/palladium on rutile: 1. Reaction kinetics of catalyst pellets. International Journal of Hydrogen Energy, June 2014.