Evaluation of a catalytic fixed bed reactor for sulphur trioxide decomposition

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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**

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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

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 SO_2 with a GC, O_2 with a paramagnetic cell analyser, acid/base titrations with sodium hydroxide, SO_2 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-

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

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 proseskondisies 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 verdure 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 regresssie. 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 konsentrasieprofiele 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 buitediameter), verhit deur ‘n omliggende elektriese oond, wat gevolg is deur ‘n reeks kondenseer flesse vir produkanalise, is gebou en bedryf. Drie proses veranderlikes is ondersoek, wat insluit: die inlaattemperatuur tot katalisor-bed, die gewig-uur-ruimte-snelheid (WHSV) en die residensietyd 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 reactor 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.

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 prosestoestande: WHSV = 15 h^{-1}, T = 903-1053 K, τ=0.1-0.076 s. Die voordeel van die gebruik van ’n gevorderde heterogene reaktormodel is dat realistiese vloeipatrone en hitte-en massa-oordrag in ag geneem word.

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

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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

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	-

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	-
$X_{\mathrm{mod},i}$	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

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

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 TiO_2 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 TiO_2 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.

"Spent Catalyst" – Refers to 0.5 wt% platinum 0.5 wt% palladium on TiO_2 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

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