Catalytic steam gasification of large coal particles

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Declaration

I, Sansha Nel, hereby declare that the dissertation entitled: **“Catalytic steam gasification of large coal particles”**, submitted in fulfilment of the requirements for a Masters degree in Chemical Engineering (M. Eng.), is my own work, unless otherwise specified in text, and that this dissertation has not been submitted to any other tertiary institution either in part or as a whole.

Signed at Potchefstroom, on the .... day of ...., 2011.

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Sansha Nel

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Abstract

Catalytic gasification has been studied extensively in order to develop more efficient and economic coal conversion processes. Fundamental studies regarding catalytic gasification have thus far focused on experimentation with small coal particles and powders. The lack of knowledge regarding the application of large coal particles in steam gasification studies, in particular catalytic steam gasification, is the motivation behind this investigation.

A washed bituminous, medium rank-C Highveld coal (seam 4) was selected for this study, and a general characterisation of the coal was conducted. It was found that the ash content of the washed coal is 12.6 wt.% (air-dried basis). Based on the gross calorific value of 26.6 MJ/kg (air-dried basis), the coal sample was graded as a grade B coal. XRF analysis of the ash indicated that the coal is rich in SiO_2 and Al_2O_3, with a low potassium oxide content (0.53 wt.%) which is typical for South African coal.

Potassium carbonate (K_2CO_3) was selected as catalyst, and the excess solution impregnation method was used to impregnate large coal particles (5 mm, 10 mm, 20 mm and 30 mm). The pH of the impregnation solution stabilised after three weeks, which led to the assumption that impregnation is complete. Two methods were used to determine the catalyst loading obtained after impregnation: XRF was used to determine the wt.% K in the ash, while ion specific electrode (ISE) was used to measure the $[K^+]$ decrease in the impregnation solution. XRF results indicated the maximum catalyst loading obtainable for large coal particles, with the specific impregnation method, to be between 0.68 – 0.83 wt.% K (coal basis). XRF can be used to determine the catalyst loading by measuring the K content in the ash, while ISE can be used to semi-quantitatively predict the catalyst loadings of large coal particles. The catalyst distribution was studied using SEM and tomography analyses. SEM scans showed that the formation of cracks occurred as a result of impregnation, and EDS analysis indicated that the majority of the catalyst is concentrated around the outer surface of the particles. Tomography scans, and mineral volume analysis, indicated that the mineral matter of the coal particles increased after impregnation.

The effect of catalyst addition on reactivity was investigated by conducting steam gasification experiments with 5 mm and 10 mm particles, in a large particle TGA. The 20 mm and 30 mm particles did not remain intact after impregnation and were therefore not used for the reactivity experiments. Reactivity experiments were performed at temperatures ranging from 800 °C to 875 °C, with a steam concentration of 80 mol%. Graphs illustrating conversion as a function of time indicated that the addition of K_2CO_3 to the coal samples increased the reaction rate. This was quantified by determining the reactivities of the raw and catalysed samples using linearised homogeneous model plots. The reaction rate was found to be temperature sensitive, and independent of particle size, which indicated that experiments were conducted in the chemical reaction control regime. A slight decrease in activation energy was observed with the addition of K_2CO_3, from 191 kJ/mol (raw coal) to 179 kJ/mol (catalysed coal). Microscope images of raw and catalysed chars indicated that the addition of a catalyst may reduce agglomeration.

Opsomming

Katalitiese vergassing is voorheen al breedvoerig ondersoek met die doel om meer doeltreffende en ekonomiese steenkool vergassingsprosesse te ontwikkel. Fundamentele studies aangaande katalitiese vergassing het tot dusver gefokus op eksperimentering met klein steenkool partikels en poeiers. Die gebrek aan kennis rakende die aanwending van groot steenkool partikels vir steenkool vergassing studies, in besonder katalitiese vergassing, is die motivering agter dié ondersoek.

‘n Bitumineuse, medium rang-C Hoëveld steenkool (laag 4) is gekies vir die studie, en ‘n algemene karakterisering van die steenkool was gedoen. Dit was gevind dat die as-inhoud van die steenkool 12.6 % (massa basis) is, wat relatief laag is vir Suid-Afrikaanse steenkool. Die steenkool was gegradeer as ‘n graad B steenkool, volgens ‘n verbrandingswarmte waarde van 26.6 MJ/kg. XRF analise het getoon dat die steenkool ryk is in SiO_2 and Al_2O_3, met ‘n lae kalium oksied inhoud (0.53 %, massa basis), wat kenmerkend is van Suid-Afrikaanse steenkool.

Kalium karbonaat (K_2CO_3) was die gekose katalis, en die groot steenkool partikels (5 mm, 10 mm, 20 mm and 30 mm) was geïmpregneer deur middle van die oormatige oplossing metode. Die pH van die impregneringsoplossing het gestabiliseer na drie weke, wat gelui het tot die aanname dat impregnering klaar is. Twee metodes was gebruik om die katalisinhoud in die steenkool te bepaal na impregnering: XRF was gebruik om die massa % K in die as te bepaal, terwyl ISE gebruik was om die afname in [K^+] in die oplossing te bepaal. XRF resultate het aangedui dat ‘n maksimum katalisinhoud van tussen 0.68 – 0.83 % K (massa basis) vergrygbaar is vir die impregnering van groot steenkool partikels. XRF kan gebruik word om die katalisinhoud te bepaal deur die K inhoud in die as te analiseer, terwyl die katalisinhoud op ‘n semi-kwantitatiewe manier voorspel kan word d.m.v. ISE. Die katalis verspreiding was bestudeer met SEM en tomografiese analises. SEM foto’s het gewys dat die impregneringsmetode die vorming van krake veroorsaak in die partikels, en EDS analise het aangedui dat die meerderheid van die katalis rondom die buite oppervlakte van die steenkool partikels gekonsentreerd is. Tomografiese foto’s, en mineral volume analises, het gewys dat die mineraalinhoud van die partikels vermeerder na impregnering.

Die effek van katalis byvoeging op die reaktiwiteit van die steenkool was bestudeer deur stoom vergassing eksperimente te doen met die 5 mm en 10 mm partikels, in ‘n groot partikel TGA. Die 20 mm en 30 mm partikels was nie gebruik vir stoom

vergassingseksperimente nie, aangesien hulle verbrokkel het na impregnering. Eskperimente was uitgevoer by temperature in die omgewing van 800 ℃ tot 875 ℃, met ‘n stoomkonsentrasie van 80 mol.%. Grafieke wat die omsetting as ‘n funksie van tyd vooorstel het aangedui dat die byvoeging van K_2CO_3 tot die steenkool partikels, die reaksie tempo verhoog. Dit was gekwantifiseer deur die reaktiwiteite van die rou en gekataliseerde partikels te bepaal deur gebruik te maak van gelineardiseerde homogene model grafieke. Dit was ook gevind dat die reaksie tempo temperatuur-sensitief is en onafhanklik van partikelgrootte, wat aandui dat die eksperimente uitgevoer is in die chemiese-reaksie beherende regime. ‘n Afname in aktiveringsenergie is ook waargeneem met die toevoeging van K_2CO_3, van 191 kJ/mol (rou) na 179 kJ/mol (gekataliseerd). Mikroskoop foto’s van rou en gekataliseerde steenkool het ook gewys dat die byvoeging van katalis agglomerasie verminder.

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Roman Symbols

Symbol	Description	Units
A	Pre-exponential factor	$min^{-1}.bar^{-m}$
E_a	Activation energy	kJ/mol
ΔH^0	Enthalpy of reaction	kJ/mol
k	Reaction rate constant/ reactivity	h^{-1}
k_{cat}	Reactivity of catalysed coal samples	h^{-1}
k_{raw}	Reactivity of raw coal samples	h^{-1}
$K_2O_{initial}$	Mass K_2O present in coal before impregnation	wt.%/g ash
K_2O_{loaded}	Mass K_2O impregnated	wt.%/g ash
K_2O_{total}	Total mass K_2O present in coal after impregnation	wt.%/g ash
K_{mass}	Mass K impregnated	g/g coal
K_{loaded}	Mass K impregnated	wt.%/g coal
$[K_2CO_3]$	K_2CO_3 concentration decrease	mol/L
$[K_2CO_3]_i$	Initial K_2CO_3 of impregnation solution	mol/L
$[K_2CO_3]_f$	Final K_2CO_3 of impregnation solution	mol/L
$[K_2CO_3]_{adsorbed}$	K_2CO_3 concentration impregnated/adsorbed	mol/L
$[K^+]_{adsorbed}$	K^+ concentration impregnated/adsorbed	mol/L
M_0	Initial mass of coal sample	g
M_t	Mass of coal sample at time t	g
M_{ash}	Mass of residual ash after gasification	g
r	Reaction rate	$mol_{gas}/mol.s$
R	Molar gas constant	J/mol.K
t	time	hr or s
T	Temperature	K or ℃
X	Conversion	-
X_c	Carbon conversion	-

Nomenclature

Abbreviations	Description
AFT	Ash fusion temperature
ASTM	American Society for Testing Materials
CCG	Catalytic coal gasification
CT	Computer tomography
DAEM	Distributed activation energy model
d.a.f.	Dry ash free basis
ECI	Excess co-impregnation
EDS	Energy dispersive spectrometry
ESI	Excess solution impregnation
FSI	Free swelling index
FTIR	Fourier transform infrared spectroscopy
GCV	Gross calorific value (MJ/kg)
HM	Homogeneous model
IM	Inherent moisture
ISE	Ion-specific electrode
ISO	International Standards Organization
LH	Langmuir-Hinshelwood rate equation
PVI	Pore volume impregnation
RCM	Random capillary model
ROM	Run-of-mine
RPM	Random pore model
SABS	South African Bureau of Standards
SANS	South African National Standards
SCM	Shrinking core model
SEM	Scanning Electron Microscope
SNG	Substitute natural gas
SS-NMR	Solid-state nuclear magnetic resonance
TGA	Thermogravimetric analyser
TG-DTA	Thermogravimetric/Differential Thermal Analyser
VM	Volatile matter
WCI	World Coal Institute
WCIM	Wetness co-impregnation method
WSI	Wetness sequential impregnation
XRD	X-ray diffraction

XRF	X-ray fluorescence analysis