Separation of SO_2/O_2 using membrane technology

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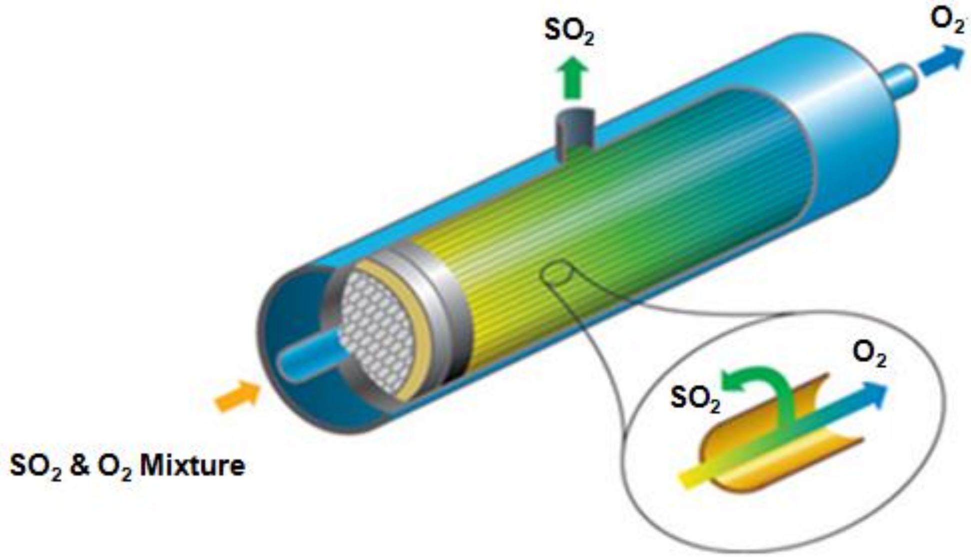

Dissertation submitted in partial fulfillment of the requirements of the degree Master of Engineering in Chemical Engineering of the North West University in Potchefstroom

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ABSTRACT

The Hybrid Sulphur process is one technology out of a multitude of known technologies responsible for hydrogen production. Within the latter hydrogen production cycle, it is pivotal to recover O_2 as a by-product from a sulphuric acid decomposition reaction that produces SO_2, H_2O and O_2. It is assumed that a simple phase separation stage carried out on the reaction products would liberate SO_2 and O_2 as a gaseous mixture leaving behind H_2O in the liquid state.

Several separation technologies are available to effect SO_2/O_2 separation, but membrane technology has proved to be dearer due to simplicity of the technology, low capital and energy costs. It is a pity though that insignificant work has been done that considers the SO_2/O_2 binary system in the membrane technology context. Of the insignificant work done, non – commercial membranes were employed. It is on the latter background that the present study was proposed.

Six commercial membranes were selected from literature, two (Udel Polysulfone and Teflon AF 2400) of which are currently used in gas separation applications and the remainder (Hyflon M, Hyflon F, Halar and Nafion 117) not necessarily used as gas separation membranes but present a potential of separating SO_2/O_2. The inclusion of the latter four membranes sought to unearth unknown gas separation potentials of the membranes based on hypothetical 1 µm thick membranes.

A screening technique was employed to eliminate poor performing membranes through pure component permeation of SO_2, O_2, N_2 and CO_2. The use of the additional gases (N_2 and CO_2) was meant to allow the generation of a pool of data that would be used as a yardstick to compare to literature and thus validate the authenticity of the designed set up. The single permeation experiments were carried out at 25°C and at absolute gas feed pressures of 1 bar, 2 bar and 3 bar, with the exception of Hyflon F experiments that were carried out at 3.85 bar, 2.85 bar and 1.85 bar also at 25°C. The effect of pressure on gas permeability and ideal selectivity of all gases against O_2 was investigated. Udel Polysulfone and Nafion 117 presented clearly evident pressure dependant SO_2 permeabilities whilst CO_2, N_2 and O_2 permeabilities were sluggishly dependant on pressure in all membranes. Gas flux in general increased with increasing pressure as pressure is essentially the driving force for permeability. Membrane screening for further investigation was then performed based on a compromise between SO_2/O_2 ideal selectivity and SO_2 flux in hypothetical 1 µm thick membranes. Membranes that presented the best SO_2/O_2 selectivity include, Udel Polysulfone with SO_2/O_2 selectivities of 46, 58 and 314 at 1 bar, 2 bar and 3 bar respectively, Nafion 117 with SO_2/O_2 selectivities of 30, 35 and 40 at 1 bar, 2 bar and 3 bar respectively and Halar with a SO_2/O_2 selectivity of 17 at 3 bar. The best SO_2 flux through hypothetical 1 µm thick membranes was manifested in Teflon AF 2400 with SO_2 fluxes of 3.6 $m^3.m^{-2}.hr^{-1}$, 5.9 $m^3.m^{-2}.hr^{-1}$ and 9.9 $m^3.m^{-2}.hr^{-1}$ at trans-membrane pressures of 1 bar, 2 Bar and 3 Bar respectively, Udel Polysulfone with SO_2 fluxes of 0.13 $m^3.m^{-2}.hr^{-1}$, 0.32 $m^3.m^{-2}.hr^{-1}$ and 2.56 $m^3.m^{-2}.hr^{-1}$ at trans-membrane pressures of 1 bar, 2 bar and 3 bar respectively and Nafion 117 with SO_2 fluxes of 0.48 $m^3.m^{-2}.hr^{-1}$, 1.03 $m^3.m^{-2}.hr^{-1}$ and 1.79 $m^3.m^{-2}.hr^{-1}$ at 1 bar, 2 bar and 3 bar trans-membrane pressures respectively. Despite Teflon AF 2400 presenting the highest SO_2 flux, the poor SO_2/O_2 ideal selectivity ≈ 1 rendered the membrane unfit for further investigation. The low SO_2 flux (0.02 $m^3.m^{-2}.hr^{-1}$) presented by Halar also rendered the membrane unfit for further investigation despite the relatively fair SO_2/O_2 ideal selectivity of 17.

Binary permeation experiments were then performed on Udel Polysulfone and Nafion 117 after passing the single permeation screening test. Gas mixture compositions of (25 wt %:75 wt %, SO_2:O_2), (50 wt %:50 wt %, SO_2:O_2) and (75 wt %:25 wt %, SO_2:O_2) were employed. The binary permeation experiments were carried out at a temperature range of 15°C to 55°C and a SO_2 feed partial pressure range of 1.1 ± 0.1 bar to 2.3 ± 0.1 bar.

The SO_2 permeate composition increased with pressure and decreased with temperature in both Udel Polysulfone and Nafion 117. Udel Polysulfone presented a superior SO_2/O_2 separation potential, concentrating a (25 wt %:75 wt %, SO_2:O_2) gas mixture to (94 wt %:6 wt %, SO_2:O_2) in a single step at 15°C and 2.2 ± 0.1 bar SO_2 feed partial pressure. Nafion 117 concentrated the same gas mixture to (87 wt %:13 wt %, SO_2:O_2) also in a single step at 15 °C and 2.4 ± 0.1 bar SO_2 feed partial pressure. Based on hypothetical 1 µm thick membranes, Nafion 117 presented generally high SO_2 molar fluxes in mixture with O_2 of about a magnitude higher than the SO_2 molar fluxes presented in Udel Polysulfone. Also, Nafion 117 proved to be less prone to plasticisation within the pressure range considered. Despite Udel Polysulfone presenting generally lower SO_2 molar fluxes, Udel Polysulfone was deemed to be the ideal membrane for the current SO_2/O_2 separation application as thicknesses of 1 µm of Nafion the perfluorosulfonic acid based membrane are currently unknown and also Udel Polysulfone presented the best SO_2/O_2 separation capability. The latter findings are envisaged to prompt further research on the production of ultra-thin perfluoro-sulfonic acid based membranes for the current application.

Key words: Sulphur dioxide, membrane, Hybrid-sulphur, Udel Polysulfone, Nafion 117

DECLARATION

I hereby declare that all the content compiled in this dissertation is my original work with the exception of referenced work. The current study has not been presented in any form to any institution.

Signed at ________________________ on the _______ day of __________________

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Bongibethu. M. Hlabano-Moyo

ACKNOWLEDGEMENTS

I would like to acknowledge the efforts of the following individuals that contributed to the fruition of this study. Many thanks to my supervisor Dr Percy van der Gryp for the unfathomable guidance he afforded me. Thanks to my Co-supervisors Dr Dmtri Bessarabov and Prof Henning Krieg. I am grateful for the technical advice from Professor Hein Neomagus and Dr Kaitano Rufaro at the commencement of the project. Vital analytical work done by Dr L. Tiedt and Dr Annine Jordan is acknowledged. The administrative assistance from Mr. Frikkie van der Merwe, Mrs Hestelle Stoppel, Mrs. Eleanor De Koker and Miss Annieta Bok is not negated. The technical support from Mr. Adrian Brock, Mr Jan Croez, Mr Johan Broodryk, Mr. Dawie Branken and Mr. Andries Kruger was invaluable. A big thank you to Hydrogen South Africa Infrastructure for the financial support, particularly Dr Dmtri Bessarabov for his benevolence. Many thanks to my colleagues:

- Bothwell Nyoni
- Liberty Mapamba
- Steven Chiuta
- Sandile Madonsela
- Dursman Mchabe
- Hope Baloyi
- Gregory Okolo
- Leonard Ndlovu
- Wisdom Dube

Special thanks go to my beloved parents and family, above all I place all my gratitude to the Almighty God.

TABLE OF CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Description	Unit
A	Membrane area	m^2
b	Langmuir affinity constant	Kpa^{-1}
C	Concentration of gas	$mole.cm^{-3}$ of polymer
C*	Saturation concentration of gas	$mole.cm^{-3}$ of polymer
C_D	Dissolved gas concentration in polymer	$mole.cm^{-3}$ of polymer
C_H	Adsorbed gas concentration in polymer	$mole.cm^{-3}$ of polymer
C'_H	Langmuir capacity constant	$mole.cm^{-3}$ of polymer
CO	Carbon Monoxide	-
CO_2	Carbon Dioxide	-
D	Diffusivity	$cm^2.s^{-1}$
D_0	Pre-exponential constant for diffusivity	$cm^2.s^{-1}$
$(dp/dt)_{leak}$ $\Delta p/\Delta t)_{leak}$	Pressure build up in permeate due to leakage	$mbar.s^{-1}$
$(dp/dt)_{ss}$ $\Delta p/\Delta t)_{ss}$	Steady state pressure build up in permeate	$mbar.s^{-1}$
(dv/dt)	Volumetric displacement	$cm^3.s^{-1}$
E_D	Diffusion activation energy	$KJ.mol^{-1}$
E_P	Permeation activation energy	$KJ.mol^{-1}$
H_2	Hydrogen	-
H_2O	Water	-
H_2S	Hydrogen Sulfide	-
H_2SO_4	Sulphuric acid	-
$\Delta H_{condensation}$	Enthalpy of condensation of gas in Polymer	$KJ.mol^{-1}$
ΔH_{mixing}	Enthalpy of creating polymer gas molecular gaps	$KJ.mol^{-1}$
ΔH_s	Enthalpy of solution	$KJ.mol^{-1}$
J	Flux	$mole.m^{-2}.s^{-1}$
K_D	Henry's law constant	$mole.cm^{-3}.pa^{-1}$
l	Membrane thickness	µm
NaOH	Sodium Hydroxide	-
N_2	Nitrogen	-
P, P_A	Permeability coefficient	Barrer
p_{atm}	Atmospheric pressure	Pa, Bar, atmosphere
p_1	Downstream pressure	Pa, Bar, atmosphere

Symbol	Description	Unit
p_2	Upstream pressure	Pa, Bar, atmosphere
p_{so2}	Sulphur dioxide partial pressure	Pa, Bar, atmosphere
p_{o2}	Oxygen partial pressure	Pa, Bar, atmosphere
Δp	Trans-membrane pressure	Pa, Bar, atmosphere
R	Molar gas constant	$J.K^{-1}.mol^{-1}$
S	Solubility	$mole.cm^{-3}$ of $polymer.pa^{-1}$
S_0	Pre-exponential factor for solubility	$mole.cm^{-3}$ of $polymer.pa^{-1}$
S_F	Sweep gas flow rate	$cm^3.s^{-1}$
T	Temperature	°C, °F, K
T_C	Critical temperature	°C, °F, K
Tg	Glass transition temperature	°C, °F, K
V′	Volumetric flowrate	$m3.hr^{-1}$
V_d	Downstream volume	cm^3
x_i	Gas mole fraction	-

Greek symbol	Description	Unit
α	Selectivity	-
$\prod_{SO2}$	Sulphur dioxide pseudo permeability coefficient	$mol.m.s^{-1}.m^{-2}.pa^{-1}$
$\prod_{O2}$	Oxygen pseudo permeability coefficient	$mol.m.s^{-1}.m^{-2}.pa^{-1}$

Abbreviation	Description
ASTM	American Standard Testing Method
AF	Amorphous polymer
BPR	Back Pressure Regulator
CSIR	Council for Scientific and Industrial Research
ECTFE	Ethylene-Chlorotrifluoro ethylene
GC	Gas Chromatograph
HP	Hewlett Packard
HySA	Hydrogen South Africa
MD	Machine Direction
MFC	Mass Flow Controller
PFA	Perfluoroalkoxy fluorocarbon

Abbreviation	Description
ppm	Parts per million
P_R	Pressure regulator
P_T	Pressure transducer
SEM	Scanning electron microscope
SILM	Supported Ionic Iiquid Membrane
TD	Transverse Direction
UPS	Udel Polysulfone
VLE	Vapour Liquid Equilibrium

LIST OF TABLES

LIST OF FIGURES