

CHAPTER 1 : INTRODUCTION

OVERVIEW

Chapter 1 constitutes of 3 main Sections namely Background and Motivation (Section 1.1), Objectives (Section 1.2), and Scope of the study (Section 1.3). Section 1.1 presents the problem at hand and the proposed route to the solution. Section 1.2 gives an outline of the work to be achieved in the current study. Section 1.3 then gives detail on aspects covered in the study.

1.1 BACKGROUND AND MOTIVATION

In recent years, there has been an increase in the desire to replace fossil based fuels for vehicle propulsion with alternative types that would reduce the emission of the detrimental greenhouse gases and supplement the expensive and dwindling oil reserves (Lattin & Utgikar, 2007:3230). In 2006 the rate of oil consumption was 30.6 billion barrels per year and over 875 billion oil barrels have been consumed since the late 19th century (Lattin & Utgikar, 2007:3230). The worldwide oil reserves have been estimated to be 2.6 trillion barrels, and at the current rate of oil and natural gas consumption, these reserves may last for the next forty years (Lattin & Utgikar, 2007:3230). The increasing world population could even reduce this period.

The average global temperature is increasing with the years, alterations in the rates of both precipitation and evaporation and the rising sea levels are attributable to industrial activities that emit green house gases such as methane, carbon dioxide and nitrous oxide (Lattin & Utgikar, 2007:3231). The CO₂ content in the atmosphere has increased from 280ppm in the pre industrial era to 380ppm at present due to the combustion of fossil fuels (Lattin & Utgikar, 2007:3231). The global energy needs and population are on an upward trend as such the green house gas emissions will likewise follow an upward trend save a cleaner fuel source is employed (Lattin & Utgikar, 2007:3231).

The South African government in May 2007, realising the need of a hydrogen economy approved in cabinet a 15 year strategy proposed by the Department of Science and Technology of South Africa (Bessarabov *et al.* 2012). The strategy was successfully implemented in September 2008 and dubbed Hydrogen South Africa (HySA) which is divided into three centres of competency (Bessarabov *et al.* 2012). The competency centres are HySA Infrastructure which is jointly hosted by the North West University in Potchefstroom and the Council for Scientific and Industrial Research (CSIR), HySA Catalysis Competence centre jointly hosted by the University of Cape Town and the South Africa's Mineral Research Technology Organisation (Mintek) and the third being HySA Systems which is hosted by the University of Western Cape (Nyoni, 2011:5).

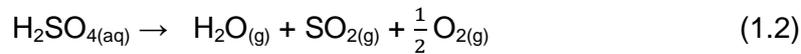
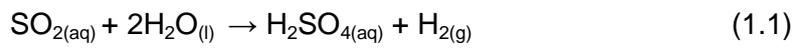
HySA Infrastructure's main focus is to devise and improve hydrogen production, storage and distribution technologies through the use of much cleaner and economic methods (Bessarabov *et al.* 2012).

Diverse methods of hydrogen production are available inclusive of steam reforming of hydrocarbons, coal gasification and partial oxidation of hydrocarbons (Stiegel & Ramezan,

2005:174). The common major set-back of the latter methods is their contribution to the release of green house gas pollutants. HySA in its quest to utilize clean technology proposed research focus on the Hybrid Sulphur Process, a thermo chemical cycle with carbon free characteristics first proposed by Brecher and Wu at Westinghouse Electric Corp (Gorensek & Summers, 2009:4098). The process seeks to address the green house gas emission problem through the clean production of hydrogen, a fuel that combusts to produce water which is not of detriment to the environment (Gorensek & Summers, 2009:4097; Stiegel & Ramezan, 2005:174).

Despite the availability of clean H₂ production technologies and the clean combustion thereof, one major setback of this dubbed “Hydrogen Economy” is the lower energy density in comparison with fossil fuels (Poling *et al.* 2008:195-200). However ongoing research seeks to thwart the latter setback so as to bring to reality the hydrogen economy.

The Hybrid Sulphur Cycle is hinged on two major processes and other auxiliary processes. Equation 1.1 represents the electrolysis reaction which is a major process, and Equation 1.2 which represents the decomposition of sulphuric acid which also is a major process. The remaining processes may be rendered as auxiliary processes.



A summary of the whole hybrid sulphur process is presented in Figure 1.1

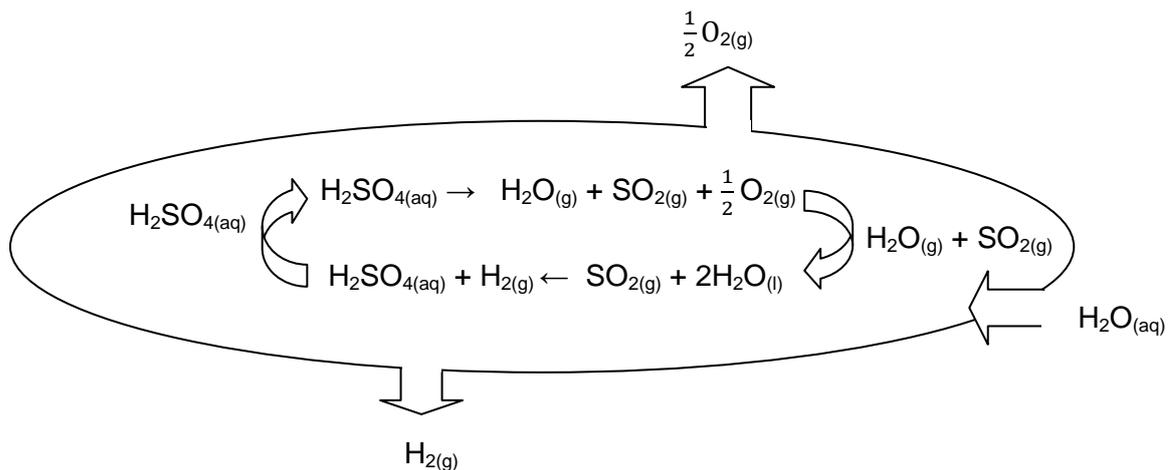


Figure 1.1 Hybrid sulphur process

Some component mixtures in the Hybrid Sulphur cycle need to be separated so as to recover product and also improve process efficiency. A list of the streams is outlined.

- H₂/H₂O stream from electrolyser cathode to recover H₂ product.
- H₂O/H₂SO₄/SO₂/O₂ stream from anode so as to pre-concentrate H₂SO₄ prior to decomposition.
- H₂O/H₂SO₄/SO₂/O₂ streams from the decomposition reactor, and the knock out drums so as to recover oxygen as by-product and recycle SO₂, H₂SO₄ and H₂O back to the process.

However in the present study, focus has been drawn to the product streams constituting of O₂, as it is intended that O₂ is removed from the process. The presence of SO₂ in the O₂ by-product stream serves as an impurity and thus would deny the industrial entity of revenue that could be received from the sale of pure oxygen. The loss of SO₂ along with by product O₂ would translate to the need for continual sulphuric acid dosing so as to account for the lost SO₂. An increase in the raw material cost would result. The need to separate SO₂/O₂ is thus validated.

It is envisaged that any H₂SO₄(aq) and H₂O(l) in the streams in question would be eliminated through phase separation, leaving behind a SO₂/O₂ gas mixture which will then have to be separated. Several methods inclusive of cryogenic distillation, pressure swing adsorption, temperature swing adsorption, absorption into ionic liquids and water absorption as is proposed by Gorenssek & Summers, (2009:4110) have the capability to effect SO₂/O₂ separation. A greater bias towards membrane technology however exists.

A comparison by Amo *et al.* (1998:6) unearthed the desirability of polymeric membrane technology over absorption units in natural gas sweetening. Membrane units are light in weight and are often skid mounted as such can easily be set offline for the introduction of a replacement unit in the case of a break down. The latter fact translates to reduced capital/installation costs. The absence of moving parts and the reduced need of supporting units reduces the probability of malfunctioning of the membrane separation unit. One major factor not to be negated in the absorption of SO₂ in water is the strong dependence of SO₂ solubility on solvent pH. Dudekova *et al.* (2006) presented a study on the influence of diverse operating parameters on the SO₂ absorption process. Results showed that a slight change in absorbent pH from 5 to 3 drastically lowered the SO₂ absorption efficiency (Dudekova *et al.* 2006). pH fluctuations in the Hybrid Sulphur process absorber would directly impact SO₂ recovery as such lots of monitoring would be needed. pH control in absorption units is often achieved through buffering with alkaline solutions such as NaOH (Dudekova *et al.* 2006). However in the Hybrid Sulphur process case, introduction of a basic solution to the absorption tower would consume H₂SO₄ and SO₂ which are both prime inputs for subsequent

sub-processes in the main process. The latter introduces complexity to the SO₂ water absorption process control. In contrast Amo *et al.* (1998:6) went on to state that membrane units require less monitoring and are versatile to parameter fluctuations.

Physical adsorption technologies, that is, pressure and temperature swing adsorption are alternative technologies that could eliminate the O₂ by product from the Hybrid Sulphur process. However, Kim *et al.* (2007) suggest that the latter two technologies are highly energy intensive to be employed in large systems such as the separation of SO₂/O₂ in the Sulphur-Iodine process which may be comparable to the Hybrid Sulphur process. The major energy requirement in membrane separation systems would be for compression of feed gas and recompression of the permeated gas for further purification in multistage membrane separation. Membrane separation technology may be deemed to be less energy intensive since the compression energy is significant only when high pressures are required (Wong & Bioletti, 2002; Park & Lee, 2008:634). Moreover, the regeneration or desorption stage in physical adsorption processes often employs part of the non-adsorbing gas to aid in flushing out the adsorbed gas. Either way, whether the non-adsorbing gas is SO₂ or O₂, contamination of either stream is undesirable through the regeneration step. On the contrary, membrane separation systems do not require regeneration separation agents (Wong & Bioletti, 2002; Amo *et al.* 1998:6).

Cryogenic distillation, also known as low temperature distillation is a potential candidate to achieve the separation in question. For the separation of components to take effect, a gas to liquid phase change is required. The change of phase that occurs adds significantly to the separation cost (Freemantle, 2005). Conversely, no phase change is required in membrane gas separation systems (Freemantle, 2005). The presence of the trace higher boiling H₂SO₄ and H₂O vapors in the SO₂/O₂ stream, would cause blockage of system pipelines due to freezing since the distillation unit would operate below 0°C. Introduction of a dryer prior to distillation would be paramount and would translate to increased capital and energy costs.

The use of ionic liquids for SO₂/O₂ separation in thermo-chemical processes has been proposed by Lee *et al.* (2008:6031). The technology is deemed to be environmentally friendly, however it is relatively new, as such a fair comparison with membrane separation systems is not possible at this stage.

The use of polymeric membranes has also been supported by several authors inclusive of Pandey & Chauhan, (2001:853), Bernardo *et al.* (2009:4638) and Robeson, (1999:552) and is thus the proposed solution to the problem at hand.

1.2 OBJECTIVES

The main objective of the present study was to effectively separate SO₂/O₂ mixtures through membrane technology. In this realm there are tributary objectives that contribute to the main objective namely to:

- Investigate the effect of process parameters, i.e, pressure on single permeation of gases in different membranes.
- Fully characterize the final membranes of choice, by investigating the effect of process parameters inclusive of pressure, temperature and feed composition on binary gas permeation.

1.3 SCOPE OF THE STUDY

The present study comprises of four distinct parts that are set to achieve the separation of SO₂ from O₂. A consolidated summary of the scope is given in Figure 1.2. Aspects covered in the present study entail:

1. An extensive outline of the research affiliated to the present study and diverse aspects of gas separation through membrane technology are presented in the literature overview (Chapter 2). Experimental work that has been performed on preferential SO₂ membrane permeation is also presented in the literature overview all in an effort to introduce the reader to the study and identify the missing links.
2. Design and development of an SO₂/O₂ membrane separation unit, which is outlined in the experimental section (Chapter 3).
3. Use of experimental methods to obtain permeation results from the separation apparatus at diverse experimental conditions (temperature, pressure and gas mixture feed composition). The experimental methods were hinged on screening criteria that aided in zeroing down to the membrane that offered the best separation capability. The respective results were then discussed and interpreted in Chapter 4.
4. Conclusions and recommendations are then presented in Chapter 5.

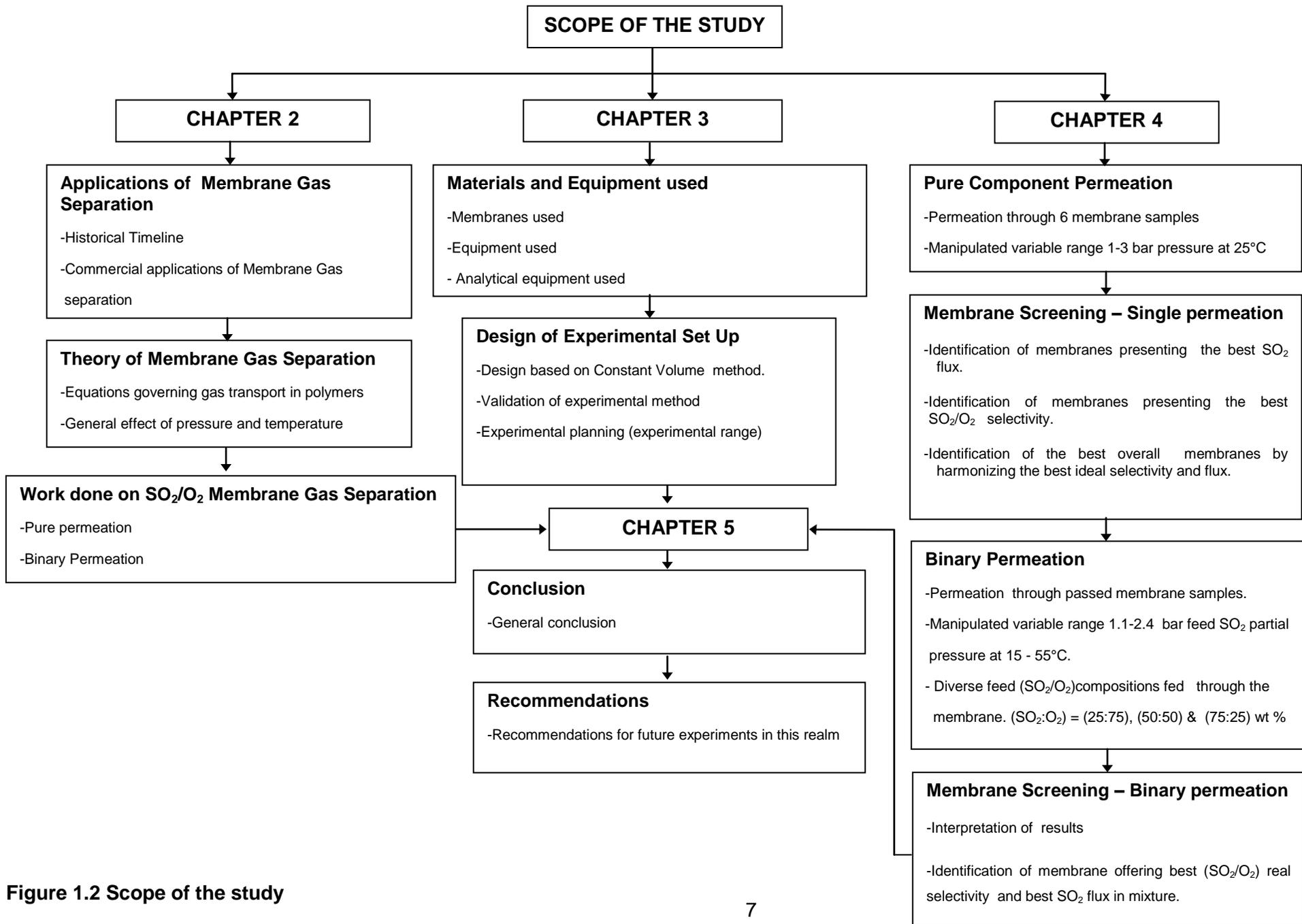


Figure 1.2 Scope of the study

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