EFFECT OF CO$_2$-INDUCED PLASTICIZATION AND MEMBRANE CONFIGURATION ON THE PERFORMANCE OF ASYMMETRIC POLYSULFONE HOLLOW FIBER MEMBRANE FOR CO$_2$/CH$_4$ GAS SEPARATION

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A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Engineering (Gas)

Faculty of Chemical and Natural Resources Engineering
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JUNE 2005
To my beloved parents

(Encik Yaacob bin Awang Ahmad and Puan Kartini binti Roseley),

My husband

(Nur Shamriman bin Abdul Rahman)

And my siblings

(Yusnaini Yaacob and Muhammad Akmal Yaacob)

Who gave me inspiration, encouragement and valuable support
toward the success of this study.
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ABSTRACT

The present study focuses on the effect of CO₂-plasticization and membrane configuration on the performance of asymmetric polysulfone hollow fiber membrane for CO₂/CH₄ separation. Heat treatment method to suppress plasticization effect and membrane module configurations in series and cascades arrangement for the CO₂/CH₄ gas separation was investigated. The membranes were prepared using polysulfone (Udel P1700) and tested using pure CO₂ and CH₄ and CO₂/CH₄ gas mixture. Gas permeation experiments were conducted for single, two and three-stage configurations. The produced membranes were characterized by pure gas permeation experiments, density measurement, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). In pure gas permeation experiment for both untreated and treated membranes, the pressure-normalized flux of CO₂ decreases with increasing of the membrane stages. In addition, the selectivities of the asymmetric polysulfone hollow fiber membrane showed a more constant trend with increasing feed pressure. Treated membrane exhibited lower pressure-normalized flux than untreated membranes due to skin layer densification which increases the gas transport resistance which lead to the reduction in the CO₂ pressure-normalized flux values. Among all configurations studied, two-stage series configuration showed the most constant trend of selectivity values. The selectivity is slightly below the intrinsic selectivity. However, three-stage cascade configuration produced the highest CO₂/CH₄ selectivity especially when tested at low feed pressure range. Some of the selectivity even surpasses the intrinsic selectivity of polysulfone. Effect of stage cut on feed pressure showed an increasing trend with increasing of CO₂ and CH₄ feed pressure in all configurations. This is due to the increase of the permeation driving force, which causes the passage of larger amounts of more permeable gas through the membrane. This study showed that, three-stage cascade configuration exhibited the smallest stage cut values than other module configurations. Hence, cascade configuration produces higher purity of CO₂ in the permeate stream. In mixed gas permeation experiment, increasing trend of CO₂ pressure-normalized flux was also observed but exhibited lower value due to competition among the penetrant species. As a result, the selectivity and the stage cut achieved are also lower in values. As a conclusion, the results of this work served as a platform in determining the most suitable module configuration to be used for gas separation processes.
Fokus utama kajian ini adalah ke atas kesan pemplastikan teraruh CO\textsubscript{2} dan konfigurasi membran terhadap prestasi membran gentian geronggang asimetrik polisulfona bagi pemisahan gas CO\textsubscript{2}/CH\textsubscript{4}. Kaedah rawatan pemanasan untuk merencat kesan pemplastikan dan modul konfigurasi membran secara bersiri dan menirus untuk pemisahan gas CO\textsubscript{2}/CH\textsubscript{4} turut dikaji. Membran disediakan menggunakan polisulfona (Udel P1700) dan diuji menggunakan gas tulen CO\textsubscript{2} dan CH\textsubscript{4} serta campuran gas CO\textsubscript{2}/CH\textsubscript{4}. Ujikaji penelapan gas dijalankan untuk konfigurasi satu, dua dan tiga tahap. Membran yang dihasilkan diciri dengan ujian penelapan gas, pengukuran ketumpatan, Mikroskop Elektron Imbasan (SEM), Permeteran Kalori Pengimbasan Kebezaan (DSC) dan Analisis Termogravimetri (TGA). Dalam ujian penelapan gas tulen bagi kedua-dua membran yang tidak dirawat dan yang dirawat, fluk tekanan ternalnormal CO\textsubscript{2} menurun dengan peningkatan bilangan membran. Tambahana pula, kememilihan membran gentian geronggang asimetrik polisulfona menunjukkan keadaan tetap dengan peningkatan tekanan masukan. Membran yang dirawat menunjukkan penurunan dalam fluk tekanan ternalnormal berbanding membran yang tidak dirawat disebabkan penebalan lapisan kulit membran yang meningkatkan rintangan pengangkutan gas yang membawa kepada penurunan nilai fluk tekanan ternalnormal CO\textsubscript{2}. Di antara kesemua konfigurasi, konfigurasi dua tahap secara bersiri menunjukkan nilai kememilihan yang paling tetap. Kememilihan yang terhasil adalah sedikit rendah berbanding kememilihan intrinsik polisulfona. Walaubagaimanapun, konfigurasi tiga tahap secara menirus menunjukkan kememilihan CO\textsubscript{2}/CH\textsubscript{4} yang tertinggi turutamanya apabila diuji pada jual tekanan masukan yang rendah. Terdapat juga kememilihan yang mengatasi kememilihan intrinsik polisulfona. Kesan keratan aras ke atas tekanan masukan meningkat dengan peningkatan tekanan masukan CO\textsubscript{2} dan CH\textsubscript{4} dalam semua konfigurasi. Ini adalah disebabkan peningkatan daya peresapan yang menyebabkan sejumlah besar gas yang mudah meresap merentasi membran. Kajian ini menunjukkan yang konfigurasi tiga-tahap secara menirus menunjukkan nilai keratan aras yang termurah berbanding konfigurasi yang lain. Oleh itu, konfigurasi menirus menghasilkan ketulenan CO\textsubscript{2} yang tinggi dalam aliran peresapan. Bagi ujikaji gas campuran, fluk tekanan ternalnormal CO\textsubscript{2} didapati meningkat tetapi menunjukkan nilai yang lebih rendah disebabkan saingan di antara kumpulan gas. Hasilnya, nilai kememilihan dan keratan aras yang terhasil juga adalah rendah. Kesimpulannya, keputusan ujikaji ini bertindak sebagai satu cara untuk menentukan konfigurasi modul yang paling sesuai untuk kegunaan proses pemisahan gas.
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<td>$A$</td>
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<td>$A_1$</td>
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<td>$A_2$</td>
<td>Porous surface area</td>
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<td>$b$</td>
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<tr>
<td>$L_i$</td>
<td>Coefficient of proportionality</td>
</tr>
<tr>
<td>LPM</td>
<td>Liter per minute</td>
</tr>
<tr>
<td>$m$</td>
<td>Mean hydraulic radius or mean pore size</td>
</tr>
<tr>
<td>$m^2/m^3$</td>
<td>Surface to volume ratio unit</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass (g/mol) of the monomer unit</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular weight (g mol$^{-1}$)</td>
</tr>
<tr>
<td>$N$</td>
<td>Avogadro constant</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure, atm</td>
</tr>
</tbody>
</table>
$p_A$ - External partial pressure of A

$p_f$ - CO₂ average partial pressure in the feed absolute pressures

$p_r$ - CO₂ average partial pressure in the reject absolute pressures

$p_{if}$ - Partial pressure of $i$ on the feed side of the membrane

$p_{ip}$ - Partial pressure of $i$ on the permeate side of the membrane

$p_{ds}$ - Downstream pressure of the gas

$p_{us}$ - Upstream pressure of the gas

$p$ - Mean pressure

$P$ - Pressure-normalized flux of $i$ in the membrane polymer

$P_A$ - Pressure-normalized flux of gas A in a membrane material

$P_1$ - Intrinsic pressure-normalized flux of the membrane material

$P_2$ - Effective pressure-normalized flux characteristic of pore

$P/l_i$ - Pressure-normalized flux

$Q$ - Volumetric flow rate (cm³ (STP) s⁻¹ or mol s⁻¹)

$Q_i$ - Total gas flux for permeant $i$

$Q_p$ - Permeate flow rate (cm/s)

$s$ - Second

$S$ - Stage cut

$S_A$ - Solubility coefficient

$R$ - Gas constant

$T$ - Temperature (K)

$T_c$ - Critical temperature

$T_g$ - Glass transition temperature

$v_i$ - Mean molecular speed of permeant $i$

$V$ - Total molar volume of the monomer unit (cm³/mol)

$V_e$ - Equilibrium volume of densified glass

$V_g$ - Actual glassy specific volume

$V_w$ - Van der Waals volume

$V_0$ - Volume occupied by the chains (cm³/mol)

wt% - Weight percentage

w/w - Weight per weight

$x$ - CO₂ mole fractions in the retentate stream

$x_f$ - CO₂ mole fractions in the feed streams
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tr>
<td>$y$</td>
<td>CO$_2$ mole fraction in the permeate stream</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Selectivity</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>$^\circ$C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>$^\circ$C/min</td>
<td>Degree Celsius per minute</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Numerical factor for a particular system</td>
</tr>
<tr>
<td>$\delta^-$</td>
<td>Negative charge</td>
</tr>
<tr>
<td>$\delta^+$</td>
<td>Positive charge</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of the film (g/cm$^3$)</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pressure difference (bar or cmHg)</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>$\gamma_i c_i$</td>
<td>Solvent activity</td>
</tr>
<tr>
<td>$\mu$m</td>
<td>Micrometer</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Viscosity (N s m$^{-2}$)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Turtousity factor</td>
</tr>
</tbody>
</table>
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CHAPTER 1

INTRODUCTION

1.1 Membrane for Gas Separation

Membrane separation processes is a well-established technology. The process essentially involves contacting one side of a semi-permeable gas separation membrane with a feed gas mixture containing at least the gas whose enrichment is desired, along with one or more other gases. The membranes divide a separation chamber into a high-pressure side into which the feed gas mixture is fed at a low-pressure side. A pressure differential is maintained across the membrane under conditions such that at least one of the gases in the feed gas mixture selectively permeates through the membrane from the high-pressure side to the low-pressure side of the membrane. Then the gas mixture which is relatively enriched in the first group of gases and depleted in the second different group of gases is removed from the low-pressure side of the membrane. While, gas depleted in the first group of gases is removed from the high-pressure side of the membrane (Stern et al., 1997).

The application of membranes to gas separation problems has grown rapidly since the installation of the first industrial plants in the early 1980s. Membranes have gained an important place in chemical process industries and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. Removal of CO\textsubscript{2} is the only natural gas separation currently practiced on a large scale (more than 200 plants have been installed). Most were installed by Grace (now Kavanaugh-GMS), Separex (UOP) and Cynara. All of these plants used
cellulose acetate membranes in hollow fiber or spiral wound module form. More recently, hollow fiber polyaramide (Medal) and polyimide (Ube) membranes have been introduced due to their higher selectivity (Baker, 2000). A list of the principal gas separation markets, producers and membrane systems is given in Table 1.1.

These market estimates are based on the new membrane equipment produced each year. Currently, only eight or nine polymer materials that are listed above are used to make at least 90% of the total installed gas separation membrane base. Plasticization problems, aging phenomena, low process ability and high cost are the main reasons why only eight to nine different polymers are used in 90% of the commercial applications (Barsema, 2003). The table shows that, to date, two thirds of the total gas separation market is in the separation of hydrogen from ammonia purge gas or syngas. These are clean gas streams, generally free of components that might foul or plasticize the membrane, which means that hollow fiber modules work well. However, the growing application areas are in natural gas treatment and in refining and petrochemical plants. The gas streams often contain high levels of plasticizing and condensable vapors, which degrade membrane performance.

**Table 1.1: Principal gas separation markets, producers and membrane systems**

(Baker, 2000)

<table>
<thead>
<tr>
<th>Company</th>
<th>Principal membrane material used</th>
<th>Module type</th>
<th>Principal markets/ Estimated annual sales</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permea (Air Products)</td>
<td>Polysulfone</td>
<td>Hollow fiber</td>
<td>Large gas companies; N&lt;sub&gt;2&lt;/sub&gt;/air at US$75 million per year; hydrogen separation at US$25 million per year.</td>
</tr>
<tr>
<td>Medal (Air Liquide)</td>
<td>Polyimide/Polyaramide</td>
<td>Hollow fiber</td>
<td></td>
</tr>
<tr>
<td>Generon (MG industries)</td>
<td>Tetra bromo polycarbonate</td>
<td>Hollow fiber</td>
<td></td>
</tr>
<tr>
<td>IMS (Praxair)</td>
<td>Polyimide</td>
<td>Hollow fiber</td>
<td></td>
</tr>
<tr>
<td>Kvaerner</td>
<td>Cellulose acetate</td>
<td>Spiral wound</td>
<td>Mostly natural gas separations at US$30 million per year.</td>
</tr>
<tr>
<td>Separex (UOP)</td>
<td>Cellulose acetate</td>
<td>Spiral wound</td>
<td></td>
</tr>
<tr>
<td>Cynara (Natco)</td>
<td>Cellulose acetate</td>
<td>Hollow fiber</td>
<td></td>
</tr>
<tr>
<td>Parker-Hannifin</td>
<td>Polyphenylene oxide</td>
<td>Hollow fiber</td>
<td>Vapor/gas separation, air dehydration and other at US$25 million per year.</td>
</tr>
<tr>
<td>Ube</td>
<td>Polyimide</td>
<td>Hollow fiber</td>
<td></td>
</tr>
<tr>
<td>GKSS Licensees</td>
<td>Silicone rubber</td>
<td>Plate and frame</td>
<td></td>
</tr>
<tr>
<td>MTR</td>
<td>Silicone rubber</td>
<td>Spiral wound</td>
<td></td>
</tr>
</tbody>
</table>
Therefore, robust membrane modules, which are able to handle ‘upsets’, are required (Baker, 2001).

Developing processes such as CO₂ separation from natural gas, Volatile Organic Compound (VOC) separation from air and nitrogen and recovery of light hydrocarbons from refinery and petrochemical plant purge gases are performed on a commercial scale and in total several hundred plants have been installed. Some predictions of the future for the membrane gas separation market are given in Table 1.2. It seems that the total market will grow, but perhaps not uniformly in all the areas that are shown. Natural gas sales have reached about USD 30 million per year and should increase rapidly, perhaps reaching USD 90 million by 2010.

CO₂ removal from natural gas has been practiced using cellulose acetate membranes for more than 10 years and the introduction of more selective polyimide membranes has begun and in time is likely to make membrane processes much more competitive with amine absorption. In the area of CO₂/CH₄ separation membranes,

<table>
<thead>
<tr>
<th>Separation</th>
<th>Membrane market (USD million, 2,000 dollars)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2000</td>
</tr>
<tr>
<td>Nitrogen from air</td>
<td>75</td>
</tr>
<tr>
<td>Oxygen from air</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>25</td>
</tr>
<tr>
<td>Natural gas</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>30</td>
</tr>
<tr>
<td>NGL</td>
<td>&lt;1</td>
</tr>
<tr>
<td>N₂/H₂O</td>
<td>0</td>
</tr>
<tr>
<td>Vapor/nitrogen</td>
<td>10</td>
</tr>
<tr>
<td>Vapor/vapor</td>
<td>0</td>
</tr>
<tr>
<td>Other</td>
<td>15</td>
</tr>
<tr>
<td>Total</td>
<td>155</td>
</tr>
</tbody>
</table>

Table 1.2: Predicted sales of membrane gas separation in the main target market (Baker, 2001)
natural gas sweetening, the removal of CO$_2$ in landfill gas recovery processes and CO$_2$ removal from fractured wells as well as the removal of CO$_2$ in enhanced oil recovery applications (EOR) are of interest (Staudt-Bickel and Koros, 1999). CO$_2$ produced can be injected into adjacent oil fields to enhance oil recovery (Lonsdale, 1982). In order to achieve excellent performance in membrane processes, the process reliability needs to be enhanced to make CO$_2$ removal technology the ultimate choice in a variety of processing conditions. It is crucial to transport the field gas through the conventional pipeline without catastrophic corrosion problems. Hence, an efficient method to reduce the composition of CO$_2$ gas is critically in need and membrane gas separation processes was found to be the best solution.

Nowadays, there are wide varieties of acid gas removal technologies available. Membrane separation processes have been shown to be very effective for natural gas processing. An efficient separation of CO$_2$ and hydrogen sulfide from natural gas can be achieved by selective permeation through polymer membranes (Lee et al., 1995). However, membrane technologies have been chosen for applications that have large flows, have high CO$_2$ contents or are in remote areas. The removal of CO$_2$ from off gas and reinjection into the oil field is desirable but the recycle gas must have a CO$_2$ purity of at least 95%. This minimum level is necessary in order to maintain the solvent power of the CO$_2$ (Dortmundt and Doshi, 1999). When the CO$_2$ content of the feed was above 75% CO$_2$, the separation could be achieved in a single membrane stage. In this case, the compressor was no longer needed (Ho and Sirkar, 1992).

Even though the separation of CO$_2$/CH$_4$ using polymeric membranes is growing rapidly, the plasticization of the membrane material is always a problem. This is due to the pressure-normalized flux of the slower gas which is facilitated by the highly soluble, faster gas. This phenomenon is attributed to plasticization effects caused by the high CO$_2$ solubility or interactions between CO$_2$ and the polymer material. As the membrane is plasticized the pressure-normalized flux increases significantly but the selectivity for gaseous mixtures decreases (Barsema et al., 2003). A good asymmetric membrane for natural gas separation can be achieved if it possesses the following material and performance characteristics: (1) inherently high
selectivity for CO$_2$ and CH$_4$ gas pair and (2) immunity to plasticization induced by CO$_2$. The CO$_2$-induced plasticization usually causes a severe deterioration of membrane separation performance in the natural gas application loss (Cao et al., 2003).

An understanding of the plasticization phenomenon is crucial to develop and achieve a high performance membrane in order to make membrane separation application attractive. Therefore, a thorough investigation of CO$_2$-induced plasticization phenomenon must be carried out in order to reduce the extent of plasticization phenomena in glassy polymer membranes.

1.2 Problem Statement

The problem encountered in the CO$_2$/CH$_4$ separation was the swelling of the polymer matrix by the highly sorbed CO$_2$, which resulted in an increase in CO$_2$ pressure-normalized flux. This behavior is related to the so-called plasticization effects that occur during the separation process. This phenomenon took place since CO$_2$ that falls into the category of acid gas such as hydrogen sulfide (H$_2$S) is commonly found in natural gas streams and hydrocarbon gases at levels as high as 40% to 60% and sometimes up to 80% as hydrocarbon capacities decline, and up to a feed pressure of 60 atm. These extreme operation conditions were the result of the swelling and plasticization of most membrane materials by the CO$_2$ present in the feed stream (Ho and Sirkar, 1992, Scott, 1998, Staudt-Bickel and Koros, 1999). In other words, degraded the membrane performance. As a result, pressure-normalized flux of CH$_4$ increases. As it increases more than the pressure-normalized flux of CO$_2$, the selectivity decreases (Bos et al., 1998). Since plasticization is a major problem that occurs in CO$_2$/CH$_4$ separation, it is necessary to develop a membrane that has less plasticization effect besides maintaining the separation performance at elevated pressure conditions.
1.3 Research Objectives

As stated above, the separation of CO$_2$ from CH$_4$ customarily takes place in the processes of natural gas treatment, enhanced oil recovery, landfill gas and also in digester gas upgrading and flue gas recovery in order to reduce pipeline corrosions induced by CO$_2$ as well as to produce high-purity energy products. Polymer membrane based technology is competitive for this kind of application in view of the following facts: (1) the high pressure of feed gas is a ready-made driving force for permeation and (2) CO$_2$ is more permeable than CH$_4$ in most membranes. Thus, the enriched CH$_4$ as the residual stream still retains at a high pressure for other operations without a significant pressure loss (Cao et al., 2003). Many polymers used for the CO$_2$/CH$_4$ gas separation show the typical trend of a decreasing pressure-normalized flux with increasing pressure at low feed pressures and an increasing pressure-normalized flux as the CO$_2$ pressure is further elevated. The increase of pressure-normalized flux with increasing pressure is cause by plasticization (Bos et al., 1998).

From the literature, few researchers reported on asymmetric membrane film, in addition very few researchers report on plasticization in asymmetric hollow fiber membranes. This phenomenon is mainly due to the fact that the dense selective layer of the hollow fibers is very thin and the inception of plasticization in the hollow fibers may occur at a very low feed pressure (Wang et al., 2002a). Many researchers studied polyimide membranes. However, polyimide trade off is not attractive to be used commercially and is expensive compared to polysulfone. On the other hand, the trade-off for polysulfone is favorable for commercial applications. This can help to reduce the cost of using membrane separation systems with condensable gases such as CO$_2$.

Developing a better membrane that has less plasticization effect besides maintaining the membrane performance is essential for the future application of membrane based gas separation. Not much attention was given to overcoming the plasticization effect in hollow fiber membranes especially on polysulfone. As such, it is necessary to reduce the effect caused by the dissolved CO$_2$ that will alter the
polymer matrix, resulting in an increase in pressure-normalized fluxes and a reduction of selectivities. From the discussion above, the objectives of this research are:

1. To develop and characterize asymmetric polysulfone hollow fiber membranes.
2. To study the effect of plasticization in asymmetric polysulfone hollow fiber membranes for CO$_2$/CH$_4$ gas separation systems.
3. To determine the optimize operating conditions for suppression of plasticization in hollow fiber membranes for CO$_2$/CH$_4$ separation system.

1.4 Scope of Thesis

In order to achieve the objective as stated above, the following scopes of work are identified:

1. Fabricating asymmetric polysulfone hollow fiber membrane and membrane modules for testing purposes.
2. Designing and fabricating a high-pressure three-stage gas permeation testing system in order to determine the separation performance of the asymmetric polysulfone hollow fiber membranes.
3. Investigating the plasticization effect using pure CO$_2$ and CH$_4$ as well as CO$_2$/CH$_4$ mixture permeation experiments.
4. Performing a mild heat treatment process below polysulfone glass transition temperature in order to suppress CO$_2$-plasticization.
5. Conducting membrane characterizations using density measurement, Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) that can provide an indirect evidence of plasticization.
LIST OF PUBLICATIONS


2. N. Yaacob, A. F. Ismail, Effect of Membrane System Configuration on the Performance of Polysulfone Hollow Fiber Membrane System for CO₂/CH₄ Separation, Symposium of Malaysian Chemical Engineers (SOMChE), 13th-14th December 2004, Universiti Teknologi Petronas, Tronoh.


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