Hybrid Membrane-Distillation Separation for Ethylene Cracking

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Hybrid membrane-distillation separation for ethylene cracking
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Abstract – PhD Thesis

Gas separations are often required in chemical processes, e.g. air separation, ethylene production, etc. These are often challenging and costly processes because of the low temperature and high pressure needed if vapour-liquid phase separations are involved. This thesis focuses on hybrid membrane-distillation separations as an opportunity to develop more energy-efficient separation processes.

In a typical ethylene plant, recovery, the separation and purification of the cracked product are economically important. The focus of this thesis is on the ‘C₂ splitter’ which separates the desired product, ethylene, from ethane. Cryogenic distillation, which is currently used to separate the binary ethylene-ethane mixture, is extremely expensive in terms of both capital and operating costs, especially because of refrigerated cooling requirements.

Hybrid membrane-distillation processes are able to effectively separate low-boiling compounds and close-boiling mixtures and to reduce energy consumption, relative to cryogenic distillation. However, hybrid membrane-distillation processes present challenges for process modelling, design and operation. There are two major challenges associated with the modelling of hybrid processes for low temperature separations: i) the complex interaction between the process and the refrigeration system and ii) the large number of structural options, e.g. conventional column, membrane unit or hybrid membrane-distillation separation, where the distillation column can be integrated with the membrane unit to form a sequential, parallel, ‘top’ or ‘bottom’ hybrid scheme.

This thesis develops a systematic methodology to design, screen, evaluate and optimise various design alternatives. Schemes are evaluated with respect to energy consumption, i.e. power consumption of process and refrigeration compressors, or energy costs. In the methodology, process options are screened first for feasibility, based on numerous simulations and sensitivity analyses. Then, the feasible options are evaluated in terms of energy consumption and compared to the performance of a conventional distillation column. Finally, economically viable schemes are optimised to identify the most cost-effective heat-integrated structure and operating conditions.

The methodology applies models for multi-feed and multi-product distillation columns, the membrane, compressor and refrigeration system; heat recovery opportunities are systematically captured and exploited. For the separation of relatively ideal mixtures, modified shortcut design methods, based on the Fenske-Underwood-Gilliland method are appropriate because they allow fast evaluation without needing detailed specification of column design parameters (i.e. number of stages, feed and side draw stage locations and reflux ratio). The modifications proposed by Suphanit (1999) for simple column design are extended to consider multi-feed and/or multi-product columns. The complex column designs based on the
approximate calculations method are validated by comparison with more rigorous simulations using Aspen HYSYS.

To design the hybrid system, a reliable and robust membrane model is also needed. To predict the performance of the module model, this work applies and modifies detailed membrane model (Shindo et al., 1985) and approximate method (Naylor and Backer, 1955) to avoid the need for initial estimates of permeate purities and to facilitate convergence.

Heat integration opportunities are considered to reduce the energy consumption of the system, considering interactions within the separation process and with the refrigeration system. A matrix-based approach (Farrokhpah, 2009) is modified to assess opportunities for heat integration. The modified heat recovery model eliminates the need to design the refrigeration cycle and uses a new simple, linear model that correlates the ideal (Carnot) and a more accurately predicted coefficient of performance.

This work develops a framework for optimising important degrees of freedom in the hybrid separation system, e.g. permeate pressure, stage cut, side draw molar flow rate and purity, column feed and side draw locations. Heat recovery options between: i) column feeds and products; ii) the membrane feed and products and iii) the associated refrigeration system are considered. A deterministic and a stochastic optimisation algorithm are applied and compared for their efficiency of solving the resulting nonlinear optimisation problem.

The new approach is demonstrated for the design and optimisation of heat-integrated sequential and parallel hybrid membrane-distillation flowsheets. Case study results show that hybrid scheme can reduce energy cost by 11%, compared to distillation, and that parallel schemes have around 8% lower energy costs than sequential hybrid schemes. These results suggest hybrid membrane-distillation processes may be competitive with distillation when applied for ethylene-ethane separations, but that further development of suitable membranes may still be needed.
Declaration

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institution of learning.

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Nomenclature and Abbreviations

\( \overline{P_M} \) Component permeance

\( C_{steam}^k \) Steam cost in the range of temperature \( k \)

\( A \) Membrane area, \( m^2 \)

\( B \) Bottom molar flow rate

\( C \) Set of cold/sink streams

\( C' \) Set of partitioned sink process streams

\( C^C \) Molar concentration of the carrier in the membrane

\( C^C_{i,f} \) Molar concentration of the silver-component complex in the feed

\( C^C_{i,p} \) Molar concentration of the silver-component complex in the permeate

\( C_{elec} \) Is the cost of electricity

\( C_{i,f} \) Is the molar concentration of component \( i \) in the feed side

\( C_{i,p} \) Is the concentration of component \( i \) in the permeate side

\( C_{ij} \) Is the utility cost of the match between source \( i \) and sink \( j \) per unit of heat load

\( C_{ij}^{power} \) Is the cost of power of the heat pump system operating between source stream \( i \) and sink stream \( j \) per unit of heat absorbed

\( C_{ij}^{utility_cw} \) Is the cost of cooling water utility for the match between source stream \( i \) and sink stream \( j \) per unit of heat rejected

\( COP: \) Coefficient of performance of refrigeration system

\( COP_{act} \) Is an actual coefficient of performance

\( COP_{ideal} \) Is an ideal coefficient of performance

\( CP: \) Heat capacity

\( C_P: \) Molar heat capacity

\( C_T \) The total carrier concentration inside the membrane

\( D \) Diffusion coefficient

\( D \) Distillate molar flow rate

\( D_C \) Diffusion coefficient of the complex

\( D_i \) Is the diffusivity constant of component \( i \) in the membrane

\( e \) Local error \( e \) of component

\( F \) Feed Molar flow rate

\( f \) Is the dimensionless flow rate on the feed stream

\( F_f \) Molar flow rate of the feed stream
$F_M$ Membrane feed molar flow rate
$F_n$ Inlet volumetric flow rate
$F_P$ Molar flow rate of the permeate stream
$g$ Is the dimensionless flow rate on the permeate stream
$G$ Molar flow rate of vapour on the permeate side of the membrane
$H$ Enthalpy
$H$ Hot/Source stream
$H'$ Set of partitioned source process streams
$H_B$ Is the enthalpy of the bottom product
$H_D$ Molar enthalpy of the distillate
$H_i$ Henry’s coefficient of component $i$
$H_L$ Molar enthalpy of the liquid at the top of the column
$H_{L,\infty}$ Molar enthalpy of the liquid at the rectifying pinch
$H_M$ Is the molar enthalpy of the membrane stream
$H_P$ Is the molar enthalpy of the permeate stream
$H_V$ Molar enthalpy of the vapour at the top of the column
$H_{V,\infty}$ Molar enthalpy of the vapour at the rectifying pinch
$J_i$ Flux of component $i$
$K$ Is the annealing parameter
$K_{eq}$ Equilibrium constant
$K_{i,\infty}$ Equilibrium constant of component $i$ at the rectifying pinch
$L_{\infty}$ Liquid molar flow rate at the rectifying pinch
$m$ Number of streams cooled using ambient cooling utility
$M$ Match matrix
$n$ Number of component
$nc$ Is the number of compressors in the flowsheet
$N_i$ Is the flux of component $i$
$N_{min}$ Minimum number of stages at total reflux condition
$N_{min,I}$ Is the minimum number of theoretical stages required in section I
$n_{sink}$ Is the number of sink streams
$n_{source}$ Is the number of source streams
$P$ Pressure, bar
$P_{COL}$ Distillation column pressure
$P_f$  Membrane feed stream pressure

$P_i$  Partial pressure of component $i$ on the feed side or permeate side

$P_{in}$  Inlet pressure of the compressor

$P_M$  Membrane feed stream pressure

$P_{Mi}$  Is the permeability of component $i$

$P_{Mj}$  Is the permeability of component $j$ (the fast permeating component)

$P_{out}$  Outlet pressures of the compressor

$P_P$  Permeate stream pressure

$P_R$  Retentate stream pressure

$Q$  Duty, kW

$q$  Feed quality

$Q_C$  Cooler or condenser duty

$Q_{evap}$  Evaporator duty

$Q_H$  Heater duty

$Q_{ij}$  Heat duty exchanged between source $i$ and sink $j$

$Q^k$  The heat load of segment $k$ belonging to source $i$ or sink $j$

$Q_R$  Reboiler duty

$Q_{sink}$  Heat sink

$Q_{source}$  Heat source

$r$  Pressure ratio

$R$  Reflux ratio of distillation column

$R_{act}$  Actual reflux ratio

$R_{min}$  Minimum reflux ratio

$S$  Dimensionless membrane area

$s_i$  Solubility coefficient of component $i$ (cm$^3$(STP) cm$^{-3}$ bar$^{-1}$)

$S_0$  Dimensionless inlet membrane area

$T$  Temperature, °C

$T^*_k$  Is the shifted inlet temperatures of segment $k$ belonging to the process stream $j$ or $i$

$T^*_{k+1}$  Is the shifted outlet temperature of segment $k$ belonging to the process stream $j$ or $i$

$T_0$  Is an initial annealing temperature

$T_{cond}$  Is the condensing temperature (K)
\( T_{\text{evap}} \) Is the evaporating temperature (K)
\( T_{\text{in}} \) Inlet stream temperature
\( T_{\text{out}} \) Outlet/target temperature
\( T_{\text{part}} \) Partitioned temperature
\( T_{\text{sink}} \) Cold stream temperature
\( T_{\text{source},} \) Hot stream temperature
\( v \) Is the pattern vector
\( V \) Vapour flow rate at the top of the column
\( V_{\infty} \) Vapour flow rate at the rectifying pinch
\( V_{\text{min}} \) Minimum vapour flow in top section of distillation column
\( W_{\text{c}} \) Compressor shaft power
\( W_{\text{act}} \) Actual shaft work
\( W_{\text{f}} \) Feed shaft work
\( W_{\text{HP}} \) Heat pump shaft work
\( W_{\text{ideal}} \) Ideal shaft work
\( W_{\text{P}} \) Permeate shaft work
\( W_{\text{R}} \) Retentate shaft work
\( W_{\text{total}} \) Total process shaft work
\( x_{0} \) Is the initial guess point
\( x_{\infty} \) Mole fraction of a component in liquid at pinch
\( x_{B,H} \) Mole fraction of the heavy key component in the bottom
\( x_{B,L} \) Mole fraction of the light key component in the bottom
\( x_{D,H} \) Mole fraction of the heavy key component in the distillate
\( x_{D,L} \) Mole fraction of the light key component in the distillate
\( x_{i} \) Mole fraction of component \( i \) in the feed side
\( x_{i,D} \) Mole fraction of component \( i \) in the distillate
\( x_{i,F} \) Mole fraction of component \( i \) in the feed
\( x_{i,P} \) Mole fraction of component \( i \) in the permeate stream (Upper feed)
\( x_{i,R} \) Mole fraction of component \( i \) in the retentate stream (lower feed)
\( x_{M,H} \) Mole fraction of the heavy key component in the membrane feed
\( x_{M,L} \) Mole fraction of the light key component in the membrane feed
\( x_{R,H} \) Mole fraction of the heavy key component in the retentate
\( x_{R,L} \) Mole fraction of the light key component in the retentate
Mole fraction of a component in vapour at the rectifying pinch
Mole fraction of component $i$ in the permeate stream
Mole fraction of component $i$ in membrane feed stream
Vapour mole fraction of component $n$ in at the rectifying pinch

**Abbreviations:**

AbsTol  Absolute error tolerance
CMS    Carbon Molecular Sieve Membrane
FTMs   Facilitated transport membranes
GPS    Generalized Pattern Search
GSS    Generalized Set Search
ILM    Immobilized Liquid Membrane
LP     Linear programming
MADS   Mesh Adaptive Direct Search
MILP   Mixed integer linear programming
MINLP  Mixed integer nonlinear programming
NLP    Nonlinear programming
Ode    Ordinary differential equations
PMs    Polymeric Membranes
RelTol Relative error tolerance
SA     Simulated annealing
SPEM   Solid Polymer Electrolyte Membrane
SQP    Sequential quadratic programming
TOC    Total operating cost
TolFun Tolerance on the objective function
TSPC   Total shaft power cost

**Greek letters:**

$\alpha_{ij \ avg}$ Geometric average relative volatility
$\emptyset$ The Underwood root
$\alpha$ Relative volatility of a component also used for representing the membrane selectivity
$\alpha_{ij}$ Relative volatility of a component $i$ with respect to $j$
\( \gamma \)  Pressure ratio
\( \delta \)  Membrane thickness
\( \Delta P \)  Pressure difference across the membrane
\( \Delta T_{\text{min}} \)  Minimum approach temperature
\( \varepsilon \)  Membrane porosity
\( \zeta \)  Polytropic efficiency
\( \eta \)  Refrigeration cycle efficiency
\( \theta \)  Stage cut
\( \tau \)  Membrane tortuosity
\( \Psi \)  Inlet heat capacity ratio
\( \Omega \)  Polytropic coefficient
\( \omega \) & \( \beta \)  Are parameters of refrigeration model

**Subscripts:**

f  Feed
HK  heavy key component in distillation
i  Counter for cold streams, also used for component indication
I, II  Number of column section
in  Stream supply condition
j  Counter for hot streams, also used for component indication
k  Counter for portioned segments of process stream
LK  light key component in distillation
out  Stream target condition
p  Permeate
r  Retentate

**Superscripts:**

C  Complex
L  lower bound
U  upper bound
Chapter 1 Introduction

1.1 Background to the Research

Ethylene is one of the most important petrochemical products used in many commercial industrial derivatives (Ethylene Product Stewardship Guidance Manual, 2004; Faiz and Li, 2012). The global demand of ethylene is expected to increase to 160 million tons by the year 2015 (Shi et al., 2011).

Ethylene is mainly produced by two processes: steam cracking of paraffinic hydrocarbons, which is the predominant process used to produce ethylene, and separation from refinery gases. In cracking, a hydrocarbon feed forms a mixture of hydrogen, methane, ethylene, ethane, acetylene, propane, propylene and heavier components. These are compressed, cooled, and partially condensed in a train of heat exchangers and recovery units (Bernardo et al., 2004). The condensate is separated and passed to a demethanizer column, while the gaseous stream is treated for acid gas removal (H₂S, CO₂) and processed through a drying unit for moisture removal. The demethanizer unit separates the lighter gases (H₂ and CH₄) into an overhead product and a bottom stream rich in ethylene, ethane, propane and propylene hydrocarbons. The bottom hydrocarbon stream is further fractionated to yield a high purity ethylene product, an ethane product, a stream of C₃ and heavier hydrocarbons (Nunes and Peinemann, 2001). Figure 1.1 shows a simplified block diagram of a separation train in an ethylene plant (Zimmermann and Walzl, 2012).
The separation and purification process of ethylene and other products from the cracked gas represents a large percentage of the capital investment and energy costs for the ethylene plant (Eldridge, 1993; Bernardo et al., 2004; Eldridge et al., 2005). The conventional distillation column for the separation of ethylene from ethane consumes about 26% of the refrigeration energy in a front-end demethanizer ethylene plant (Zimmermann and Walzl, 2012). For this difficult fractionation, the net amount of work done by the refrigeration system is high because of the high reflux ratio required (around 4) and the low temperatures involved (Zimmermann and Walzl, 2012). In addition to the high energy consumption, a series of stages is required to achieve the high purity demanded for ethylene (approximately 99.9%), which results in high capital cost. The capital cost associated with the column is relatively high due to the close relative volatility between the components being separated together with the refrigeration shift power requirement.

In order to increase the thermodynamic efficiency of separation and decrease the energy consumption of the distillation column, three approaches have been proposed (Humphrey and Seibert, 1992).

1. Improve the energy-efficiency of the distillation process.
2. Completely replace the distillation technology.
3. Augment the distillation technology with other separation technologies to form efficient hybrid systems.
The first approach has been investigated in some depth (Kaiser et al., 1979; Verma et al., 2007). Process integration and complex column configurations have proven to be very successful in reducing the energy requirements for conventional distillation arrangements (Umeda et al., 1979; Dhole and Linnhoff, 1993; Castillo and Dhole, 1995; Shah, 1999; Wang and Smith, 2005).

In the second approach, different separation technologies such as extractive distillation, physical and chemical adsorption/absorption have been proposed as means of saving energy (Eldridge, 1993). A comparison of these technologies is shown in Table 1.1 (Eldridge, 1993; Eldridge et al., 2005; Ravanchi et al., 2009).

However, several limitations have prevented these processes from replacing cryogenic distillation processes (Eldridge, 1993; Faiz and Li, 2012). For instance, membranes have limited capabilities with respect to recovery and purity. Also, there are issues with recompression of permeate and membrane stability. In practice, membranes are sensitive to the presence of contaminants such as acetylene and sulphur. These compounds reduce membrane separation efficiency due to their interaction with silver. However, pre-treatment can reduce the concentration of these compounds to an acceptable low level (Faiz and Li, 2012).

A combination of cryogenic and membrane technologies could represent an alternative option. Hybrid membrane distillation processes offer an opportunity to exploit the characteristics of both technologies in an efficient way. A number of hybrid membrane-distillation applications in an ethylene plant have been highlighted by Al-Rabiah (2001), Nunes and Peinemann (2001) and Bernardo et al. (2004). Possible applications include hydrogen separation and olefin-paraffin separations (ethylene-ethane and propylene-propane). In such applications, hybrid membrane-distillation separation systems, which are the main focus of this thesis, have been shown to improve product purity at a reduced energy requirement. They have also been shown to lower capital and production costs (Roberts and Gottschlich, 1990; Al-Rabiah, 2001; Nunes and Peinemann, 2001; Barakat et al., 2008; Caballero et al., 2009; Ploegmakers, et al., 2013).
Table 1.1: Comparison of gas separation technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-temperature distillation</td>
<td>• High recovery of products</td>
<td>• High capital cost</td>
<td>Eldridge, 1993; Ravanchi et al., 2009; Faiz and Li, 2012; Rungta et al., 2012</td>
</tr>
<tr>
<td></td>
<td>• High purity</td>
<td>• High energy consumption</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Can operate at high pressures</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Large flow rates can be accommodated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption (pressure swing)</td>
<td>• Very high purity of light product</td>
<td>• Low recovery</td>
<td>Ravanchi et al., 2009</td>
</tr>
<tr>
<td></td>
<td>• Simple process</td>
<td>• Operates most favourably at lower pressures</td>
<td></td>
</tr>
<tr>
<td>Extractive distillation</td>
<td>• Separation enhanced</td>
<td>• High capital and operating costs</td>
<td>Eldridge, 1993; Eldridge et al., 2005</td>
</tr>
<tr>
<td></td>
<td>• Easy operation</td>
<td>• Limited solvent selectivity/capacity</td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>• Accomplish the selective transport of specific component</td>
<td>• Trade-off between purity and recovery constrains</td>
<td>Eldridge, 1993; Faiz and Li, 2012; Rungta et al., 2012</td>
</tr>
<tr>
<td></td>
<td>• Low energy requirements and low cost</td>
<td>• May require compression (high capital cost)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Operable</td>
<td>• Sensitivity to traces of hydrogen sulfide and acetylene</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Can be combined with other separation processes</td>
<td>• Short life time</td>
<td></td>
</tr>
</tbody>
</table>

1.2 Motivation and Research Objectives

The majority of published research on olefin-paraffin hybrid separation processes focuses on propylene-propane separation. There are few studies on ethylene-ethane separation. Hybrid membrane-distillation processes are not yet well established for ethylene-ethane separation due to the poor chemical stability and/or performance of
relevant membranes. However, it is of great interest to verify whether a hybrid system is economically attractive if a proper and stable membrane material is available. In addition, research studies on hybrid systems for ethylene-ethane separations can provide insight into membrane development needs, as shown recently by Motelica et al. (2012) and Ploegmakers, et al. (2013). Therefore, this thesis explores the potential advantages of hybrid separation processes for ethylene-ethane separation.

The scope of this thesis is to systematically explore the performance of various hybrid membrane-distillation schemes, as well as to generate conceptual process designs which could help in deciding quickly whether an alternative flowsheet is economically attractive. Most of the published research carried out to date on the design of hybrid membrane-distillation process seeks to identify the most cost-effective design option using previous design experience, heuristic rules (e.g. Roberts and Gottschlich, 1990) and conventional design approaches (e.g. Al-Rabiah, 2001; Motelica et al., 2012; Ploegmakers, et al., 2013). This is due to the large number of structural and operative degrees of freedom. Hybrid flowsheet design using conventional process simulation software is computationally extensive for a complex column design (trial and error required) and thus few alternative design options can be explored. Furthermore, the global optimum is difficult to find by carrying out extensive runs of process simulation. Therefore, there is a need for a systematic approach to exploit the performance of hybrid systems (Eldridge et al, 2005; Koch et al., 2013 and Bravo-Bravo, et al., 2013).

The major challenge in developing a systematic method for hybrid membrane-distillation system design and optimisation comes from the following aspects: selecting a proper membrane modelling algorithm and solution procedure that is convenient for carrying out process design and optimisation; adjusting shortcut methods for column design to provide more accurate predictions; a large number of design alternatives; complex trade-offs within the separation flowsheet; and heat integration opportunities. Existing hybrid membrane-distillation design and optimisation methodologies (Caballero et al., 2009 and Koch et al., 2013) do not consider the opportunity for heat integration. In low-temperature processes, there might be a great opportunity to reduce the energy cost of the process by recovering
heat between the separation systems and between the refrigeration system and the separation systems. However, heat integration makes the design more complex due to the requirement of a heat recovery model and refrigeration design model in addition to the separation unit models. This research aims to overcome some of the shortcoming of the previous work by developing a systematic approach to model, evaluate and optimise hybrid membrane-distillation processes, while taking into account heat recovery opportunities.

The objectives of this work are to:

1. Establish models for all relevant unit operations. Develop a simple and robust membrane model for multicomponent mixtures and different flow patterns. Adapt existing shortcut models for distillation columns.

2. Develop a systematic design methodology for identifying technically and economically attractive separation flowsheets composing membrane separations, and/or a conventional distillation column.

3. Develop a systematic approach to incorporate heat recovery options during process design.

4. Develop an optimisation framework to find the optimum flowsheet structure and operating conditions to achieve the desired separation specifications. Important degrees of freedom in design, including membrane types, membrane permeate pressures, fraction of feed permeated or membrane area, side draw rate and column operating pressure will be variables to be optimised.

5. Implement the optimisation approaches in a suitable software environment.

6. Propose a modelling approach to represent the refrigeration performance. The refrigeration model should be simple, reliable and suitable for application within an optimisation framework for screening and evaluation of process design alternatives.

7. Apply the design framework to different case studies.

### 1.3 Outline of the Thesis

Chapter 1 presents a general background, describes the motivation and objectives of the research. Chapter 2 then reviews previously published work on hybrid
membrane-distillation systems and existing approaches to membrane and distillation modelling. In addition, a summary is provided of a literature search on membrane materials and models of transport mechanism for olefin/paraffin separations.

Chapters 3 and 4 propose mathematical models for vapour-phase membrane separation and a modified shortcut method for distillation column design, respectively. Model validation is also presented. The effect of stage cut and permeate pressure on membrane performance is discussed and an effective solution strategy is proposed for the membrane model. In Chapter 4, the shortcut distillation design method is modified to improve the performance of the Underwood equations, which tend to underestimate the minimum reflux ratio.

Chapter 5 introduces a systematic design methodology that has been developed to simulate, screen and evaluate various separation flowsheets, including stand-alone distillation and membrane units, and several hybrid membrane-distillation configurations. Opportunities for heat recovery between the separation processes and the refrigeration system are considered in the approach. In order to demonstrate the effectiveness of the design approach, a case study involving the separation of ethylene-ethane mixtures is presented.

Chapter 6 describes the methodology for carrying out heat integration and introduces a new model for predicting the performance of refrigeration systems. Heat integration opportunities between the separation processes and the refrigeration system are considered and an illustrative example is provided to demonstrate the application of the methodology.

In Chapter 7, an optimisation framework for process synthesis and evaluation is proposed. The nonlinear optimisation problem is solved using a ‘global optimisation method’, where the design variables to be optimised and their boundaries are chosen based on a sensitivity analysis. Case studies are presented to demonstrate the applicability of the approach to the design of heat-integrated low temperature hybrid membrane-distillation systems. Chapter 8 presents the conclusions of the thesis and presents recommendations for future work.
Chapter 2 Literature Review

2.1 Introduction

The separation of close-boiling mixtures using conventional columns is still a challenging issue in process design. This separation is extremely expensive in terms of both capital and operating costs, especially because of refrigerated cooling requirements. As introduced in Chapter 1, three approaches can be used to improve the thermodynamic efficiency of the conventional distillation column. Among these, the combination of two separation units has gained considerable attention recently. Various studies have shown the economic advantages of implementing a hybrid membrane-distillation system for separating mixtures with low relative volatilities. This work will focus on ethylene-ethane separation. In this chapter, relevant research on the design and modelling of hybrid membrane-distillation systems are reviewed and discussed.

Membranes relevant to ethylene-ethane separation, such as facilitated transport membranes, are reviewed first. The limitations and advantages of ethylene-ethane separation using facilitated transport membranes are then discussed. The discussion is further extended to include membrane modelling and solution methods. Following this, the design methods for distillation columns are discussed. In addition, there is a description of research work on the extension and application of these design methods to the design of distillation columns with various hybrid membrane-distillation configurations. Finally, published work on hybrid membrane-distillation separation process design and optimisation is reviewed. It is seen here various researchers have applied these methods for the structural and parametric optimisation of hybrid separation systems. The shortcomings of previous work on the design and optimisation methods for hybrid systems are identified.
2.2 Membrane-based ethylene-ethane separation

Membranes are defined as permselective barriers or interfaces between two phases (Mulder, 1996). Transport across the membrane produces two streams: the retentate, which is depleted in some of its original components, and the permeate, which is concentrated in these components. This process is described schematically by the figure below. The driving force for transport of a species, in the case of gas or vapour membrane separation processes, is the pressure difference across the membrane (Mulder, 1996).

![Figure 2.1: Schematic process flow diagram of a simple membrane separation](image)

To achieve a high separation performance in terms of recovery and purity, a membrane must possess high permeance and a high selectivity or separation factor, which is defined as the ratio of the individual permeability, as shown in equation 2.1.

\[
\alpha_{ij} = \frac{P_{Mi}}{P_{Mj}}
\]  \hspace{1cm} (2.1)

\[
P_{Mi} = \delta \overline{P_{Mi}}
\]  \hspace{1cm} (2.2)

Where \(P_{Mi}\) is the permeability of component \(i\), \(\alpha_{ij}\) is the membrane selectivity, \(\delta\) is the membrane thickness and \(\overline{P_{Mi}}\) is the permeance of component \(i\). The permeance is defined similarly to a mass transfer coefficient (Smith, 2005) that is the flux per driving force (partial pressure):

\[
\overline{P_{Mi}} = \frac{N_i}{\Delta P}
\]  \hspace{1cm} (2.3)

Where \(N_i\) is the flux of component \(i\), which is the flowrate of component \(i\) per unit area of membrane, and \(\Delta P\) is the partial pressure difference across the membrane.
The separation factor identifies the degree of separation that can be achieved for a given membrane. For instance, if \( \alpha_{ij} = 1 \), separation is not possible; if \( \alpha_{ij} > 1 \), this implies that separation is easy. In this case, the permeate stream will be concentrated in \( i \) and the retentate stream concentrated in \( j \) and if \( \alpha_{ij} < 1 \), meaning that the permeate stream is concentrated in \( j \) and the retentate stream is concentrated in \( i \) (Kohl and Nielsen, 1997).

Selectivity indirectly impacts membrane area and directly impacts the recovery of products. The higher the selectivity, the higher the permeate purity of the fast permeating component \( i \). Meanwhile, the lower the recovery, the smaller the required membrane area and therefore, the lower the operating and capital costs of the membrane system (Korros and Mahajan, 2000).

Other important parameters that determine the performance of a membrane gas separation system are the stage cut and pressure ratio. Stage cut is the fraction of the feed that permeates the membrane, as given by equation 2.4. Pressure ratio is the ratio of permeate pressure to the feed side pressure across the membrane.

\[
\theta = \frac{F_p}{F_f}
\]  

Where \( \theta \) is the stage cut, \( F_p \) and \( F_f \) are the molar flow rates of the permeate and feed streams, respectively. In a membrane gas separation there is a trade-off between the permeate purity and recovery. A high permeate purity or high recovery can be achieved, but not both. This trade-off is characterised by stage cut.

Membrane selectivity is influenced by membrane materials, feed composition, temperature and pressure. In the literature, several membranes have been reported to separate ethylene and ethane, as summarised in Table 2.1. The membrane materials of these membranes range from inorganic solids such as carbon membranes to polymeric materials. In general, polymeric membranes have low selectivity for ethylene-ethane separation due to the similar molecular sizes and solubility of ethylene and ethane (Faiz and Li, 2012). Adding a carrier solution to the polymeric membranes enhances their separation performance. The carrier accelerates the transport of ethylene in the membrane; therefore, higher selectivity can be achieved compared to polymer membrane. This type of transport is called carrier-mediated
transport or facilitated transport (Mulder, 1996). Facilitated transport membranes can be classified as asymmetric composite membranes. Asymmetric membranes contain pores which increase in size from one side of the sheet to the other (Ismail et al., 2002). Composite membranes consist of a thin dense layer called the ‘permselective’ layer and a porous support. The selective layer needs to be thin to achieve high fluxes.

Table 2.1: Membrane types for ethylene-ethane separation

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Selectivity $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMs</td>
<td>3.3 – 3.4</td>
<td>Tanaka et al., 1996; Staudt-Bickel and Koros, 2000</td>
</tr>
<tr>
<td>CMS</td>
<td>2 – 11</td>
<td>Hayashi et al., 1996; Yoshino et al., 2003; Fuertes and Menendez, 2002; Xu et al., 2011; 2012; Rungta et al., 2012; 2013</td>
</tr>
<tr>
<td>ILM</td>
<td>1000 – 1100</td>
<td>Teramoto et al., 1986; Hayashi et al., 1996</td>
</tr>
<tr>
<td>IEM</td>
<td>243</td>
<td>Hughes et al., 1986</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>LeBlanc et al., 1980; Kraus, 1986</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Ericksen et al., 1993</td>
</tr>
<tr>
<td>SPEM</td>
<td>26</td>
<td>Morisato et al., 2002</td>
</tr>
<tr>
<td></td>
<td>260 – 120</td>
<td>Pinnau and Toy, 2001</td>
</tr>
<tr>
<td></td>
<td>18 – 68</td>
<td>Merkel et al., 2007; Merkel et al., 2013</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Hamza, et al., 2013</td>
</tr>
</tbody>
</table>


Facilitated transport membranes (FTMs), particularly immobilized liquid membranes and solid polymer electrolyte membranes are among the most promising with respect to their selectivity. Immobilized liquid membrane can be defined as pores membrane that held a carrier solution within its pores by capillary force (Faiz and Li,
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The carrier solution facilitates selectively for olefin transport across the membrane.

Immobilized liquid membranes incorporate the metal ions into membranes where the ions form a selective complex with olefin molecules and provide them with a pathway across the membrane. It has been reported that copper and silver are the most viable metals for use in olefin separation because of the reversibility of the complexes, as well as their safety and low cost (Azhin et al, 2008).

The ability of a carrier to form a complex depends significantly on its electronegativity and its salt’s lattice energy (Ravanchi et al., 2010). In the literature, silver nitrate was mostly used as a carrier solution because it has a relatively low cost; it reacts reversibly with ethylene; it is highly soluble in water; and solutions of up to 8.5M in silver ions can easily be prepared (Norman and Joseph, 1992). Another potential ethylene-ethane separating agent is silver tetra fluoroborate (AgBF$_4$). A high concentration of this carrier solution effectively frees more silver ions to complex with olefins when dispersed in a polymer electrolyte (Azhin et al., 2008). This, in turn, helps to increase the membrane selectivity.

Solid polymer electrolyte membranes are membranes in which a metal salt is dissolved in a polymer matrix (Faiz and Li, 2012). The metal salt dissociates into anions and cations that are sufficiently mobile, so no solvent or plasticizer is required to promote ionic motion and conductivity (Rungta et al., 2013a). Salt ions facilitate the transport of olefin across the membrane, which results in an increase in permeability and selectivity of the membrane.

There are different mechanisms by which the transport of olefin occurs in facilitated transport membrane. Mass transfer mechanisms that have been suggested for olefin-paraffin transport through facilitated transport membranes are discussed below.

2.2.1 Transport mechanisms through facilitated transport membranes

2.2.1.1 Immobilized liquid membranes

In this type of membrane, two processes occur simultaneously. Part of the olefin is transported by diffusion whilst another part is transported by solute-carrier
complex diffusion (Pinna and Toy, 2001). On the feed side (high-pressure side) of
the membrane, both olefin and paraffin sorb into the membrane. However, only
olefins such as ethylene form a complex with the silver-ion carrier, as shown in
equation 2.6, providing a significantly increased solubility of olefin compared to
paraffin (Mulder, 1996) and enhancing olefin movement across the membrane
(Merkel et al., 2013).

When the complex reaches the permeate side (low-pressure side) of the
membrane, the complex decomposes, releasing the olefin (e.g. ethylene) molecules
into the low-pressure side (Pinna and Toy, 2001). At the same time as the olefin
molecule is transported selectively by silver complexation, both olefin and paraffin
(e.g. ethane) permeate by ordinary solution-diffusion (Mulder, 1996).

**Transport equations**

The total flux in immobilized liquid membrane is not directly proportional to the
concentration gradient due to the existence of two transport mechanisms in the
membrane: solution diffusion and diffusion of the carrier-solute complex (Mulder,
1996).

Equation 2.5 describes the flux equation when fast reaction takes place in the
membrane. Olefins such as ethylene can only react with the carrier, e.g. silver ions,
confined in the membrane.

\[
J_i = D_i \frac{(C_{i,f} - C_{i,p})}{\delta} + D_c \frac{(C_{i,f}^C - C_{i,p}^C)}{\delta}
\]  

(2.5)

Where

- \(D_i\): is the diffusivity constant of component \(i\) in the membrane.
- \(D_c\): is the diffusivity coefficient of the complex.
- \(C_{i,f}\): is the concentration of component \(i\) in the feed side.
- \(C_{i,p}\): is the concentration of component \(i\) in the permeate side.
- \(C_{i,f}^C\): molar concentration of the silver-component complex in the feed.
- \(C_{i,p}^C\): molar concentration of the silver-component complex in the permeate.
The ethylene flux depends on the concentration of the silver ions and the equilibrium constant for the reaction between the silver ion and ethylene as indicated in equation 2.6 (Teramoto et al., 2002).

\[
\text{C}_2\text{H}_4 + \text{Ag}^+ \rightleftharpoons [\text{AgC}_2\text{H}_4]^+ \quad \text{(Complex)} \quad (2.6)
\]

The equilibrium constant in equation 2.6 can be calculated as follows:

\[
K_{eq} = \frac{C^C}{C_{C_2H_4} C_{Ag^+}} \quad (2.7)
\]

Where

- \(K_{eq}\): equilibrium constant.
- \(C^C\): molar concentration of the silver-ethylene complex in the membrane.
- \(C_{Ag^+}\): molar concentration of the carrier in the membrane.
- \(C_{C_2H_4}\): molar concentration of ethylene in the membrane.

The total carrier concentration, \(C_T\), inside the membrane can be obtained from the following mass balance equation (Teramoto et al., 1986 and Teramoto et al., 2002):

\[
C_T = C^C + C_{Ag^+} \quad (2.8)
\]

Combining equations 2.7 and 2.8, and solving for the concentration of complex, yields equation 2.9.

\[
C^C = \frac{K_{eq} C_{C_2H_4} C_T}{1 + K_{eq} C_{C_2H_4}} \quad (2.9)
\]

The solute concentration in the membrane can often be related to the gas phase partial pressure using Henry’s law or a similar equilibrium relationship (Ho and Sirkar, 1992). Equation 2.10 describes the relationship between the concentration of and the partial pressure component \(i\):

\[
C_i = \frac{P_i}{H_i} \quad (2.10)
\]

Where

- \(H_i\): Henry’s coefficient of species \(i\).
- \(P_i\): partial pressure of component \(i\) on the feed side or permeate side.
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For a constant membrane permeability and approximately ideal vapour-phase behaviour, equation 2.10 at the feed and permeate sides can be described as follows:

\[ C_{i,f} = H_{i}P_{f}x_{i,f} \]  
(2.11)

\[ C_{i,p} = H_{i}P_{p}y_{i,p} \]  
(2.12)

Where \( P_{f} \) is the membrane feed pressure; \( P_{p} \) is the membrane permeate pressure; \( x_{i} \) is the mole fraction of component \( i \) at the feed side and \( y_{i} \) is the mole fraction of component \( i \) at the permeate side.

By assuming that reaction equilibrium holds at the feed-side and permeate-side (Gottschlich et al., 1988), equation 2.9 can be described as follows:

\[ C_{C_{2}H_{4},f}^{\text{eq}} = \frac{K_{eq}C_{C_{2}H_{4},f}C_{T}}{1 + K_{eq}C_{C_{2}H_{4},f}} \]  
(2.13)

\[ C_{C_{2}H_{4},p}^{\text{eq}} = \frac{K_{eq}C_{C_{2}H_{4},p}C_{T}}{1 + K_{eq}C_{C_{2}H_{4},p}} \]  
(2.14)

Substituting equations 2.11 to 2.14 into equation 2.5 yields the transport equation of ethane and ethylene across the membrane. The assumptions used to obtain equations 2.15 and 2.16 are: steady state operation, isothermal process, instantaneous reaction, the reversible reaction inside the membrane is at equilibrium, constant membrane permeability and pressure drop is negligible along the membrane. The porosity and tortuosity factors are included in equations 2.15 and 2.16 to account for the possibility of membrane consisting of microporous and tortuous path filters immersed in liquid membrane (Gottschlich et al., 1988).

\[ J_{C_{2}H_{6}} = \frac{\varepsilon}{\delta \nabla H_{C_{2}H_{6}}} D_{C_{2}H_{6}} \left( \frac{P_{C_{2}H_{6},f} - P_{C_{2}H_{6},p}}{\delta} \right) \]  
(2.15)

\[ J_{C_{2}H_{6}} = \frac{\varepsilon D_{C_{2}H_{6}} \left( P_{C_{2}H_{6},f} - P_{C_{2}H_{6},p} \right)}{\delta \nabla H_{C_{2}H_{6}}} + \frac{\varepsilon D_{C_{2}H_{6}}K_{eq}C_{T}}{\tau \nabla H_{C_{2}H_{6}}} \left[ \frac{P_{C_{2}H_{6},f}}{1 + K_{eq} \left( \frac{P_{C_{2}H_{6},f}}{H_{C_{2}H_{6}}} \right)} \right] - \frac{P_{C_{2}H_{6},p}}{1 + K_{eq} \left( \frac{P_{C_{2}H_{6},p}}{H_{C_{2}H_{6}}} \right)} \]  
(2.16)
Where

\[ \varepsilon: \text{ membrane porosity (a measurement of the open space in a membrane).} \]
\[ \tau: \text{ membrane tortuosity (the membrane tortuosity reflects the length of the average pore compared to the membrane thickness).} \]

2.2.1.2 Solid polymer electrolyte membranes

The mechanism proposed for transport across a solid polymer electrolyte membrane occurs via random jumps or hops by olefin molecules from one salt ion site to the other in a rubbery polymer matrix (Pinna and Toy, 2001; Merkel et al. 2007; Faiz and Li, 2012).

Vapour permeation can be described in the following steps:

- Adsorption and dissolution of vapour molecules at the polymer membrane interface.
- Diffusion of the molecules in and through the bulk polymer. In the diffusion stage, the silver ions, which originated from the dissociation of a metal salt such as AgBF\(_4\) that is dissolved into the polymers matrix, form a complex with olefin.
- The olefin-silver ion complex then transports from site to site by a hopping mechanism until it reaches the low-pressure side, where the silver releases the olefin (Faiz and Li, 2012). The uncomplexed molecules, which cross the membrane by diffusion, also desorb into the low-pressure side of the membrane. The rate of facilitated transport of olefin is much faster than the rate of solution-diffusion of uncomplexed molecules across the membrane. Therefore, the olefin diffuses faster than paraffin through the membrane.

Transport equations

The movement of vapour molecules in a solid polymer electrolyte membrane can be described by Fick’s first law (Pinna and Toy, 2001; Morisato et al., 2002). The assumption here is that a concentration gradient is the driving force across the membrane. Accordingly, the transmembrane flux \( J_i \) of component \( i \) is defined as shown in equation 2.17.
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\[ J_i = \frac{D_i(C_{i,f} - C_{i,p})}{\delta} \]  

(2.17)

Where

- \( J_i \): is the flux (mole flow per unit area).
- \( D_i \): is the diffusivity constant of component \( i \) in the membrane.
- \( C_{i,f} \): is the concentration of component \( i \) in the feed side.
- \( C_{i,p} \): is the concentration of component \( i \) in the permeate side.

When the solubility of a penetrant gas in a membrane is sufficiently low, the concentration of the penetrant is proportional to the pressure of penetrant in the membrane (Mulder, 1996). This relationship is expressed as shown in equation 2.18.

\[ C_i = s_i P_i \]  

(2.18)

Where

- \( C_i \): is the concentration of component \( i \) (mole cm\(^{-3}\)).
- \( s_i \): is the solubility coefficient of component \( i \) (cm\(^3\) (STP) cm\(^{-3}\) bar\(^{-1}\))
- \( P_i \): is the pressure of the penetrant (bar)

Under the assumption of constant diffusivity and solubility (i.e. membrane permeability is independent of temperature, pressure and concentration) and applying Henry’s law, then equation 2.17 can be rearranged to yield

\[ J_i = \frac{P_{Mi}(P_f x_i - P_p y_i)}{\delta} \]  

(2.19)

Equation 2.19 describes the steady state flux of component \( i \) in a passive transport membrane (solution-diffusion is the controlling mechanism of molecule transport). The other basic assumptions that have been made in driving equation 2.19 are the system operates at isothermal conditions and pressure drop is negligible along the membrane.

\[ P_{Mi} = D_i s_i \]  

(2.20)

Where

- \( P_{Mi} \): is the permeability of component \( i \)
- \( P_f \): is the feed pressure (high-pressure side)
\( P_p \): is the permeate pressure (low-pressure side)
\( x_i \): is the mole fraction of component \( i \) in the feed side
\( y_i \): is the mole fraction of component \( i \) in the permeate side

### 2.2.2 Flow patterns

The performance of a membrane separator is affected by the relative flow directions of the bulk feed and permeate streams (Ho and Sirkar, 1992). Figure 2.2 shows the four idealized flow patterns in membrane separation. In the perfect mixing configuration, as shown in Figure 2.2(a), both the feed and permeate sides of the membrane are well mixed. Figure 2.2(c) shows a co-current flow pattern in which the flow of fluid on the high-pressure side is parallel to the flow of fluid (the permeate stream) on the low-pressure side. In cross-flow, the fluid permeates to the low-pressure side of the membrane and flows perpendicular to the membrane, while the fluid on the high-pressure side of the membrane flows parallel to the membrane surface, as shown in Figure 2.2(b). In the counter-current flow case, as illustrated in Figure 2.2(d), the permeate and feed streams flow in opposite directions along the membrane.

Counter-current provides the highest purity and the lowest membrane area compared with the other flow patterns for a given separation problem (Shindo et al., 1985). The next best separation performance can be achieved by cross-flow,
followed by co-current. In practice, it is not consistently clear as to which idealized flow pattern is assumed (Ho and Sirkar, 1992). The flow pattern depends on the membrane configuration, the permeation rate and, therefore, the stage cut (Smith, 2005). For example, in asymmetric composite membranes, the permeate purity is a function only of the material passing through the membrane, and it is not a function of the bulk permeate stream. In this case, a cross-flow can be used to describe the module performance (Kohl and Nielsen, 1997).

### 2.2.3 Membrane module configurations

Mainly, two types of membrane module are used for membrane gas separation processes including hollow-fibre membranes and spiral-wound membranes (Smith, 2005). In the spiral wound module, a set of flat membrane envelopes is rolled into a cylinder. ‘The flat membranes envelopes are separated by spacers for the flow of feed and permeate are wound into a spiral and introduced in a pressure vessel’ (Smith, 2005). In a hollow-fibre configuration, cylindrical membranes are bundled together in an arrangement like a shell-and-tube heat exchanger (Smith, 2005). Hollow-fibre modules can be operated in three different configurations, as shown in Figure 2.3 (Ho and Sirkar, 1992). Generally, the choice between these configurations is based on the separation to be performed. For example, in hydrogen separation, shell-side feed is usually used. This configuration minimizes the pressure drop between the feed and retentate streams (Ho and Sirkar, 1992).

![Figure 2.3: Flow schemes for hollow-fibre permeators (Ho and Sirkar, 1992)](image_url)

Hollow-fibre membranes are used commonly for gas separation due to their high surface area, compactness, lack of support requirements, optional positioning of feed flow, i.e., the feed flows inside or outside the fibre tubes (Ho and Sirkar, 1992 and...
Shamsabadi et al., 2012), and low investment and operating costs (Ferraz et al., 2007). Hollow-fibre membranes have approximately three times as much area per unit volume as spiral-wound units (Ho and Sirkar, 1992). Therefore, this configuration has been investigated in the application of olefin-paraffin gas separation processing by Hughes et al., 1986; Teramoto et al., 2005; Faiz et al., 2013 and Hamza et al., 2013.

The shortcomings and advantages of the facilitated transport membranes presented in Table 2.1 are discussed in detail in the following section.

2.2.4 Review of key features of facilitated transport membranes

Steigelman and Hughes (1973) and Teramoto et al. (1986) were the first to investigate immobilized liquid membrane for ethylene-ethane separation. Teramoto et al. (1986) reported that the permeability ratio of ethylene to ethane was 1000 when a carrier silver nitrate concentration was 4 mole /l. However, ILMs were considered to be impractical for industrial applications due to evaporation of carrier solution from the membranes during operation and also because of transmembrane pressure and chemical stability issues (Teramoto et al., 1986 and Teramoto et al., 2002). ILMs suffer from chemical stability problems due to chemical degradation of the carrier by irreversible reactions with some components in the feed mixture such as acetylenes, hydrogen and hydrogen sulphide (Hughes et al., 1986). The presence of acetylene and sulphur compounds in the feed stream might cause damage or series operation problems in the membrane. For instance, when the silver ion reacts with acetylene, it forms silver acetylide, an explosive compound (Pinnau and Toy, 2001).

In order to overcome the aforementioned shortcomings, different approaches have been proposed. Hughes et al. (1986) used a dense surface skin on the hollow-fibre to reduce the availability and mobility of the carrier solution. They presented the results of a bench and pilot-scale study of ethylene and propylene transport using aqueous silver ion solutions immobilized in asymmetric, porous hollow-fibre reverse osmosis membrane at ambient temperature. Although hollow-fibre membrane was used, the high membrane thickness reduces the olefin permeation rate. Another major issue with this membrane was the need to humidify the membrane periodically with water vapour (Hughes et al., 1986). Humidification is needed to stabilise the membrane,
which used an aqueous silver solution. If silver salts lose their solvent, the silver ions will no longer be available to facilitate olefin transport. This is turn will lead to a drop in membrane selectivity.

To prevent the membrane from drying out, Teramoto et al. (2002) proposed using a bulk flow liquid membrane, where a carrier solution is circulated between the feed and the permeate side of the ultrafiltration membrane. The transport of ethylene as a free molecule and also as a complex across the membrane occurs by solution-diffusion as well as by convection. Teramoto et al. (2002) reported an ethylene permeability of $4 \times 10^{-5}$ mole m$^{-2}$ s$^{-1}$ kPa$^{-1}$ and selectivity of 1100 when the partial pressure of ethylene was 9 kPa. Although the bulk flow liquid membrane was more stable than immobilized liquid membrane, both the low gas permeance per module volume and its chemical instability significantly affect the bulk flow liquid membrane separation performance, as well as its life time (Faiz and Li, 2012). As a solution to part of the chemical instability problem, particularly silver ion poisoning by sulphur compounds, Keller et al. (1992) proposed a feed pre-treatment.

Solid polymer electrolyte membranes have overcome most of the limitations of FTM s, including poor mechanical stability, the adversity in advancing high-flux composite membrane and the requirement to operate in a humidified environment (Pinnau and Toy, 2001). In contrast to ILMs, solid polymer electrolyte membranes can handle a higher pressure difference across the membranes without the loss of the complexing agent (Rungta et al., 2013). In ILM, the high pressure difference across the membrane can lead to pushing a carrier solution out of the membrane pores, causing a drop in selectivity. In SPEM, no solvent is required because the salt dissolves into a polymer matrix in a solid state. The polymer matrix is rubbery and provides enough chain flexibility to facilitate olefin transport across the membrane (Pinnau and Toy, 2001).

The performance of a solid polymer electrolyte membrane depends on the selection of polymer material, the metal salts, and the carrier concentration (e.g. Pinnau and Toy, 2001; Morisato et al., 2002; Faiz and Li, 2012; Merkel et al., 2013; Hamza et al, 2013).
Pinnau and Toy (2001) investigated experimentally the effects of AgBF$_4$ carrier concentration and feed pressure on pure and mixed gas permeation properties of a rubbery polyethylene oxide/AgBF$_4$ composite membrane. Pinnau and Toy (2001) obtained a high selectivity using AgBF$_4$ in polyethylene oxide (PEO) for an ethylene-ethane mixture. The best performance was achieved when the concentration of AgBF$_4$ was 80 wt%. However, significantly lower ethylene-ethane selectivity was achieved for mixed gases compared to pure gases. The ethylene-ethane selectivity was 120 for mixed gases (feed composition: 50 vol% C$_2$H$_4$ and 50 vol% C$_2$H$_6$) and 5500 for pure gases when the concentration of AgBF$_4$ was 80 wt%, while feed pressure was 100 psig and temperature was 23°C. The reduction in membrane selectivity was attributed to the increase of paraffin permeance (Pinnau and Toy, 2001 and Merkel al at., 2013). The movement of the olefin particles through the membrane causes more motion in the chain of polymer matrix, allowing easier transit to the paraffin particles (Pinnau and Toy, 2001).

In PEO/AgBF$_4$ membrane, olefin permeance and selectivity were reported to decrease with increasing feed pressure due to a partial saturation of the membrane (Pinnau and Toy, 2001). The mixed ethylene-ethane selectivity decreased from 260 to 120 when the feed pressure increased from 25 to 100 psig. Although solid polymer electrolyte membranes have exhibited a practical physical stability, their chemical instability caused by degradation of silver ion, remains a problem (Morisato et al., 2002 and Merkel et al., 2007). For example, exposure to light or water can accelerate the reduction of silver ion to silver nanoparticle, which is an inactive olefin carrier (Faiz and Li, 2012 and Merkel al at., 2013). Furthermore, silver ions are very sensitive to traces of hydrogen sulphide, and regeneration of silver-containing solid polymer electrolyte membranes is difficult (Merkel al at., 2013).

Morisato et al. (2002) also studied a solid polymer electrolyte membrane based on a rubbery nylon-12/tetramethylene oxide block copolymer (PA12-PTMO) matrix material containing silver tetra fluoroborate (AgBF$_4$). PA12-PTMO/ 90 wt% AgBF$_4$ was tested using a mixed gas of 70/30 vol% (C$_2$H$_4$/C$_2$H$_6$) at 50 psig and 22°C. This membrane showed long-term stability of ethylene-ethane selectivity, with a range of 25 - 20 and high ethylene flux of 2 ×10$^{-5}$ cm$^3$ (STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$ lasting 14 days.
Unfortunately, the drawbacks mentioned previously, such as chemical instability, still exist.

Merkel et al. (2007) extended the laboratory work of Pinnau and Toy (2001) and performed further investigation on solid polymer electrolyte membranes. A polyether-polyamide block copolymer (Pebax® 2533) doped with 80 vol% of AgBF$_4$, as facilitation salt, was found to provide a suitable ethylene permeance and selectivity. With an ethylene molar feed purity of 65%, the ethylene permeance decreased from $8 \times 10^{-5}$ to $2 \times 10^{-5}$ cm$^3$ (STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$ and selectivity from 68 to 20 when the operating pressure increased from 50 to 125 psig. Merkel et al. (2007) reported a new phenomenon called ‘olefin-condition’ which was the main cause of instability in these membranes, in addition to the carrier poisoning. To date, there is no an effective strategy to mitigate the impact of this phenomenon (Rungta, et al., 2013), except working at a low temperature, such as 5ºC, or low olefin feed pressure (Merkel et al., 2007).

Recently, Merkel et al. (2013) suggested an in-situ regeneration technique to mitigate the effect of light and/or reduced silver salts such as hydrogen and acetylene. They used a peroxide/acid liquid or vapour phase to stabilise silver ions within the membrane. The results they published illustrated the ability of their proposed technique to restore Pebax 2533 plus 80 wt% AgBF$_4$ membrane performance. This new finding can contribute to solving series issues that prevent the commercial application of solid polymer electrolyte membranes. However, the performance of the membrane exposed to H$_2$S cannot be restored by treatment with liquid or vapour mixtures of hydrogen peroxide/tetrafluoroboric acid. Therefore, more research needs to be carried out.

The long-term stability issues of solid polymer electrolyte have been addressed by Hamza et al. (2013) through the use of ‘Chitoson based Imex membrane’ and AgNO$_3$ as a facilitation agent for ethylene-ethane separation. Two units with small coupons and spiral wound elements were used. The membrane performance in terms of permeate purity and selectivity was tested for range of ethylene feed mole fractions from 20 to 90 % and operating feed pressure range 60 to 360 psig. The membrane showed stable performance for 1500 hours and ethylene purity was as high as 99.5%. Using a spiral wound module, selectivity of greater than 100 was
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achieved for a (80/20) mol% \( C_2H_4/C_2H_6 \) mixture, with a feed pressure of 60 psig at ambient temperature. However, the impact of carrier poisoning on membrane performance has not been investigated by Hamza et al. (2013).

2.2.5 Summary of membrane materials for ethylene-ethane separation

The literature review demonstrates that FTMs can increase both permeability and selectivity. FTMs can be configured in hollow-fibre geometry, which are the most common practical arrangements for use in membrane gas separation processes. However, long-term stability is the major issue preventing the commercial use of these membranes. FTMs generally work at ambient temperature; however, ILMs can operate at temperatures as low as \(-30^\circ\text{C}\) at an operating pressure of 20 bar (Al Rabiah, 2001). However, below this temperature, the carrier solution freezes (Al Rabiah, 2001), thereby losing its function as a facilitation agent. In contrast to ILMs, SPEMs are able to work at lower temperature because the olefin molecule forms a complex with silver ions that is available in the polymer matrix. The ability to operate at low temperature is a distinct characteristic that is very useful for separating below ambient temperature mixtures, and this needs to be investigated.

From the foregoing, it is clear that further study of facilitated transport membranes is required to improve their stability and develop a reasonable lifetime. Nevertheless, the potential advantages of this type of membrane in membrane-assisted hybrid separation system could provide an incentive to further research.

To predict and analyse the separation performance of the membrane module, and thereafter to carry out the design and optimisation of hybrid membrane-distillation systems, an appropriate membrane model and a robust solution method are needed. The following section provides a review of published research on membrane modelling.

2.2.6 Membrane modelling

Extensive research has been conducted on modelling single membrane stages and membrane networks. Mathematical modelling of membrane gas separators was first addressed by Weller and Steiner (1950). Since then, various mathematical models and calculation methods have been reported in the literature. The membrane model
analysed here is the one based on the transport mechanisms discussed in Section 2.2.1

The literature contains exact and approximate models for describing the separation performance of membrane modules. Approximate models are used for quick design calculations and these involve making certain assumptions to simplify the models. For instance, Naylor and Backer (1955) derived an analytical expression to calculate permeate purity for a binary mixture in a cross-flow module. The derived equations were based on the assumptions of constant pressure ratio and constant separation factor. The film mass-transfer coefficient on either side of the membrane was also assumed to be negligible. These assumptions helped to develop simple analytical expressions that were used to calculate the permeate purities and the membrane area requirement. A detailed description of the approximate model of Naylor and Backer (1955) can be found in the textbook of Seader and Henley (1998). Although the rate of molecules diffusion is expressed in terms of Fick’s law, the approximate model of Naylor and Backer (1955) can be used to describe other types of transport.

Teramoto et al. (1986) presented an approximation method for calculating the flux rate of facilitated transport accompanied by an instantaneous reversible reaction for ethylene separation. The expression for total flux of \( \text{C}_2\text{H}_4 \) through the membrane is introduced as a function of ethylene and complex \( (\text{C}_2\text{H}_4-\text{Ag}^+) \) concentrations on both sides of the membrane. To solve the flux equation, it is assumed that the concentration profiles of the complex and carrier \( (\text{Ag}^+) \) are linear. This assumption helps to obtain the concentration of the complex and carrier in the sweep gas-membrane interface as a function of the concentration of the permeate species \( (\text{C}_2\text{H}_4) \) in feed and permeate sides. The approximation method of Teramoto et al. (1986) requires knowing the ethylene concentration in the feed and permeate sides and therefore cannot be applied to predict the separation performance.

Krovvidi et al. (1992) provided approximate solutions to the governing equations that describe the membrane module performance with co-current and counter-current flow pattern. However, their model was limited to ordinary diffusive transport, binary mixtures and the model equations are complex and highly non-linear
(Pettersen and Lien, 1994), making it difficult to extend their approximate method to other types of transport.

In the detailed model, the membrane module is divided into small elements where the variation in fluid properties throughout the module is measured (Marriott et al., 2003). Separation performance is described by differential equations, which are derived from mass balance and flux equations. Different techniques are used to solve the governing equations that describe the membrane separation performance. The selection of solution method depends on the type of problem and the operating conditions (Tessendorf et al., 1999; Coker and Freeman, 1998).

In this section, exact models are reviewed and various solution methods are discussed. The review is not restricted to binary mixtures since practical systems involve multicomponent mixtures.

Shindo et al. (1985) developed mathematical models and calculation methods for a multicomponent gas separation for five flow patterns: co-current, counter-current, crosscurrent flow, perfect mixing and one-side mixing. The model was based on the assumption of negligible pressure drops in the feed-side and permeate-side. The model equations were solved using both the Newton method to calculate the permeate composition, and the Runge-Kutta-Gill method for solving the ordinary differential equations.

The numerical methods used by Shindo et al. (1985) have some shortcomings. Among them are slow convergence, sensitivity to initialisation and inaccurate prediction at a range of operating conditions. To solve the model of Shindo et al. (1985), an initial guess of permeate purities inside the module was required in the case of co-current, counter-current and cross-flow patterns. It is difficult to assume initial estimates of permeate purities inside the module, especially for multicomponent mixtures. Mathematical modelling the membrane problem for the purpose of designing it results in nonlinear differential equations. Very fast permeating component with a small feed purity can cause stiffness in the differential equations (Tessendorf et al., 1999) and varying feed compositions and permeabilities at high stage cuts or low pressure ratios can cause convergence problems (Coker and Freeman, 1998). Still, the solution method of Shindo et al. (1985) is good for the
prediction of permeate and retentate purities as long as the problem is stable and good initial guesses are given.

Gottschlich et al. (1988) investigated a spiral-wound facilitated transport membrane for the separation of a CO$_2$/CH$_4$ mixture. They compared the performance of ion exchange membrane including ethylenediamine, as a facilitation agent, and the conventional solution-diffusion cellulose membrane module. The model presented by Gottschlich et al. (1988) was developed using the procedure of Shindo et al. (1985). The developed model was based on the assumption of negligible pressure drops and applied for a cross-flow pattern. To solve the model equations, the integration solution method used by Shindo et al. (1985), particularly Runge-Kutta, is implemented. A similar approach has been used by Pettersen et al. (1996) and Al-Rabiah (2001) for solving the governing equations that describe molecules transport through a facilitated transport membrane unit. However, the sensitivity of the solution method to initial estimates and to the operating conditions was not discussed.

To develop the equations that describe the flux characteristic and to possibly overcome the drawbacks of the conventional numerical methods of Shindo et al. (1985), different approaches and solution methods have been suggested. The proposed solution methods are: fourth order Runge-Kutta method (David, 2007), trial and error shooting technique (Lin., 1996), finite element and orthogonal collocation (Marriott et al., 2001; 2003).

Coker et al. (1998) presented mathematical models for various flow patterns, taking into account pressure drop on the bore side of the hollow-fibre membrane. The flux through the membrane is described by solution-diffusion theory. In their work, the membrane area is divided into incremental area, where the resulting system of equations is solved using ‘Newton- Raphson’ method.

Although the method proposed by Coker et al. (1998) provides a rapid and stable solution for multicomponent mixtures at high stage cuts with wide variations in permeability coefficients, an initial estimate of the flow rates on each stage in the algorithm is necessary. For the counter-current model, an initial estimate of the component flow rate is obtained by solving a cross-flow model. In process synthesis
and design, it is not practical to run cross-flow first to get an initial estimate of the flow rate or purity profile inside the module. Therefore, what is required is another solution strategy that does not need to carry out a detailed simulation model for calculating the flow rate profile inside the module.

Furthermore, a higher number of incremental areas are needed in order to obtain an accurate solution at high stage cut as reported by Coker et al. (1998). A high number of incremental areas prolongs the solution convergence time. Therefore, a more efficient computation algorithm is needed. The algorithm should be robust enough to give accurate predictions for a variety of mixtures, membrane materials and operating conditions.

For the same separation problem investigated by Coker et al. (1998), David (2007) proposed a new approach to solve the nonlinear differential equations using what he called ‘start-up algorithm’. In this method, the nonlinear membrane model is first solved with a permeate pressure of zero. Then, the permeate pressure increased by an increment. The permeate composition profile obtained from the first iteration was used as an initial estimate in the next iteration. The procedure is repeated until the predefined permeate pressure is reached. Although the ‘start-up’ method does not require an initial estimate of the permeate purities, David (2007) found that the algorithm is unstable at low pressure ratios and failed to converge at high recovery for the fast permeating component.

Lin. (1996) developed a model for predicting the gas separation performance of a hollow fibre module with facilitated transport membrane taking into account pressure drop inside the fibre. However, the model was limited to a binary mixture. To solve the counter-current and co-current mode, a trial and error ‘shooting method’ is suggested. The shooting method is robust as long as the problem is stable, and a good initial estimate is provided (Tessendorf et al., 1999). Providing an initial estimate is not trivial in the counter-current case or for a multicomponent mixture, thus, a more robust algorithm for solving such type of flow pattern mode is needed.

Kaldis et al. (2000) presented a mathematical model for multicomponent mixtures using asymmetric hollow-fibre membranes, whereby the transport mechanism through the membrane was described by solution-diffusion theory. Kaldis et al.
(2000) implemented the orthogonal collocation technique to approximate differential equations and to solve the resulting system of nonlinear algebraic equations by the Brown method (Brown, 1967). Orthogonal collocation technique offers more accurate solutions, with less computation time, as compared to Runge-Kutta (Finlayson, 1980; Villadsen and Michelsen, 1978 cited in Kaldis et al., 2000). Reducing the simulation time allows exploration of more design variables (e.g. feed composition, stage cut and pressure ratio) that influence the membrane separation performance. In addition, the reduction in execution time enables fast prediction, something that helps in performing an economic evaluation of separation alternative. Although the approach proposed by Kaldis et al. (2000) might not suffer from the disadvantages of conventional techniques, such as sensitivity to the initial estimate of the permeate composition profile and permeate pressure, as reported by Kaldis et al. (2000), the accuracy of the solution depends on the number of collocation points, which is not obvious (Lefevre et al., 2000).

Marriott et al. (2001; 2003a; 2003b) developed a detailed membrane model that is used for a range of applications such as pervaporation, gas separation and reverse osmosis. The model considers many challenging issues such as two-dimensional flow patterns, non-isothermal temperature, multicomponent mixtures, steady-state and dynamic conditions and variable physical properties. Finite difference and orthogonal collocation methods are used for the solution. The orthogonal collocation method was better than finite difference for solving the model equations, as it uses fewer equations and that reduces solution time (Marriott et al., 2001).

However, these numerical methods are normally unbounded (i.e. no limit is employed on the variable). Unbounding could permit the appearance of unphysical oscillations (e.g. negative mole fraction) in the computed solution (Cruz et al., 2005). The permeate purity should be bounded between zero and one to avoid convergence to a physically unfeasible solution and to eliminate computational failure (i.e. the algorithm will no longer be able to proceed the calculations with negative mole fraction). Another limitation is that the model requires knowledge of two important properties—molecular diffusivity and solubility—that are difficult to measure in asymmetric membranes (Mohammad et al, 2005).
Recently, Azhin et al. (2010), Ravanchi et al. (2010b) also applied orthogonal collocation methods to facilitated transport membrane. However, the main focus of these researchers was on the calculation of facilitation factor across the membrane in the case of an instantaneous reaction between the olefin and carrier. Facilitation factor is defined as the ratio of permeate flux with carrier to the ratio of permeate flux without carrier.

### 2.2.7 Summary - Mathematical models of membrane

Membrane performance has been described by both detailed and approximate methods. The accuracy and complexity of the models depend on their assumptions: type of flow configurations (Shindo et al., 1985 and Coker and Freeman, 1998), the influence of pressure drop (Kaldis et al., 2000), temperature (Marriott et al., 2001; 2003), dynamic state, i.e. steady-state or not, (Marriott et al., 2001; 2003) and system behaviour, i.e. real or ideal system, (Tessendorf et al., 1999).

To solve the differential equations governing the molecules transport across the membrane, it is necessary to make an initial estimate for composition or flow rate (e.g. Kaldis et al., 2000; Coker and Freeman, 1998; Shindo et al., 1985). Coker et al. (1998) and Shindo et al. (1985) generated the initial estimates for counter-current flow from cross flow. Tessendorf et al. (1996) obtained the initial estimate of counter-current model from a perfect mixing flow pattern. Random assumptions without bounding on the compositions \(0 \leq \text{mole fractions} \leq 1\) could lead to oscillations and an unfeasible solution (i.e. negative mole fraction), particularly at high stage cuts and low permeate to feed pressure ratios in counter-current and cross-flow models, as will be shown in Chapter 3. None of the aforementioned works suggested how this problem might be solved.

Moreover, most of the numerical methods reviewed, such as fourth order Runge-Kutta, Newton- Raphson and finite element are sensitive to the initial guess, especially at extremely high stage cut values (David, 2007; Tessendorf et al., 1999; Coker and Freeman, 1998). Another problem associated with solving differential equations using fourth order Runge-Kutta method is the issue of instability due to the stiffness of differential equations. To design the membrane and exploit operating variables, a robust computation strategy that works accurately for a wide range of
operating conditions is required. The calculation method should not require user intervention during the simulation process and also should present low sensitivity to the initial guess.

In this thesis, a simple mathematical model for membrane will be selected. This reduces the modelling complexity and makes it easy to exploit the impact of various process design variables on overall process performance. In the present work, therefore, the model developed by Shindo et al. (1985) is adopted, although more robust solution methods will be proposed in Chapter 3. Although the modelling procedures presented by Shindo et al. (1985) were not used for olefin-paraffin separation mixtures, the transport of gases through the membrane is defined by an ordinary diffusive mechanism. This permits to apply their calculation methods for some type of facilitated transport membranes like ILMs. In addition, their modelling approach is not restricted to binary systems, and it is not difficult to extend the approach to consider of the trans-membrane flux with carrier (i.e. carrier diffusion).

Based on the literature review, there is a lack of approximate membrane model available for facilitated transport membrane which includes a facilitation agent that preferentially and chemically interacts with a desired component to facilitate their transport across the membrane. Approximate models help to analysis, simulate and evaluate separation system and design alternative within an efficient period of time. An approximate model proposed by Naylor and Backer (1955) is selected to be modified and extended to be applicable to the above mentioned transport phenomena, as will be presented in Chapter 3.

2.3 Distillation column design methods

The distillation column is the main separation unit of the distillation-based hybrid system. Therefore, a robust model is required to design and simulate the column within the hybrid flowsheet, to predict the column minimum reflux ratio, temperature and heat duties in the condenser and reboiler for a given separation task. Methods for the design of distillation column can be categorised into two main groups: shortcut methods and rigorous methods. This section briefly presents details of these methods.
2.3.1 Shortcut methods

Shortcut methods have been employed for both simple and complex column design. The most common shortcut methods for column design are those developed by Fenske (1932), Underwood (1948) and Gilliland (1940).

Fenske (1932) derived an equation to calculate the minimum number of equilibrium stages at total reflux.

\[ N_{min} = \frac{\log \left( \frac{x_{LD} \times x_{HB}}{x_{HD} \times x_{LB}} \right)}{\log(\alpha_{LH})} \]  \hspace{1cm} (2.21)

Where:
- \( x_{LB} \) is the mole fraction of the light key component in the bottom product
- \( x_{HB} \) is the mole fraction of the heavy key component in the bottom
- \( x_{LD} \) is the mole fraction of the light key component in the distillate
- \( x_{HD} \) is the mole fraction of the heavy key component in the distillate
- \( \alpha_{LH} \) is the relative volatility between the heavy key and light key components
- \( N_{min} \) is the minimum number of stages

The relative volatility is defined as the \( K \)-value ratio of the more volatile to the less volatile component (Kister, 1992).

\[ \alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i / x_i}{y_j / x_j} \]  \hspace{1cm} (2.22)

Geometric average relative volatility, which is estimated by equation 2.23, can be used in equation 2.21 (King 1981; Seader and Henley, 1984; Kister, 1992; Smith, 2005).

\[ \alpha_{ij_{avg}} = \sqrt{\alpha_{ij_{top}} \cdot \alpha_{ij_{bottom}}} \]  \hspace{1cm} (2.23)

Joyner et al. (1962) presented equations that can be extended in order to estimate the minimum number of stages at total reflux for multiple feeds and side draw columns by dividing the column into a number of sections. The principles of calculation of the minimum number of stages in each section of the column is similar.
to that used by Fenske (1932). For example, consider the sketch of the complex column shown in Figure 2.4 in which the column is divided into three sections. Section 1 is the section of the column between the distillate (D) and the feed, F. Section 2 is the section of the column between the feed and the side draw, M. Section 3 is the section of the column between the side draw and the bottom product, B.

![Figure 2.4: Schematic of a complex column for total reflux](image)

The equations for sections 1, 2 and 3 respectively are

\[
\alpha_{N_{\text{min},I}} = \frac{x_{D,L} x_{F,H}}{x_{D,H} x_{F,L}} \quad I = 1 \tag{2.24}
\]

\[
\alpha_{N_{\text{min},I}} = \frac{x_{F,L} x_{M,H}}{x_{F,H} x_{M,L}} \quad I = 2 \tag{2.25}
\]

\[
\alpha_{N_{\text{min},I}} = \frac{x_{M,L} x_{B,H}}{x_{M,H} x_{B,L}} \quad I = 3 \tag{2.26}
\]

Where \(N_{\text{min},I}\) is the minimum number of theoretical stages required in section \(I\). \(x_{D,L}, x_{M,L}, x_{R,L}\) and \(x_{B,L}\) represent the mole fraction of the light key component in the distillate, membrane feed, retentate and the bottom streams, respectively. The terms \(x_{D,H}, x_{M,H}, x_{R,H}\) and \(x_{B,H}\) are used to represent the mole fraction of the heavy key component.

The total minimum number of stages which will be required in a complex column, is
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\[ N_{\text{min}} = \sum N_{\text{min},l} \]  

(2.27)

Underwood (1948) derived correlations to calculate the minimum reflux ratio at an infinite number of stages. The basic assumptions underlying the Underwood calculation method are constant relative volatility throughout the column and constant molar flow within each section of the column (Seader and Henley, 1998 and Smith, 2005). The relative volatility values in connection with the Underwood equations are based on the feed conditions because the location of the pinches is often close to the feed (Smith, 2005).

\[ \sum_{i=1}^{n} \frac{\alpha_{ij}x_{i,F}}{\alpha_{ij} - \emptyset} = 1 - q \]  

(2.28)

\[ \sum_{i=1}^{n} \frac{\alpha_{ij}x_{i,D}}{\alpha_{ij} - \emptyset} = R_{\text{min}} + 1 \]  

(2.29)

Where \( \alpha_{ij} \) is relative volatility
\( x_{i,F} \) is mole fraction of component \( i \) in the feed
\( x_{i,D} \) is mole fraction of component \( i \) in the distillate
\( \emptyset \) is the root of equation (2.28)
\( q \) is thermal state of feed stream
\( n \) is number of components
\( R_{\text{min}} \) is the minimum reflux ratio

For a mixture of \( n \) components there are \( (n - 1) \) real positive values of \( \emptyset \) that satisfy equation 2.28. Therefore, for a binary separation, one root needs to be calculated for equation 2.28. The root lies between the relative volatility of the light and heavy key components, so: \( \alpha_{\text{LK}} > \emptyset > \alpha_{\text{HK}} \).

For multicomponent and non-ideal mixtures, the two aforementioned assumptions of the Underwood method do not hold (Seader and Henley, 1998; Suphanit, 1999). In such cases, the Underwood method underestimates the minimum reflux ratio (Suphanit, 1999; Smith, 2005). However, The Underwood method gives good estimates for relatively ideal system and binary mixtures (Rose, 1985).
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Gilliland (1940) developed an empirical correlation to relate the number of stages at finite reflux ratios with the minimum number of stages and to the minimum reflux ratio. The original form of the Gilliland correlation was graphical and various attempts have been made to represent the correlation analytically. One formulation representing the Gilliland correlation is equation 2.30 (Rusch, 1999). Another simpler formulation is the Eduljee correlation, equation 2.31 below (Eduljee, 1975).

\[
Y = 0.2788 - 1.3154X + 0.4114X^{0.2190} + 0.8268\ln X + 0.9020\ln \left( X + \frac{1}{X} \right) \tag{2.30}
\]

\[
Y = 0.75(1 - X^{0.5668}) \tag{2.31}
\]

\[
X = \frac{R - R_{\text{min}}}{R + 1} \tag{2.32}
\]

\[
Y = \frac{N - N_{\text{min}}}{N + 1} \tag{2.33}
\]

Where \(N\) is the theoretical number of stages and \(R\) is the actual reflux ratio, which is generally estimated at some multiple of the minimum reflux ratio. For below-ambient temperature (cryogenic) columns, a reflux ratio of between 1.05 and 1.1 times the minimum value is used because of high utilities costs (Ray and Sneesby, 1998; Douglas, 1988).

\[
R = f_r \times R_{\text{min}} \quad \text{i.e. } R = 1.05 \, R_{\text{min}} \text{ to } 1.1 \, R_{\text{min}} \tag{2.34}
\]

The Gilliland correlation can predict the number of stages with modest accuracy at low values of the thermal condition of the feed (e.g. superheated vapour), and can result in wrong predictions when there is large difference in stage requirements above and below the feed (Coker, 2010). Caballero et al. (2009) suggested using the method proposed by Stephan et al. (1995), which used Smoker’s equation to obtain accurate predictions of theatrical number of stages in each section for binary mixtures. Still, the Gilliland correlation can be used to calculate the number of stages with a reasonable accuracy and can be used for a preliminary exploration of design variables. A rigorous model can then be used to refine the results and achieve accurate predictions.
Nikolaides and Malone (1987) modified the Underwood method so that it can be applied to a complex column design (i.e. a column with multiple feed streams and multiple products). Nikolaides and Malone (1987) derived approximate expressions for minimum reflux calculations for multicomponent mixtures. To model a complex column, Nikolaides and Malone (1987) proposed a column decomposition approach, i.e., the complex column decomposed into a number of hypothetical simple single-feed columns. The Underwood equations were then applied to each column to calculate the minimum reflux ratios. The largest minimum reflux ratio is the one that is used for carrying out the design of the distillation column. The approach presented by Nikolaides and Malone (1987) provides a simple way to design and analyse complex column configurations, although it is based on simplified assumptions such as constant relative volatilities and constant internal molar flows across the column.

Suphanit (1999) improved the accuracy of the Underwood method for a simple column design by taking into account the two limiting assumptions of the Underwood method. Suphanit (1999) calculated the vapour flow rates from Underwood equations at the feed stage because the pinch zone is located close to the feed stage (Smith, 2005). Constant vapour mole flow was only assumed in the pinch zone and the regions where the component compositions are constant, but not throughout the whole column (Suphanit, 1999). An energy balance was then performed around the top column section to estimate condenser duty and vapour flow rate at the top of the column. Although the method by Suphanit (1999) extended to consider complex column design (e.g. steam-stripped columns, columns with thermal coupling and side heat exchanger), columns with multiple feed streams and multiple products were not addressed by using the Fenske-Underwood-Gilliland with enthalpy balance.

2.3.2 Rigorous methods

Rigorous models are widely used for the design and analysis of simple and complex columns. Rigorous models represent the material balance, enthalpy balance and equilibrium relationship for each stage in the column (Hines, et al., 1985). Stage-by-stage calculations are based on two assumptions:

1. Vapour and liquid are at equilibrium condition in each stage.
2. The entrainment of liquid drops in the vapour phase and vapour bubbles in the liquid phase are negligible.

In a computational sense, stage-by-stage calculations are time-consuming because they require solving large number of linear and nonlinear equations simultaneously. The number of equations increases according to the number of components in the system. Usually, an iterative algorithm, with a good starting point in order to converge, is used to solve the set of equations. The solver algorithms of rigorous models could be the bubble-point method, the sum-rates method, the simultaneous correction method, or the inside-out method (Seader and Henley, 1998). The rigorous models and the solvers have been incorporated in commercial simulation packages, such as HYSYS, ASPEN Plus, ChemCAD, etc., and used by researchers for the design and analysis of various column configurations, e.g., conventional column, double-feed column, column-based hybrid systems, etc.

Simulation packages such as HYSYS can be integrated with mathematical and programming tools such as MATLAB through an automation mode (HYSYS 2006.5 Customization Guide). The combination of MATLAB with a rigorous simulator has been recently used for the design of distillation processes (e.g., Nawaz, 2011; Liu, 2012) and column-based hybrid separation processes (Beronich et al., 2008; Benail and Aydin, 2010). A rigorous simulator was used to calculate thermophysical property data, whereas MATLAB was employed as a programming tool in which shortcut methods are implemented.

The combination of the two tools (MATLAB and HYSYS) reduces problem complexity, convergence problems and solution time in the design of complex distillation columns. Shortcut methods can be used to decompose complex columns to simple column arrangements, thus reducing the problem complexity and eliminating the requirement to solve a large number of highly linear and nonlinear equations. The use of a thermodynamic models and physical properties database available in the process simulation package reduces the computational time requirement. The combination design approach also allows evaluation and screening of the operating variables and column structural options, e.g., feed and side-draw arrangements, in a systematic way. These characteristics show the combination approach to be a promising design method. For this reason, it was selected for the
design of a conventional column as well as the column-based hybrid systems to be presented in Chapter 5.

### 2.3.3 Summary of distillation column design

Two methods have been proposed for column design; namely shortcut methods and rigorous methods. Compared to shortcut methods, rigorous models provide more accurate predictions, but trial and error and high CPU time is required for a complex column. The design of a distillation column with a process simulator requires a large number of individual computer runs to locate the optimal feed stage locations at which a minimum reflux ratio value occurs. Further iteration is also required to converge the recycle stream or side draw of a complex column.

Furthermore, rigorous methods demand more effort for the evaluation of the operating variables that have a significant impact on overall process performance. For a given separation problem and reflux-to-minimum reflux ratio value, there are many design variables, including operating pressure, side-draw flowrate and its compositions, feed and side-draw locations, which influence the column duties and the number of stages required. To determine the optimal operating conditions for various process configurations, an enormous number of simulations need to be carried out.

Therefore, for the purposes of this thesis, shortcut methods were selected for modelling both the conventional column and the distillation column of hybrid membrane-distillation systems. In particular, the approach developed by Nikolaides and Malone (1987) and Suphanit (1999) were selected because of their following advantages: simplicity; the complexity of the complex column design can be reduced; the underlying drawbacks of shortcut methods are overcome; computational efficiency, making it suitable for use in process optimisation; opportunity of heat recovery between separation processes and utility system, e.g., a refrigeration system can be exploited simultaneously in a systematic way. Low temperature processes need refrigeration to provide cooling at below ambient temperature. The refrigeration shaft power requirement is directly related to the temperatures and cooling and heating duties in the column. When the reflux ratio of a column is decreased, the condenser duty decreases, and consequently the refrigeration power
also decreases. An implication of this decrease is that the refrigeration design may change. By using shortcut methods, the complexity of the design and optimisation of heat-integrated separation processes can be reduced.

2.4 Hybrid membrane-distillation systems

Hybrid membrane-distillation is a combination of two separation units with different separation principles. Distillation separates components according to the difference in their boiling points, while membrane separates components due to the difference in their permeability. The combination of the two separation technologies integrates the advantages of distillation, specifically its high recovery and purity, with the advantages of membrane separation, namely its high selectivity. In addition, the integration of two separation units allows crossing of the distillation boundaries like azeotropes, and improving the thermodynamic efficiency of the column by breaking the pinch, which, consequently, facilitates savings in energy, operating costs and capital costs (Caballero et al., 2009; Lutze and Gorak, 2013).

In general, a large number of possible configurations for a hybrid membrane-distillation can be generated. Section 2.4.1 describes the main schemes that have been reported in the literature for ethylene-ethane separation. Methodologies that have been developed for screening of membrane and distillation in integrated hybrid processes are reviewed and discussed in Section 2.4.2.

2.4.1 Configuration of hybrid membrane-distillation systems

A number of hybrid configurations can be generated by complementing the distillation with membrane modules. These configurations are named according to the membrane’s position, as shown in Figure 2.5. In the sequential scheme (Fig. 2.5(A)), the membrane module is placed in the process feed stream, and both the permeate and the retentate feed the distillation column. The membrane can also be located at the top of the distillation column as shown in Fig. 2.5(B). In this case, the membrane performs the final purification of the top product of the distillation column. The retentate is recycled to the distillation column at an appropriate location in the column. Fig. 2.5(C) shows the bottom hybrid system where the membrane unit performs the final purification of the bottom product of the distillation column. The permeate, as opposed to the retentate (as in the top hybrid configuration), is recycled.
to the distillation column. In the parallel configuration (Fig. 2.5(D)), the membrane feed stream is withdrawn from an intermediate stage of the distillation column. The retentate stream and permeate stream both re-enter the distillation column.

Figure 2.5: Hybrid membrane-distillation configurations. (A) sequential scheme; (B) top hybrid; (C) bottom hybrid; (D) parallel hybrid

2.4.2 Design and optimisation methods for hybrid membrane-distillation systems

Research on hybrid system design and optimisation can be grouped into shortcut methods, rigorous methods and optimisation-based methods. In this section, design and optimisation methods for hybrid membrane-distillation systems will be reviewed and discussed.

2.4.2.1 Shortcut methods

Moganti et al. (1994) investigated the use of facilitated transport membrane hybrid systems for propylene-propane separation and presented a design methodology for hybrid processes. Two design methods for a parallel hybrid membrane-distillation system were given to minimize the number of stages in a distillation column of the hybrid system: the minimum area method and the Smoker’s equation method.

The minimum area method is based on the idea that the number of stages between the vapour-liquid equilibrium curve and the operating lines is minimal in the case of total reflux; therefore, the area is zero (Stephan et al., 1995). A McCabe-Thiele diagram is employed to find the number of theoretical stages needed to minimise the
area between the operating lines and the 45 degree line for a given separation problem.

Moganti et al. (1994) proposed using an analytical correlation developed by Smoker (1983) to determine the number of stages in a column’s sections. Smoker’s equation was based on the assumption of constant relative volatility and constant molar overflow (Kister, 1992). Smoker’s equation requires knowing the slope of the operating line, the relative volatilities of the mixture components and the mole fraction range of the column section (Stephan, et al. 1995).

In the work of Moganti et al. (1994), limited design variables including stage cut, membrane area and membrane feed composition were evaluated and some conceptual results for hybrid design were proposed. However, the criterion of evaluation—minimising the area under the operating lines in a McCabe-Thiele diagram—is only restricted to the column capital cost. There is a trade-off between the number of stages and the reflux ratio, and also between permeate pressure or compressor duty and membrane area. A systematic design and optimisation method for economic evaluation is needed to find the optimal trade-offs.

Stephan et al. (1995) extended the scope of Moganti et al. (1994) and used McCabe-Thiele diagram as a basic approach to assessing different hybrid membrane-distillation configurations. Also, a shortcut method is presented to estimate the numbers of trays in a new design by placing a membrane on the distillate stream of a distillation column.

A sequential modelling approach to designing hybrid separation systems was proposed by Stephan et al. (1995). In the sequential modelling approach, the membrane and distillation column models are solved separately. For a given set of operating parameters, perfect mixing membrane model equations are solved numerically first. Then, the distillation column design is carried out.

Stephan et al. (1995) stated that the optimal membrane operating parameters are independent of the column operating parameters. However, there is a trade-off between the membrane operating conditions and the column operating variables. In order to find the optimal position of the membrane across the column, as well as the
optimal design variables, the modelling of the membrane system should be considered simultaneously with the modelling of distillation column.

Pettersen et al. (1996) extended the work of Stephan et al. (1995) on designing hybrid systems using a distillation-facilitated transport vapour permeation membrane for the separation of propane/propylene mixtures. Pettersen et al. (1996) used Smoker’s equation to calculate the theoretical number of column stages required in the hybrid processes. The pressure drop in the distillation column was assumed to be negligible. The sequential approach proposed by Stephan et al. (1995) was used to design the hybrid system. In contrast to Stephan et al. (1995), a cross-flow membrane module was investigated and the models for the membrane unit and the distillation column were implemented in C++. The theoretical comparison of Pettersen et al. (1996) for various hybrid membrane-distillation schemes shows that the parallel hybrid system gives the best operation performance in terms of compressor duty and membrane area, as compared to top and bottom hybrid configurations.

There are some limitations associated with the design method of Stephan et al. (1995); Moganti et al. (1994) and Pettersen et al. (1996). Firstly, McCabe-Thiele is not adequate for column design if a large number of stages are required. Secondly, McCabe-Thiele cannot be developed further to allow for pressure drop or multicomponent systems (Rose, 1985). However, McCabe-Thiele provides a convenient way to analyse and screen different process configurations including hybrid separation systems, and the Smoker equation can give good results for the separation of relatively ideal mixtures, i.e. systems with constant molar overflow and constant relative volatilities (Rose, 1985).

In addition, the aforementioned authors do not include economic analysis of distillation-membrane hybrid processes, and their target is to minimize the number of trays in the distillation column. This objective may not be convenient for cases where the operating and annualized capital costs are dominated by utility costs.

Caballero et al. (2009) used the column decomposition approach to design the distillation column of a parallel hybrid membrane-distillation system. The membrane model was substituted with a separator model. For a given set of operating
parameters (selectivity and the ratio of a component flow rate in the feed stream to the separator relative to that component in the top product stream from the separator), the separator model was used to calculate all the column side stream flow rates and compositions. In the decomposed approach of Caballero et al. (2009), the distillation column divided into four sections, as shown in Figure 2.6.

The Underwood method was then used to calculate minimum vapour flow in each pseudo-column. The Underwood method was adequate for use because it is applied to a relatively ideal binary mixture where the assumptions on the Underwood method are valid.

![Figure 2.6: Parallel hybrid membrane-distillation decomposed into column sections](Caballero et al., 2009)

Ayotte-Sauve et al. (2010) developed a shortcut model based on the ‘notion of power of separation’ for the evaluation of a parallel hybrid vapour membrane-distillation system. The results of the shortcut method were compared to the results of a superstructure approach for the energy intensive separation of olefins from paraffins, namely the retrofit of a C₃-splitter and the retrofit of a C₂-splitter. GAMS-CONOPT solver was used to solve the optimisation problem. In both case studies, the computation time was reduced significantly by the use of a shortcut method due to the reduction of total number of equations and the number of solver iterations. The accuracy of the results predicted by the shortcut method was acceptable, compared with optimisation results. The proposed thermodynamic approach of
Ayotte-Sauve et al. (2010) is conceptually useful for a rapid feasibility analysis and for screening of alternatives (i.e. different membrane-assisted distillation processes) in order to evaluate potential energy improvement, but it is limited to binary separations. Moreover, it is difficult to handle a complex problem (Chiu, 1982).

2.4.2.2 Rigorous methods

Roberts and Gottschlich (1990) studied a ‘bottom hybrid’ configuration for propylene-propane separation using rigorous method. In their study, the membrane proved to be superior to distillation in terms of process cost. The economic evaluations of Roberts and Gottschlich (1990) for membrane alone, distillation alone and a hybrid membrane-distillation system show the following:

- The membrane system has a capital cost of $4 million, of which only $0.3 million is for the membrane modules; most of the capital cost is for the compressor. In terms of processing cost, the membrane has a processing cost of 0.012 $/kg product of which 30% is a result of power expenses.
- The distillation system capital cost is much greater, $20 million, and the hybrid system capital cost is intermediate at $12 million. The processing cost for the distillation system is 0.06 $/kg product, of which steam accounts for over 40%.
- The hybrid process results in a processing cost of 0.035 $/kg product, of which steam is the major expense, accounting for 30%. However, to produce high purity products, the membrane alone cannot perform the separation, and a hybrid is required.

However, Roberts and Gottschlich (1990) did not develop a systematic design methodology for hybrid processes and only bottom hybrid membrane-distillation was investigated. The bottom hybrid configuration was chosen for evaluation based on engineering knowledge and rule of thumb.

Al-Rabiah (2001) also used a rigorous simulation-based approach for the evaluation of various hybrid membrane-distillation schemes. The possibility of using polyimide and polysulphone membranes for the separation of hydrogen from de-methanizer, and facilitated transport membrane for improving the separation process
of the C₂ splitter (ethylene-ethane separation) in a commercial ethylene plant are assessed in terms of total annual cost.

Al-Rabiah (2001) presented a systematic approach to the simulation and design of the various hybrid configurations shown in Figure 2.5(b), 2.5(c) and 2.5(d). However, the approach introduced by Al-Rabiah (2001) does not consider the simultaneous optimisation of configuration and/or operating conditions. In the work of Al-Rabiah (2001), in order to find the optimum operating conditions for each hybrid distillation-membrane scheme, a large number of individual simulations are performed. The optimum operating conditions are those which result in a minimum operating and capital cost.

Pinch analysis, using commercial, ASPEN PINCH software, is also performed to identify the energy saving potential considering both energy and capital targets. To design a heat exchanger network, the pinch design method is used. In the work of Al-Rabiah (2001), pinch analysis is applied to the purification section in the conventional ethylene process as well as to the modified ethylene process. The modified ethylene process was obtained by replacing the conventional separation units with the most energy efficient hybrid membrane-distillation systems and membrane separation units. These schemes constitute the series hybrid system for ethylene-ethane separation and the membrane system for hydrogen separation.

Al-Rabiah (2001) considers heat recovery within an ethylene process using pinch analysis but neglects to integrate the ethylene process with the refrigeration system. The ethylene process requires refrigeration; integrating the process with refrigeration system could result in more energy saving. Furthermore, in the work of Al-Rabiah (2001), the separation system and the heat exchanger network are optimised sequentially. The sequential approach cannot guarantee to provide the most cost-effective design. This is because the optimum operating conditions before and after heat integration might not be the same. Thus, there is a need to develop a systematic design and optimisation procedure to assess various hybrid configurations, taking into account opportunities for heat integration. The integration of the separation system should be considered simultaneously with the integration of refrigeration and separation systems.
Benali and Aydin (2010) and Salgado-Gordon and Valbuena-Moreno (2011) investigated the technical feasibility of hybrid membrane-distillation separation systems for the separation of ethylene-ethane and propylene-propane. Their work were based on a rigorous simulation-approach, similar to that of Al-Rabiah (2001), but neither systematic heat integration nor parametric optimisation were performed; only the ‘series hybrid’ configuration and a membrane cascaded configuration, as shown in Figures 2.7 and 2.8, were evaluated in the case of ethylene-ethane separation. Benali and Aydin (2010) concluded that the series hybrid system is the most suitable for the retrofit design with total savings of 61%.

Figure 2.7: Two-stage cascaded scheme for ethylene-ethane separation (Benali and Aydin, 2010)

Figure 2.8: Series hybrid scheme for ethylene-ethane separation (Benali and Aydin, 2010)
Motelica et al. (2012) and Ploegmakers et al. (2013) employed rigorous methods to evaluate different hybrid membrane-distillation configurations. The potential for increasing the energy efficiency of the separation system is determined in relation to the required membrane selectivity and permeability data.

Motelica et al. (2012) used the Aspen Plus simulator to design a conventional column as well as the sequential hybrid scheme shown in Figure 2.9.

Discrete optimisation technique was employed to optimise the feed stage location and stage cut for different membrane selectivity ranging from 4.4 to 300. The objective was to investigate the possibility of increasing ethylene production capacity. Motelica et al. (2012) reported that membrane selectivity should be
beyond 60 and ethylene permeance above $1.7 \times 10^{-4}$ mol m$^{-2}$ s$^{-1}$ kPa$^{-1}$ in order to increase ethylene production capacity. However, the membrane selectivity values were independent of ethane permeance, i.e., selectivities were calculated for a fixed value of ethane permeance $1.6 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ against variable ethylene permeance values ranging from $7 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ to $4.8 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. Motelica et al. (2012) ignored optimising the membrane pressure ratio. The hybrid membrane-distillation performance affected by the change of both the pressure ratio across the membrane and stage cut. As the permeate pressure is reduced, the membrane area required to perform the separation is reduced, and consequently the membrane cost. But reducing the pressure ratio increases the cost of recompressing and cooling the permeate stream, as well as reducing the refrigeration power required for cooling the overhead vapour of the column. There is a trade-off between the cost of the power required to recompress and cool the permeate stream and the cost of the refrigeration necessary to provide the cooling. In order to lower energy consumption and the cost of the process, the cost of the network consumption of the process needs to be determined as a function of various parameters, including the membrane pressure ratio.

In contrast to the previous research, Motelica et al. (2012) applied a heat pump to shift heat from the column condenser to the reboiler. When the distillation column has an integrated heat pump, the operating costs may decrease compared with the operating cost of providing utility for the reboiler and condenser in the distillation column (Farrokhpanah, 2009). However, heat integration opportunities between the feed cooler and the column reboiler, or between the product cooler and the column reboiler, are not considered. In addition, a systematic heat recovery approach is not presented and only the sequential hybrid scheme is explored.

Ploegmakers et al. (2013) extended the work of Motelica et al. (2012) by performing an economic evaluation of two configurations of hybrid membrane-distillation systems; namely, parallel and sequential hybrid schemes, as shown in Figures 2.5(a) and 2.5(d). However, heat integration was not considered. The influence of process and membrane parameters, such as permeate pressure, membrane area, ethane permeance and ethylene permeance, on the hybrid
configurations was considered. In order to achieve high separation performance, a counter-current flow pattern was used for membrane unit model design.

Ploegmakers et al. (2013) outlined an optimisation procedure to retrofit hybrid membrane-distillation processes using UniSim Design. The optimisation objective was to minimise the annual operating costs of the hybrid membrane-distillation process for the separation of ethylene-ethane mixture by taking the membrane properties (selectivity and ethylene permeance), the stage locations of the feed, side-draw, retentate and permeate, and process conditions including feed pressure, permeate pressure and membrane area as the optimisation variables. To reduce the complexity of the optimisation, the membrane properties and the stage locations are optimised first for the two hybrid configurations. Then, the optimum hybrid membrane-distillation scheme obtained was further optimised by using the membrane properties, stage locations and process conditions as the optimisation variables. Ploegmakers et al. (2013) concluded that the sequential hybrid system could be an attractive alternative compared to the conventional distillation column for the separation of ethylene-ethane, if the ethylene permeance and membrane selectivity exceed $2.8 \times 10^5$ mol m$^{-2}$ s$^{-1}$ kPa$^{-1}$ and 30, respectively.

2.4.2.3 Optimisation-based methods

Research on hybrid membrane-distillation optimisation can be grouped into two categories:

1) Mathematical programming methods with a deterministic optimisation algorithm. Deterministic strategies can be classified into direct-search and gradient-based methods. Direct-search methods do require a search algorithm but not numerical derivatives of the objective function with respect to the design variables. Thus, it can be applied to non-smooth optimization problems. Also, it is well suited in situations where the objective function is a result of a simulation code (Kolda et al., 2003). The gradient-based approach needs derivatives information and it can handle linear and nonlinear, convex and smooth functions.

2) Stochastic optimisation methods. Stochastic global optimisation methods can be classified into four main categories: random search techniques, which include pure random search, adaptive random search, two phase simulated annealing and
tabu search; evolutionary methods such as genetic algorithms; swarm intelligence methods and others (Rangaiah, 2010).

2.4.2.3.1 Deterministic optimisation-based methods

In process optimisation, usually a superstructure representation is applied. Superstructure representation involves various substructures that can be simultaneously optimised to obtain the optimal solution for the problem. For a given separation task, the mathematical models are formulated as linear programming (LP), mixed integer linear programming (MILP), non-linear programming (NLP), or mixed integer non-linear programming (MINLP), based on the complexities of the problems in question. The optimisation problem can then be solved with a different optimisation algorithm based on the type of objective function and its associated constraints. For example, sequential quadratic programming (SQP) solves an NLP problem.

Kookos (2003) proposed a mathematical programming methodology using a superstructure representation of a hybrid system consisting of membranes and distillation columns. The superstructure representation is based on a simple steady-state mathematical model, and assumes that all streams taken from or returning to the distillation column are vapour streams. A MINLP model for the optimal hybrid membrane-distillation scheme to separate a propylene-propane mixture was shown to reduce the energy consumption of the separation process. Kookos (2003) presented a case study in which the hybrid system reduced the operating cost by 22% if operated under optimum conditions. Although the suggested structural representation is used to optimize a hybrid membrane-distillation system, no results are given for either membrane networks or single membranes.

Naidu and Malik (2011) proposed various superstructure representations of hybrid distillation-pervaporation processes, as well as pervaporation modules in parallel, series and series parallel arrangement. For modelling the distillation column, the approach of Viswanathan and Grossmann (1990) is utilised. A mixed integer non-linear programming (MINLP) model is used to analyse the optimal number trays, feed location, and recycle streams for a design distillation column (Viswanathan and Grossmann, 1990). Plug flow along the feed side and cross-flow along the permeate
side of the membrane are assumed. In the optimisation, the structure and design parameters, including reflux ratio, the number of trays and the number of pervaporation modules, the locations of feed and recycle streams are optimised. The optimisation problem is formulated as MINLP and the objective is to minimise total annual cost for the given separation task. However, the superstructure representation is very complex, as a large number of pervaporation units with different arrangement are included in the separation flowsheet. Solving a set of mass balance and transport equations with a very small incremental area as suggested by Naidu and Malik (2011) could take a long time. In addition, important design parameters that significantly affect the total process cost, such as the permeate pressure and column pressure, are not optimised, and opportunities for heat recovery are not addressed.

Marquardt et al. (2008) present a framework for the design of separation flowsheets, which include hybrid membrane-distillation separations. In the proposed framework, different flowsheets are generated and then evaluated with shortcut methods. Finally the most energy-efficient alternatives are rigorously optimized using MINLP to calculate detailed information and obtain the most cost-effective design.

A similar approach to Marquardt et al. (2008) has been employed by Caballero et al. (2009) and Skiborowski et al. (2013) for the design of hybrid membrane-distillation systems. The approach proposed by Caballero et al. (2009) was applied to optimise and retrofit design of ethylene-ethane separation. They used a membrane model based on ideal cross-flow and selectivity-permeance relationship introduced by Fuertes and Menendez (2002). According to Fuertes and Menendez (2002), the permeability of ethylene ranges between 10 and 1000 barrer and selectivity between 2 and 11. The distillation column was simulated with a rigorous method using UniSim Design, and the membrane model was simulated in MATLAB. A superstructure representation for parallel hybrid configuration was implemented in the process simulator to determine the optimal location at which all streams must be introduced or withdrawn. The process simulator was connected to MATLAB using its ActiveX capabilities. The objective was to maximise the annualized cost saving. Caballero et al. (2009) formulated and solved the optimisation problem as MINLP, while an LP/ NLP-based ‘branch’ and ‘bound’ algorithm was employed to deal with
an ‘implicit block’, which is a combination of different blocks of equations with an input-output structure controlled within MATLAB. Caballero et al. (2009) concluded that the parallel hybrid system can lead to an energy saving of 30% in the condenser compared to the base case (conventional column).

The approach is useful in terms of accuracy, since it uses process simulators together with rigorous optimisation involving discrete variables. The main drawback is the methodology used to solve the MINLP. In the method of Caballero et al. (2009), some form of integer relaxation is used (i.e. binary variables are relaxed to continuous variables that lie between 0 and 1). Such an approach might result in numerical problems, as stated by Caballero et al. (2006). Considerable computation time might also be needed to converge the flowsheet simulation built in a commercial process simulator.

2.4.2.3.2 Stochastic optimisation-based methods

Barakat and Sørensen (2008) presented a process synthesis procedure that made it possible to determine the optimal process type (distillation, pervaporation or a hybrid of the two) as well as its configuration, design and operation for a given separation task. The optimisation procedure, which uses a genetic algorithm, applies to batch and continuous separation processes. Search stochastic methods can find global optima without using derivative information by systematically searching the solution space. Genetic Algorithms overcome many of the shortcomings of the traditional optimisation methods (e.g. non-convexity and a combination of integer and continuous variables) (Koch et al., 2012). However, Genetic Algorithms require long computational time and early convergence to a local optimal is possible (Abramson, 2002; Wang and Smith 2005; Rangaiah, 2010).

For an equimolar acetone-water mixture, the parallel hybrid continuous distillation- pervaporation process is found to produce the highest overall profit that encapsulates capital and operating costs as well as production revenues. Barakat and Sørensen (2008) reported reductions of 14% in capital costs and 4% in operating costs compared to the optimal distillation process. They concluded that the pervaporation process is best suited to small-scale operations, whereas hybrid batch distillation-pervaporation configuration is more appropriate for large-scale separations. It should be mentioned that Barakat and Sørensen (2008) did not
consider comparing batch against continuous operation. However, the mathematical programming methods of Barakat and Sørensen (2008) restrict design considerations to the proposed superstructure (i.e., to total column condensation and above ambient temperature). Furthermore, heat recovery is not considered.

2.4.2.4 Summary of design and optimisation of hybrid membrane-distillation systems

Several approaches have been reported in the literature on design, modelling and optimisation of hybrid membrane-distillation systems. The combination of mathematical programming, e.g., MATLAB, with process simulators, e.g. HYSYS, is one of the most promising approaches. This approach benefits from the availability of thermodynamic data and a wide range of process models through the use of commercial process simulators (Koch et al., 2012). In addition, the combination of MATLAB and a process simulator facilitates the study of new separation processes (e.g., membrane) that are not available within the commercial process simulator and, consequently, exploits many structural options and operation parameters systematically and enables a robust and global process optimisation through the use of the optimisation toolboxes available in MATLAB.

Caballero et al. (2009) proposed a two-stage approach. First, a shortcut model is presented to evaluate various hybrid configurations in terms of energy. However, constant relative volatilities were assumed and the recompression and cooling duties of permeate stream were negligible in this stage. Second, the most energy efficient configuration is optimised using rigorous methods. In the second stage, a superstructure-based optimization method that combined the capabilities of commercial process simulator UniSim Design and a mathematical programming method were implemented. The approach proposed by Caballero et al. (2009) was applied to optimise the parallel hybrid membrane-distillation system, which is the most energy efficient scheme. The optimisation problem was formulated as an MINLP problem. The operational and structural parameters (feed stage locations, selectivity, membrane area, side-draw molar flow rate and its composition) were simultaneously optimized for the rigorous design of the distillation column. However, the computational demands for solving the optimization problems increase significantly by the use of these modular simulators (Koch et al., 2012) due to non-
convexities in the objective function and the contraints of the MINLP model. Furthermore, finding the global optimum solution remains uncertain, as derivative-based searching methods are employed.

Simulated annealing and genetic algorithms are among the most recently used methods in chemical engineering process optimisation because they can handle non-convex optimization efficiently and converge to a global optimum. To date, few researchers have applied stochastic optimisation methods to explore the optimisation of design and operation of hybrid systems. The opportunity to apply genetic algorithms (GA) for design and optimisation of hybrid pervaporation-distillation processes has been investigated by Barakat and Sørensen (2008), whereby optimal process configuration, design and operation using a superstructure representation was obtained simultaneously based on trade-offs between capital investment, production revenue and operating costs. The long computational time was reported as a disadvantage of using genetic algorithm (Wang and Smith, 2005; Rangaiah, 2010).

So far, there is no systematic methodology that takes heat integration opportunities into consideration in the design and optimisation of membrane-distillation hybrid processes. Although Al-Rabiah (2001) applied pinch analysis and pinch design method to the purification section in both the conventional and modified ethylene plant, heat recovery between the refrigeration system and the separation system, which can provide significant energy savings, was not looked into. Moreover, the optimisation of design and operation of the hybrid systems were performed separately without considering heat integration opportunities. The optimal operating conditions for each hybrid scheme were obtained by carrying out a large number of individual rigorous simulations. Motelica et al. (2012) were the first to explore the sequential hybrid-membrane-distillation with an integrated heat pump. Integrating the column and the heat pump can result in lower shaft power consumptions. However, only indirect heat exchange between the condenser and reboiler was considered.

As discussed in Chapter 1, the objective of the present work is to develop a synthesis and design framework to screen, examine and optimise the heat-integrated hybrid membrane-distillation separation process. The opportunity for heat recovery
needs to be taken into account to minimise the utility demand of the separation system. It would be quite difficult to apply such an approach with rigorous simulations and compact superstructure representation. For this reason, it was decided to select the design and optimisation approach of Caballero et al., 2009 and modify and extend it in order to make it applicable to a heat-integrated hybrid distillation-vapour membrane separation system.

2.5 Conclusions

This chapter details a number of gaps in membrane modelling approaches that describe the transport mechanism through facilitated transport membranes, the solution method for the model equations and the process design of facilitated transport membranes (e.g. membrane material, pressure ratio, stage cut). It also notes that, although various approaches and design methodologies have been proposed for the design and optimisation of hybrid membrane-distillation processes, there are still limitations. The main features and shortcomings of the design, modelling and optimisation approaches reviewed here can be summarised as follows:

The literature review demonstrated that solid polymer electrolyte membranes and immobilized liquid membranes are highly selective for ethylene-ethane separation. Although solid polymer electrolyte membranes exhibit high selectivities (Pinna and Toy, 2001; Merkel et al. 2007), which remain stable for several days, there is no study that explores whether solid polymer electrolyte membranes are more cost-effective compared to conventional distillation or membrane-distillation hybrids in terms of energy consumption. Most of the published works on solid polymer electrolyte membranes (e.g. Pinnau and Toy, 2001; Morisato et al., 2002; Merkel et al., 2007; Merkel et al., 2013) were carried out in the lab at stage cut values of less than 1% and at atmospheric permeate pressure. Therefore, higher yields need to be investigated in order to locate the optimal working range of the membrane module and to find the optimal trade-off between the associated operating cost per membrane module, e.g., the recompression and cooling cost of the permeate stream, and column operating costs.

Exact and approximate models of membrane have advantages and disadvantages. Exact models are more accurate, but may require longer computational time and they
are more sensitive to the initial estimate. Approximate models are fast; however, they require assumptions to simplify the model. Teramoto et al. (1986) introduced an approximate method for calculating the rate of facilitated transport accompanied by an instantaneous reversible reaction inside the membrane. The reversible reaction is assumed to be at equilibrium; and averaged concentrations of the complex and carrier on both sides of the membrane is assumed. The approximation method of Teramoto et al. (1986) is restricted to a pure system and cannot be used to calculate the permeate and retentate purities. Naylor and Backer (1955) also introduced an approximate method for a binary mixture separation. The modelling approach of Naylor and Backer (1955) can be extended to include the transport mechanisms through facilitated transport membrane.

Among the detailed models reported in the literature, the mathematical model proposed by Shindo et al. (1985) is the most promising, because of the following advantages: the model is not restricted to binary; the model is simple and can be applied to design hybrid system; the mathematical model can be extended to take account of different theories that describe the transport of components through facilitated transport membranes; the model can be extended to account for pressure drop across the membrane. However, the traditional numerical technique, which was used by Shindo et al. (1985), shows high sensitivity to the initial guess and sometimes was unable to predict solutions; particularly at high stage cuts and low pressure ratios for industrially relevant flow patterns, i.e., cross-flow and counter-current flow patterns (Tessendorf et al., 1999; Coker and Freeman, 1998).

In the main, two approaches have been used to design the conventional column and hybrid membrane-distillation systems. These approaches are the shortcut method and rigorous methods. Although rigorous methods provide accurate results, they may be difficult to converge when used for simulating complex columns. Shortcut methods can overcome convergence problems and they are suitable for carrying out the design and optimisation of complex separation processes, e.g., hybrid membrane-distillation systems. The decomposition approach developed by Nikolaides and Malone (1987) for complex column design is very promising. However, the underlying assumptions of the Underwood method, including the constant relative volatilities and constant internal molar flows across the column, reduce the accuracy.
of the solutions. Suphanit (1999) improved the accuracy of the Underwood method for a simple column design working with total condenser. However, columns with multiple feed streams and multiple products were not considered.

Frameworks for systematic process design and optimisation have been introduced by Marquardt et al. (2008), Caballero et al. (2009), Koch et al. (2012) and Skiborowski et al. (2013). The important features of these approaches are that the advantages of shortcut methods and rigorous simulation are exploited. The key shortcomings are the requirement to pre-specify the number of stages for the distillation column in the process simulator and the choice of optimiser, i.e., the use of deterministic approaches. Direct-search methods are less computationally expensive and offer good performance and are a good starting point, but they can get trapped in a local optimum if that objective function is highly non-convex. Also, in the aforementioned frameworks, heat integration within the separation system and between the separation process and refrigeration system is not considered. There may be a greater opportunity to reduce the energy consumption of the system by introducing process-to-process heat recovery, and by recovering heat between the refrigeration systems and the separation process (i.e., heat can be rejected to a heat sink within the process rather to an external cooling utility).

This research aims to overcome the shortcomings of previous work by developing a systematic separation process design approach that will model, evaluate and optimise various separation process options—including membrane, distillation and hybrid membrane-distillation processes—while taking into account heat recovery opportunities.
Chapter 3 Modelling Developments for Membrane Separations

3.1 Introduction

The membrane separation process is conceptually simple; however, when evaluating a proposed membrane separation, several issues need to be considered, including the membrane material, module configurations, the membrane operating conditions, and the arrangement of membrane modules within the overall unit. In this work, the focus is on modelling a single membrane module for different permeate flow patterns. Although different solution methods have been proposed to solve the governing equations that describe a membrane module performance (e.g. Shindo et al., 1985; Krovvidi et al., 1992; Pettersen and Lien, 1994; Coker et al., 1998; Marriott et al., 2001; Cruz et al., 2005; David, 2007; Makaruk and Harasek, 2009), there is still a need for a computationally efficient and robust algorithm for the membrane design and optimisation. Therefore, it is necessary to develop a robust and stable algorithm which is insensitive to both the initial estimate and the various operating conditions.

This chapter presents a general detailed membrane model for a single-stage membrane module separating a multicomponent mixture with respect to industrial permeate flow patterns; namely a cross-flow and a counter-current flow. To solve the detailed module model equations, the proposed solution methods are based on Shindo et al. (1985) and modified to overcome the sensitivity to initializations and the long computation time. In addition to the detailed approach, a new approximate method is proposed for estimating the membrane selectivity of an immobilized liquid membrane, and the permeate purity for a binary system. The approximate solution method is based on the approximate cross-flow model developed by Naylor and Backer (1955).
The predictive accuracy of the models is studied by comparing the model’s results with published and experimental data on binary and multicomponent mixtures. The membrane models presented in this chapter are combined with a shortcut model of a distillation column in Chapter 4 in order to evaluate hybrid membrane-distillation design options and improve the separation performance of conventional distillation, as will be shown in Chapter 5.

3.2 Detailed mathematical modelling of FTM

The membrane modelling approach taken in this work is based on the theoretical formulation and calculation method developed by Shindo et al. (1985). Shindo et al. (1985) presented formulations and calculation methods for various flow patterns: one side mixing; complete mixing; cross-flow; counter-current flow; and co-current flow. The rates of permeation were described by Fick’s first law. The formulations and calculation methods developed by Shindo et al. (1985) are not restricted to binary systems and can be easily modified to account for other types of permeation rate, making it possible to predict and analyse membrane performance for various types of membrane separators.

In this thesis, the focus will be on facilitated transport membranes, as they are reported to be convenient for ethylene-ethane separation, as discussed in Section 2.2. Two transport mechanisms for ethylene-ethane across the facilitated transport membrane have been proposed in the literature, as reviewed in Section 2.2.1. In solid polymer electrolyte membrane, the flux can be described by Fick’s law (Pinna and Toy, 2001) and therefore the model developed by Shindo et al. (1985) can be implemented. To account for the solution-diffusion and solute-carrier complex diffusion within the immobilized liquid membrane separator, the formulation and calculation methods of Shindo et al. (1985) are extended. Section 3.2.1 describes the model assumptions. Section 3.2.2 introduces the basic equations that describe the performance of membrane module for cross-flow and counter-current flow patterns. Cross-flow and counter-current flow patterns are the main focus for investigation in this work because they are more likely to represent the actual flow pattern (Smith, 2005; Motelica et al., 2012; Ploegmakers et al., 2013). It should be mentioned that the membrane model equations provided in Section 3.2.2 are general because they are characterized in terms of flux.
3.2.1 Model assumptions

The following assumptions are used in the membrane model:

- Pressure drop is assumed to be negligible for feed and permeate streams (Shindo et al., 1985).
- Steady-state process (Benail and Aydin, 2010). This assumption implies that the membrane’s permeability, selectivity and flux rate are unchanged over time, and that the membrane is chemically stable.
- Membrane permeability is independent of pressure and composition, (Shindo et al., 1985; Baldus and Tillman, 1986). For the sake of simplicity, the permeability coefficient of each component is assumed to be unaffected by temperature. In general, however, permeability increases in line with temperature (Seader and Henley, 1998). Nevertheless, the opposite trend was observed by Merket et al. (2007) when using polyether-polyamide block copolymer (Pebax® 2533) for ethylene/ethane separation. In the experimental work of Merket et al. (2007) the permeability increased when the temperature decreased.
- The diffusivity and solubility coefficients of each component are constant.
- Feed and permeate streams are in plug flow, except in the permeate streams in cross-flow (Shindo et al., 1985).
- For immobilized liquid membrane, the assumption is that there is an instantaneous ethylene/silver reaction and equilibrium between the product and reactant species at the boundaries along the entire membrane (Al Rabiah, 2001; Benail and Aydin, 2010). By assuming thermodynamic equilibrium at the upstream and downstream membrane interfaces, the concentrations adjacent to the membrane faces can be related to the partial pressures by Henry’s law (Seader and Henley, 1998). Figure 3.1 shows the partial pressure and concentration profile across porous and dense membrane.
- Concentration polarisation and fouling are assumed to be negligible and the membrane material does not change when it is in use (does not age).
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Modelling Developments for Membrane Separations

Figure 3.1: Partial pressure and concentration profile across membranes (Smith, 2005)

- Ideal heat exchange is assumed (i.e. heat loss is zero in the membrane unit). Under this assumption, the permeate temperature is equal to retentate temperature (Ploegmakers et al., 2013).

- Isothermal operation is taken into account. Membrane gas (vapour) separation processes are isothermal (Marriott and Sørensen, 2003). If isothermal flow is assumed and Henry’s coefficient (cm³ (STP)/cm³ Pa) is independent of total pressure, Henry’s coefficient of component \( i \) adjacent to upstream \( H_{o,i} \) and downstream \( H_{L,i} \) membrane interfaces are identical to Henry’s coefficient of component \( i \), \( H_i \) in the bulk feed (Seader and Henley, 1998).

### 3.2.2 Model equations

The schematic diagram of the two flow patterns considered in this study is given in Figure 3.2. The overall molar balance over the differential area \( dA \) is

\[-dF = dG\]  \(\text{(3.1)}\)

Where \( F \) is the molar flow rate of vapour on the feed side of the membrane and \( G \) is the molar flow rate of vapour on the permeate side of the membrane. Alternatively, the transport of component \( i \) can be described in terms of flux, \( J \):

\[-\frac{\partial F}{\partial A} = \sum J_i\]  \(\text{(3.2)}\)
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(a) Cross-flow  
(b) Counter-current flow

Figure 3.2: Schematic diagrams of flow patterns considered for investigation

The component molar balance for component $i$ is given by

$$-d(x_i F) = d(y_i G)$$  \hspace{1cm} (3.3)

$$- \frac{\partial (x_i F)}{\partial A} = J_i$$  \hspace{1cm} (3.4)

Integrating equation 3.4 from an arbitrary point to the outlet yields the following equation (Shindo et al., 1985): Equation 3.5 used in a counter-current flow pattern.

$$y_i = \frac{f x_i - x_{i,r} (1 - \theta)}{f - (1 - \theta)}$$  \hspace{1cm} (3.5)  \hspace{1cm} \text{where} \hspace{0.5cm} g \neq 0

Where $\theta$ is the stage cut (ratio of permeate flow rate to feed flow rate); $f$ is the dimensionless flow rate on the feed stream; $x_{i,r}$ retentate mole fraction of component $i$; $g$ is the dimensionless flow rate on the permeate stream. The dimensionless transport parameters are defined as shown in equations 3.6 to 3.9 (Shindo et al., 1985).

$$\theta = \frac{F_p}{F_f}$$  \hspace{1cm} (3.6)

$$\gamma = \frac{P_p}{P_f}$$  \hspace{1cm} (3.7)
Where $F_p$ and $F_f$ are the molar flow rates of the permeate and feed streams, respectively, and $\gamma$ is the pressure ratio, $P_p$ and $P_f$ are the permeate and feed stream pressure, respectively.

The permeate mole fraction can be calculated as follows (Shindo et al., 1985):

\[
y_i = \frac{J_i}{\sum J_i}, \quad g = 0
\]  

(3.10)

Solving equation 3.4 for $dx_i$ gives:

\[- J_i = \frac{F}{A} \frac{\partial x_i}{\partial A} + x_i \frac{\partial F}{\partial A}
\]

(3.11)

Subsisting equation 3.2 in equation 3.11 yields:

\[
\frac{\partial x_i}{\partial A} = \frac{1}{F} \left[ -J_i + x_i \sum J_i \right]
\]

(g \neq 0)  

(3.12a)

Subsisting equations 3.10 and 3.2 in equation 3.11 yields:

\[
\frac{\partial x_i}{\partial A} = \frac{\sum J_i}{F} \left[ x_i - y_i \right]
\]

(g = 0)  

(3.12b)

Introducing the conservation equations gives

\[
\sum x_i - 1 = 0
\]  

(3.13)

\[
\sum y_i - 1 = 0
\]  

(3.14)
Equations 3.2, 3.12a to 3.14 along with 3.5 and 3.10 provide the whole system of equations in the counter-current flow pattern. Equations 3.2, 3.12b to 3.14 along with 3.10 and 3.15 provide the whole system of equations in the cross-flow pattern.

\[
y_i = \frac{(1-\theta)x_{i,r} - x_{i,f}}{\theta} \quad i = 1: n
\]  

(3.15)

The local flux in equations 3.2, 3.10 and 3.12a and 3.12b is calculated from transport equations 2.15 and 2.16 for an immobilized liquid membrane, and from equation 2.19 for a solid polymer electrolyte membrane.

Equations 3.2 and 3.12a are used for solving the problem for a given membrane area. To solve the problem for a given stage cut, the following equations are used:

From equation 3.2,

\[
\frac{\partial A}{\partial F} = -\frac{1}{\sum J_i}
\]  

(3.16)

Dividing equation 3.12a by equation 3.2 gives

\[
\frac{\partial x_i}{\partial F} = \frac{J_i - x_i \sum_{i=1}^{n} J_i}{F \sum_{i=1}^{n} J_i}
\]  

(3.17)

In the present study, to predict the membrane performance, equations 3.16 and 3.17, along with the equations describing the flux, permeate mole fraction and equations 3.13 and 3.14 are solved simultaneously with MATLAB. Section 3.3 introduces the proposed solution methods for cross-flow and counter-current flow patterns.

### 3.3 Solution method

The solution method is based on Shindo et al. (1985), modified to overcome the sensitivity to initializations and to retain computational efficiency. This section discusses the drawbacks of the numerical solution method of Shindo et al. (1985) and the subsections 3.3.1 and 3.3.2 suggest solutions to them.
For a single-stage membrane separating a multicomponent system, Shindo et al. (1985) used Newton method to estimate permeate stream purities. It is well known that the Newton’s algorithm is quadratically convergent (Kelley, 1995); however, it has some drawbacks, such as sensitivity to the initial guess of solution and the high cost of the computation of derivatives at each iterative step. Oscillations, divergence or even convergence to unfeasible solutions (i.e. negative mole fraction) may also appear using the conventional Newton method (Tessendorf et al., 1999). Non-convergent behaviour or convergence to non-physical solutions is strongly connected to the non-linear nature of problem. In addition to this, if the transport rate of a component through a membrane is facilitated by certain carrier solutions, coupled to the transport of other components, or activated by chemical reaction occurring in the membrane, solving the non-linear equations that govern the performance of membrane module for gas separation will be highly complicated. A good initial point is therefore necessary in the solution approach of Shindo et al. (1985).

In the calculation method of Shindo et al. (1985), for a cross-flow, the initial guesses of permeate purities are assumed randomly at each step size. The results obtained from cross-flow are used as an initial estimate for counter-current flow. For a perfect mixing, initial guesses are generated based on results for co-current flow (Shindo et al., 1985). Furthermore, the permeate mole fractions are not bounded between zero and one in the published work of Shindo et al. (1985). Hence, negative mole fractions or negative membrane area results can be obtained from the simulation.

To solve the differential equations governing the system of Shindo et al. (1985), Runge-Kutta-Gill is used. The sensitivity of the solution method to the termination criteria was not discussed by Shindo et al. (1985). The choice of termination criteria can have a considerable effect on the efficiency and accuracy of the algorithm (The Math Works Inc, 2009). In addition, Shindo et al. (1985) did not state whether the Runge-Kutta-Gill method is used with a variable or fixed step size. It is better to vary the step size during the simulation so as to reduce the overall time required to simulate the system. The step size can be reduced to increase accuracy when a model’s results change steeply and increased to avoid taking unnecessary steps when the model results have changed slowly (The Math Works Inc, 2009).
discusses the influence of the abovementioned parameters on the ordinary differential equations solver in MATLAB.

In the calculation method of Shindo et al. (1985), the counter-current flow was solved by using Powell’s nonlinear optimisation method. In this method, the permeate mole fractions are unconstrained; therefore, the optimization can be trapped at a local optimum or may converge to an infeasible solution. Therefore, it is better to use a constrained nonlinear optimisation method. It should be mentioned that Shindo et al. (1985) did not introduce the criteria for the optimization or the formula of their objective function, but they specify the optimisation variables.

The following section introduces the solution methods that overcome the aforementioned shortcoming of Shindo et al. (1985).

3.3.1 Solution strategy for solving a cross-flow model

In the cross-flow case, the model results in an initial value problem, since the boundary conditions are specified at the inlet (Tessendrof et al., 1999).

To solve the cross-flow model shown in Figure 3.2 (a), the permeate mole fractions in the initial increment need to be specified first. It is extremely important to assume a reasonable initial estimate and maintain the permeate mole fraction within a specified bound to ensure a practical design. This section describes how the permeate purities are initialised. A solution method to solve the ordinary differential equations governing the membrane unit is then introduced.

3.3.1.1 Initial estimate of permeate purity

i. Binary system

In the cross-flow case, the permeate mole fraction is a function of the local feed purity only (Shindo et al., 1985; Kohl and Nielsen, 1997). A local permeate mole fraction $y_i$ can be obtained from equation 3.10. For a binary system, the ratio between two components in the permeate stream yields:

$$\frac{y_i}{1-y_i} = \frac{J_i}{J_j}$$  \hspace{1cm} (3.18)
If the flux is described by equation 2.19, equation 3.18 can be written as follows:

\[
\frac{y_i}{1-y_i} = \frac{P_{Mj}(x_i - y_i)}{P_{Mj}(1-x_i) - \gamma(1-y_i)}
\]  

(3.19)

Equation 3.19 is quadratic in \( y_i \) (Davis and Sandall, 2003). Solving for \( y_i \):

\[
y_i = \frac{(P_{Mj} - 1) \left( x_i \frac{1}{y} + 1 \right) + \frac{1}{y} - \sqrt{\left( \frac{P_{Mj}}{P_{Mj}} - 1 \right) \left( x_i \frac{1}{y} + 1 \right)^2 - 4 \left( \frac{P_{Mj}}{P_{Mj}} - 1 \right) x_i \frac{1}{y} P_{Mj}}}{2 \left( \frac{P_{Mj}}{P_{Mj}} - 1 \right)}
\]  

(3.20)

The cross flow model equations are subject to the initial boundary conditions

\[
\begin{align*}
x_i &= x_{f,i} \\
f &= 1
\end{align*}
\]  

at \( S = 0 \)  

(3.21)

\[
S = A \frac{P_f P_{Mj}}{F_f \delta}
\]  

(3.22)

Where \( S \) is the dimensionless membrane area, \( A \) is the membrane area, and \( \delta \) is the membrane thickness.

It can be seen that neither an initial estimate nor an iteration procedure are required to calculate the permeate mole fractions in the first increment area of the membrane module when the separation system is for a binary mixture.

ii. Multicomponent system

For a multicomponent system, the key is to assume a reasonable initial value of the mole fraction for the fast permeating component. An initial estimate of the mole fraction for the fast permeating component \( j \) can be specified as follows:

\[
y_j = \frac{x_{j,f}}{\sum_{i=1}^{n} \frac{P_{Mj}}{P_{Mj}} x_{i,f}}
\]  

(3.23)

Where \( x_{i,f} \) and \( x_{j,f} \) are the feed mole fractions of component \( i \) and the most permeating component, \( j \), respectively. \( y_j \) is the mole fraction of the most permeating
component. $P_{Mi}$ and $P_{Mj}$ are the permeability of component $i$ and the most permeating component, respectively.

For a given function and its derivative with respect to $y_j$, and beginning with an initial estimate of permeate stream mole fraction, a new approximation of $y_j$ can be calculated. Therefore, the calculation method of Shindo et al. (1985) can be used to predict the mole fraction of the most permeating component. The permeate mole fraction $y_j$ for the most permeating component is obtained by solving equation 3.24 with the ‘Newton method’. In the Newton algorithm, the permeate mole fraction is bounded between zero and one to provide a feasible solution in this work. In addition, under-relaxation factors are introduced.

$$\sum_{i=1}^{n} x_{i,f} \frac{P_{Mi}}{P_{Mj}} - 1 = 0 \quad g = 0$$ (3.24)

The calculated value of $y_j$ used to find the rest of the permeate mole fractions, $y_i$, through equation 3.25. However, only $n-1$ of the permeate mole fractions are calculated, and the remaining mole fraction is determined from the summation mole fraction equation 3.14. The solutions obtained for $y_j$ are used as a new initial estimate for the next area increment in the simulations.

$$y_i = \frac{x_{i,f} \frac{P_{Mi}}{P_{Mj}}}{(\gamma + \theta - \gamma\theta) \left[ \frac{P_{Mi}}{P_{Mj}} - 1 \right] + \frac{x_{j,f}}{y_j}} \quad j \neq i$$ (3.25)

$$y_i = \frac{x_{i,f} \frac{P_{Mi}}{P_{Mj}}}{(\gamma + \theta - \gamma\theta) \left[ \frac{P_{Mi}}{P_{Mj}} - 1 \right] + \frac{x_{j,f}}{y_j}} \quad i = 1: n-1$$

### 3.3.1.2 Ordinary differential equations solution method

MATLAB provides a set of programs, known as ode solvers, which are designed for solving non-stiff ordinary differential equations, such as ode45, which is based on an explicit Runge-Kutta (4, 5) formula; and ode15s, which is intended to solve stiff differential equations and based on the numerical differentiation formulas
(first/fifth order Runge-Kutta). Ode15s is a multistep solver; the model is solved at different step sizes during the simulation.

The efficiency of these solvers can often be considerably improved by adjusting a local error \( e \) in the \( i \)th component of the solution, as shown in equation 3.26, which is a function of a relative error tolerance, \( RelTol \), and an absolute error tolerance, \( AbsTol \) (The Math Works Inc, 2009). Section 3.3.3 will discuss the influence of \( RelTol \) and \( AbsTol \) on the solution accuracy.

\[
|e_i| \leq \max\{RelTol \times |x_i|, \ AbsTol\} \quad (3.26)
\]

In this work, ode45 is applied to solve ordinary differential equations. If ode45 along with the adjusted integration properties fails to provide convergence to a feasible solution, ode15s is employed to solve the ordinary differential equations.

The algorithm for cross-flow is shown in Figure 3.3. The permeate mole fraction of the fast permeating component at the inlet is calculated by solving equation 3.24 using Newton’s method. Equation 3.25 is then used to calculate the rest of the permeate mole fractions.

In Newton’s method, the algorithm checks the termination conditions after each iteration step. The calculation is repeated until the calculated value is within a specified tolerance. In this work, the maximum number of iterations is set to 100 and the tolerance on the function value to \( 10^{-6} \). The algorithm then checks whether the calculated permeate purities are suitable. If permeate purities are not within the specified range, Newton’s method is under-relaxed and a higher number of iterations to approach a convergent solution is specified. The relaxation factor is set to 0.1 and the maximum number of iterations to 500. However, for stiffness equations, the relaxation factor is further reduced to 0.01 and the tolerance on the function value to \( 10^{-10} \) in order to obtain a convergent solution. The purpose of using the two-step approach (the classical Newton’s method and then the relaxed Newton’s method) is to avoid both divergent solutions at high stage cuts and low pressure ratios, and slow convergence (high CPU time) at low stage cuts. After that, the odes, in conjunction with summation equation, are integrated, for given boundary conditions. The permeate product purities can then be calculated from the overall mass balance equation around the membrane.
3.3.2 Solution strategy for a counter-current membrane separator

Solving the counter-current case is more difficult than the previous case because the permeate purity on the permeate side is unknown (Shindo et al., 1985; Coker, et al., 1998). An initial estimate for the permeate purity for the fast permeating
component and retentate purities is needed to solve the set of nonlinear differential equations. For a counter-current flow, as shown in Figure 3.2 (b), the integration is carried out ‘backwards’ (beginning at the feed end of the module).

The simulation flowchart for a counter-current model is schematically shown in Figure 3.4. For a given feed composition, pressure ratio, permeability values, and stage cut, the calculation is initiated by guessing the retentate purity, mole fraction of the most permeating component in the permeate stream and dimensionless membrane area.

![Simulation flowchart for the counter-current flow membrane module](Figure 3.4)

First, Newton’s method is used to calculate the mole fraction of the fast permeating component in the permeate stream at the feed end of the module by solving equation 3.24. Then, the rest of the permeate mole fractions at the feed end of the module are evaluated using equation 3.25. Following this, the set of differential equations are solved using the Runge-Kutta method (ode15s). Thereafter, the integration of the set of differential equations (3.16 & 3.17), in conjunction with equations 3.13, 3.14 and 3.5, are carried out until the end of the membrane module (i.e. to the inlet feed side). At the inlet feed side, the difference between the given feed purities $x_{i,f}$ at dimensionless inlet membrane area $S_0 = 0$ and the integration results of feed purities $x_{i,f}$ at dimensionless inlet membrane area $S_0 = S$ are evaluated by equation 3.27. When equation 3.27 is calculated, its results are returned to the optimiser. The optimiser is used to minimise the objective function (equation 3.27) by varying the process variables. In this work, sequential quadratic programming
(SQP) method is used to find the lowest possible value of the objective function, \( f \). In the SQP method, the function solves a quadratic programming sub-problem at each iteration. An estimate of the Hessian of the Lagrangian is updated using the Broyden, Fletcher, Goldfarb, and Shanno formula (The Math Works Inc, 2009). To achieve accurate predictions, a termination tolerance on the function value (\( TolFun \)) of \( 10^{-10} \), a termination tolerance on variable \( x \) (\( TolX \)) of \( 10^{-6} \), and a maximum number of function evaluation allowed (\( MaxFunEvals \)) of 600 are set for the optimization.

\[
\min(f) = (S - S_0)^2 + \sum_{i}^{n} (x_{i,r} - x_{i,f})^2
\]  

(3.27)

Where

\( x_{i,f} \): is the given value of feed mole fraction of component \( i \)

\( x_{i,r} \): feed mole fractions predicted by the model

\( S_0 \): dimensionless inlet membrane area

\( S \): dimensionless inlet membrane area predicted by the model

The objective function is subject to the following constraints

i. Equality constraints

\[
\sum_{i=1}^{n} x_{i,r} = 1
\]  

(3.28)

ii. Upper and lower bound constraint

One of the difficulties of the constrained optimisation is to choose appropriate upper and lower bound constraints for retentate mole fractions. Equation 3.29 represents the upper and lower bound constraint on retentate mole fractions at the feed end of the module. For a lower bound constraint \( (x_{i,r}^l) \), the feed mole fractions are used; except for the most permeating component, a very small value is assumed (0.001). This is because the purity of the fast permeating species in the high-pressure side at high stage cuts is small. For upper bound constraint \( (x_{i,r}^u) \), the initial estimates are higher than perfect mixing retentate mole fractions because the lowest separation performance is achieved from a perfectly mixed flow.
iii. Logical binary variables

A conditional statement with a logical binary variable \( Y_1 \) is used to check that the permeate mole fractions are in the range of 0 to 1. If the algorithm returns permeate mole fractions between 0 and 1 then the condition is true (logical 1). Otherwise, a new initial value of the permeate mole fraction is automatically estimated (by using a function that increases the permeate mole fraction by adding a small increment size: \( y_j(k+1) = y_j(k) + \Delta y_j \)) and tested again. Updating and testing guarantees that the algorithm gives a feasible solution.

This state is expressed as shown below:

\[
Y_1 = 1 \quad if \quad 0 \leq y_{i,p} \leq 1 \tag{3.30}
\]

\[
Y_1 = 0 \quad if \quad y_{i,p} > 1 \quad or \quad y_{i,p} < 0 \tag{3.31}
\]

### 3.3.3 Illustrative example: Solving numerical instability in membrane module equations

An illustrative example is presented in this section to illustrate the robustness of the proposed solution method in Sections 3.3.1 and 3.3.2 for solving the membrane model equations. The performance of the ordinary differential equation solvers available in MATLAB are compared with a fourth order Runge-Kutta (RK4) routine which uses a fixed step size. The solvers which have been used are ode45 (fourth/fifth order Runge-Kutta) and ode15s (first/fifth order Runge-Kutta). These solvers are suitable for a wide variety of initial value problems because they vary the step size, choosing the step size at each step in an attempt to achieve the desired accuracy for the permeate purities. This accuracy can be controlled by defining two parameters; the relative tolerance, \( \text{RelTol} \), and the absolute tolerance, \( \text{AbsTol} \). Thus, the influence of these parameters on the efficiency and accuracy of the odes solver is analysed.
A case study presented by Coker et al. (1998) for hydrogen separation from a refinery stream by a polysulphone membrane is taken as an illustrative example. This case is chosen because Coker et al. (1998) and David (2007) reported convergence problems at low pressure ratios and high recovery for the fast permeating component. Data for the feed stream composition and their permeance are presented in Table 3.1 (Coker et al., 1998). The effect of flow pattern including a cross-flow and a counter-current flow, pressure ratio and stage cut on membrane module performance are explored. Equations 2.19, 3.16 and 3.17 are considered for describing the performance of a polysulphone membrane.

Table 3.1: Permeability of gases in polysulphone membrane and feed conditions (Coker et al., 1998)

<table>
<thead>
<tr>
<th>Component</th>
<th>formula</th>
<th>Mole fraction</th>
<th>Permeance $\text{cm}^3$ (STP) $\text{cm}^2 \text{s}^{-1} \text{cmHg}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H$_2$</td>
<td>0.65</td>
<td>100$\times10^6$</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C$_2$H$_4$</td>
<td>0.025</td>
<td>3.03$\times10^6$</td>
</tr>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>0.210</td>
<td>2.86$\times10^6$</td>
</tr>
<tr>
<td>Ethane</td>
<td>C$_2$H$_6$</td>
<td>0.080</td>
<td>2$\times10^6$</td>
</tr>
<tr>
<td>Propane</td>
<td>C$_3$H$_8$</td>
<td>0.035</td>
<td>1.89$\times10^6$</td>
</tr>
</tbody>
</table>

3.3.3.1 Cross-flow

To solve the set of equations describing the module model performance in a cross-flow pattern, RK4, ode45, ode15s are used. The simulation results of a fourth order Runge-Kutta are shown in Table 3.2. In this case, the membrane module is divided into a number of increments of equal step size.

Table 3.2 shows that the number of increments has a strong impact on the precision of the results. It can be seen that a large number of increments needs to be used to obtain identical results to ode45, as shown in Figure 3.7 (a). The minimum number of increments in this case should be 1000. These findings are comparable to the results obtained by Coker et al. (1998). The minimum number of increments used in their simulation is 100 at low stage cut. However, the minimum required number increased to more than 1000 for high stage cuts (>90%).
Table 3.2: Effect of increment numbers on retentate purity (stage cut = 0.8; permeate pressure = 42.4 bar; feed pressure = 76.9 bar; Feed to permeate pressure ratio = 1.8)

<table>
<thead>
<tr>
<th>Increment number</th>
<th>50</th>
<th>100</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionless step size</td>
<td>0.004</td>
<td>0.002</td>
<td>0.0004</td>
<td>0.0002</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Retentate mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.2678 0.2463 0.2263 0.2236 0.2222</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.0471 0.0485 0.0499 0.0501 0.0502</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.4094 0.4219 0.4335 0.4351 0.4359</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.1901 0.1954 0.2002 0.2009 0.2012</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.0856 0.0879 0.0901 0.0904 0.0905</td>
</tr>
<tr>
<td>Simulation time, sec</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 3.2 shows that the number of increments must be determined carefully, as a large number leads to high computation time and small numbers result in an inaccurate solution. In the present illustrative example, an average dimensionless step size of flow rate on the feed stream equal to $10^{-4}$ is found to be sufficient for accurate predictions for retentate compositions at a stage cut value of 0.8. Reducing the dimensionless step size below this value does not considerably change the computed results.

As expected, ode45 provides fast and accurate prediction of the membrane performance (e.g., retentate mole fractions) compared to RK4. The simulation results in Figure 3.5 show that ode45 will probably work at a stage cut ratio below 0.5 with the default relative tolerance, RelTol, of $10^{-3}$ and absolute tolerance, AbsTol, of $10^{-6}$. However, at higher stage cuts the default values of RelTol and AbsTol should be adjusted to get a feasible answer, as shown in Figures 3.5 and 3.6. Convergence is achieved as shown in Figures 3.5 (b) and 3.6 with RelTol of $10^{-6}$ and AbsTol of $10^{-8}$ at $\theta = 0.8$, and with RelTol of $10^{-6}$ and AbsTol of $10^{-10}$ at $\theta = 0.92$.

The effect of the parameters of relative tolerance and absolute tolerance on solving the set of differential equations at low pressure ratios has also been examined. Convergence is achieved at extremely high stage cuts and low pressure ratios via ode45 with RelTol of $10^{-9}$ and AbsTol of $10^{-10}$ and by ode15s with RelTol of $10^{-9}$ and AbsTol of $10^{-10}$, as shown in Figures 3.8 (a) and 3.8 (b).
Figure 3.5: Effect of ode45 solver parameters on cross-flow simulation results: $\gamma^1 = 5.3; \theta = 0.8$
(a) $\text{RelTol} = 10^{-6}$ and $\text{AbsTol} = 10^{-8}$. Elapsed time is 0.21 sec

(b) $\text{RelTol} = 10^{-6}$ and $\text{AbsTol} = 10^{-10}$. Elapsed time is 0.1 sec

Figure 3.6: Simulation results using ode45 for cross-flow membrane module: $\gamma^{-1} = 5.3; \theta = 0.92$
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(a) ode45: RelTol = 10^{-6} and AbsTol = 10^{-10}. Elapsed time is 0.23 sec.

(b) ode45: RelTol = 10^{-9} and AbsTol = 10^{-10}, Elapsed time = 1.8 sec; ode 15s: RelTol = 10^{-8} and AbsTol = 10^{-10}, Elapsed time = 0.96 sec

Figure 3.7: Simulation results using ode45 and ode15s for cross-flow membrane module: $\gamma^{-1} = 1.8; \theta = 0.92$
3.3.3.2 Counter-current flow

For a counter-current flow, the problem becomes more complicated because the model becomes highly sensitive to initial estimates and suffers from convergence problems, as shown in Figure 3.8. Consequently, a constraint on the permeate purities needs to be introduced to force the algorithm to converge to a feasible solution (in the range of [0, 1]). The simulation results shown in Figure 3.8 illustrate that there is only one solution for the problem.

Figure 3.8: The sensitivity of Newton’s method to initial guess. Stage cut = 0.85; permeate pressure = 42.4 bar; feed pressure = 76.9 bar; Feed to permeate pressure ratio = 1.8

In addition to its sensitivity to initialization, the model is sensitive to the stiffness of ordinary differential equations and, therefore, calculations sometimes fail to converge. A comparison between ode45 and ode15s is shown in Figure 3.9. Using ode45 with the default relative tolerance, \(RelTol\), of \(10^{-3}\) and absolute tolerance, \(AbsTol\), of \(10^{-6}\), the solutions diverge from the first iteration. Clearly the default \(RelTol\) is not sufficiently small and ode45 is not able to give a feasible solution. On the other hand, ode15s performs quite well compared with ode45. Using the parameters \(RelTol\) of \(10^{-10}\) and \(AbsTol\) of \(10^{-8}\) for ode solver and the termination tolerance on the objective function, \(TolFun\), of \(10^{-10}\) for the objective function gives accurate results, as shown in Figure 3.10.
Figure 3.9: Comparison of ode45 and ode15s performance for counter-current flow. Feed to permeate pressure ratio = 1.8; Stage cut = 0.85; RelTol = $10^{-3}$ and AbsTol = $10^{-6}$
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In conclusion, this section illustrates that fine-tuning of the ode solver parameters is very important, especially when the driving force becomes very small (partial pressures on the permeate side and feed side of the membrane are virtually equal). The parameters influence the accuracy of the solution and the speed of convergence as they control the local discretization error and the integration step size. The ode solver parameters concerned are the relative error tolerance and the absolute error tolerance. Examining the computed results shows that the default relative tolerance, \( \text{RelTol} \), of \( 10^{-3} \) is not sufficient; therefore, a smaller relative tolerance should be used.

Figure 3.10: Simulation results of counter-current algorithm using odes15s. Feed to permeate pressure ratio = 5.3; stage cut = 0.85

(a) The algorithm step size and the objective function value at each iteration

(b) Retentate mole fractions profile
A relative tolerance in the range of $10^{-6}$ to $10^{-9}$ is found to be suitable along the entire range of stage cuts. Setting the relative tolerance to $10^{-9}$ gives accurate results.

The absolute tolerance is also reduced from the default value; the suitable range is $10^{-8}$ to $10^{-10}$. Although the default absolute tolerance of $10^{-6}$ seems to be adequate at low stage cuts, to account for small mole fractions, the absolute tolerance value should be further reduced than the default value.

In the counter-current flow, the termination tolerance on the objective function value should also be adjusted to a small value such as $10^{-10}$. It should be mentioned that, although the illustrative example is applied to a hydro-treatment unit operation in a refinery, the range of odes solvers parameters found here are applicable for an ethylene-ethane separation system in this thesis.

From cross-flow results, it is proved that ode45 (fourth/fifth order Runge-Kutta) and ode15s (first/fifth order Runge-Kutta) are more powerful for solving differential equations at high stage cuts and low pressure ratios than the 4\textsuperscript{th} order Runge-Kutta method.

In the counter-current flow, ode15s provides the best performance in terms of accuracy and computational efficiency compared with ode45. Ode15s works properly even when the partial pressure on both the high- and low-pressure side of the membrane become practically equal. In the case outlined above, solving the model equations takes a maximum of 2 seconds for a cross-flow module, and about 122 seconds for a counter-current flow module.

### 3.4 Model validation

To confirm that the proposed solution method provides accurate predictions of the membrane performance, the model prediction is tested and compared with published work in this Section. The membrane model performance has been validated against the experimental results of Kaldis et al. (2000) and compared with the published modelling results of Shindo et al. (1985) and Coker et al. (1998).
3.4.1 Validation of model prediction with experimental work of Kaldis et al. (2000)

Kaldis et al. (2000) used a polyimide hollow fibre asymmetric membrane for the separation and recovery of hydrogen from refinery gases. The feed and membrane specifications are given in Table 3.3. The pressures on the feed and permeate side of the membrane are 20 bar and 1 bar, respectively. Counter-current flow pattern is used to describe the module model performance.

Table 3.3: Permeability of gases in polyimide membrane and feed compositions
(Kaldis et al., 2000).

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Permeability (cm$^3$/cm$^2$.s.cmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.675</td>
<td>$2.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.167</td>
<td>$3.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.013</td>
<td>$6.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.035</td>
<td>$9.3 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

To predict the membrane performance in a counter-current flow, the solution method presented in Section 3.3.2 is used. The ode15s solver parameters are set as follows: $\text{RelTol}$ of $10^{-10}$ and $\text{AbsTol}$ of $10^{-8}$.

The present simulation results are in good agreement with the experimental data over the range of reported stage cuts and pressures. That this is good agreement can be seen in Figures 3.11 and 3.12, which show the permeate purity and retentate purity as functions of the module stage cut.

![Figure 3.11](image.png)

Figure 3.11: Comparison of modelling results with experimental data of Kaldis et al. (2000): permeate purity as a function of stage cut at a feed pressure of 20 bar.
Figure 3.12: Comparison of model predictions with experimental data of Kaldis et al. (2000): retentate purity as a function of stage cut at a feed pressure of 20 bar.

Figure 3.13 shows the effect of feed pressure on retentate purity; it can be seen that there is excellent agreement between the experimental data and the model prediction for most of the component in the mixture. However, it is noticeable that the predicted retentate mole fractions are low for hydrogen and high for methane, compared to the experimental data. This could indicate that hydrogen permeation has the effect of slightly speeding up the permeation of the slower gases or could be due to using pure permeability data. The assumption of using pure permeability values for a multicomponent system could lead to overestimation of the membrane performance for the fast permeating component. The permeability data of Kaldis et al. (2000) given in Table 3.3 was measured for pure component.

Figure 3.13: Comparison of model predictions with experimental data of Kaldis et al. (2000): retentate purity as a function of feed pressure at a stage cut of 0.5.
3.4.2 Validation of model prediction with simulation results of Shindo et al. (1985)

The model prediction is compared with the results of Shindo et al. (1985) for the separation of a mixture of NH₃, H₂, and N₂ with the four idealised flow patterns. The Permeability of gases in polyethylene membrane is provided in Table 3.4. The feed pressure and the permeate pressure are 20 bar and 2.6 bar, respectively. The ratio of permeate exit molar flow rate to the feed molar flow rate is 0.5.

Table 3.4: Permeability of gases in polyethylene membrane and feed purities (Shindo et al., 1985)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Permeability (mol/s.m.Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.45</td>
<td>$3.69 \times 10^{-15}$</td>
</tr>
<tr>
<td>H₂</td>
<td>0.25</td>
<td>$1.17 \times 10^{-15}$</td>
</tr>
<tr>
<td>N₂</td>
<td>0.3</td>
<td>$2.41 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

In this case, ode45 is the method used to solve the governing equations of the membrane. The simulation parameters used for this separation are RelTol of $10^{-3}$ and AbsTol of $10^{-6}$. The results obtained for the membrane area for various flow patterns are comparable to those reported by Shindo et al. (1985) at a stage cut of 0.5, as shown in Figure 3.14. Table 3.5 shows the permeate purities for various flow patterns. In all cases, the permeate mole fractions calculated by Shindo et al. (1985) compare very well with the mathematical model predictions of this work for stage cut 0.5. The maximum absolute error for the permeate mole fraction is 0.4%. In this case, the algorithms do not show any sensitivity to the initial estimates for various flow patterns.

Table 3.5: Model prediction and data of Shindo et al. (1985)

<table>
<thead>
<tr>
<th>Permeate mole fraction</th>
<th>Shindo et al. (1985)</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₃</td>
<td>H₂</td>
</tr>
<tr>
<td>Counter-current flow</td>
<td>0.7054</td>
<td>0.2200</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>0.7003</td>
<td>0.2241</td>
</tr>
<tr>
<td>Co-current flow</td>
<td>0.6923</td>
<td>0.2303</td>
</tr>
<tr>
<td>Perfect mixing</td>
<td>0.6393</td>
<td>0.2492</td>
</tr>
</tbody>
</table>
3.4.3 Validation of model prediction with simulation results of Coker et al. (1998)

The model predictions have also been compared to the results of the model presented by Coker et al. (1998) for hydrogen separation from a refinery stream in a counter-current operation. Coker et al. (1998) used ‘Newton-Raphson’ method to solve the model equations as discussed in Section 2.2.6.

The stream composition and the permeance of gases through a polysulphone membrane are presented in Table 3.1. Two cases with a different ratio of feed to permeate pressure were investigated by Coker et al. (1998). In the first case, the permeate pressure is assumed to be 7.9 bar and the feed pressure is 42.4 bar (feed to permeate pressure ratio = 5.3). In the second case, the permeate pressure is assumed to be 42.4 bar for a feed pressure of 76.9 (feed to permeate pressure ratio = 1.8). In both these cases, the stage cuts are varied from 0 to 1.

The sequential quadratic programming method is used to solve the counter-current membrane module, with $TolFun$ of $10^{-10}$ for the objective function of the optimisation and $RelTol$ of $10^{-10}$ and $AbsTol$ of $10^{-8}$ for ode15s solver. Figure 3.15 illustrates the effect of pressure ratio on the hydrogen purity and recovery. As the stage cut is varied, the hydrogen purity and recovery values change. As shown in
Figure 3.15, the simulation results are comparable to those presented by Coker et al. (1998) for both pressure ratios. In this case, the counter-current algorithm takes about 122 seconds to obtain a convergent solution.

![Graph showing comparison between simulation results and modelling results of Coker et al., 1998; influence of pressure ratio on hydrogen purity and recovery for counter-current unit.]

3.5 Summary– Detailed model

A new numerical solution approach for the well-known model developed earlier by Shindo et al. (1985) for multicomponent membrane gas separation process is introduced. The results of a simulation applying the proposed numerical method presented in Section 3.3.1 and 3.3.2 demonstrates low sensitivity to the initial estimate of the permeate stream composition and the program converges to an accurate solution in a reasonable time. The simulation results show the robustness of the solution method.

Coker et al. (1998) found that the shooting method was unstable and were unable to achieve convergence because the partial pressure driving force for hydrogen becomes very small at high stage cut. The new algorithm is stable at low pressure ratios and high stage cuts, and outperforms the conventional Runge-Kutta method used by of Shindo et al. (1985) and the shooting method tested by Coker et al. (1998) because the permeate purity is bounded and a robust ode solver is used.
The results of the present numerical solution approach are found to be in good agreement with published work, e.g. the model results reported by Coker et al. (1998), the experimental work of Kaldis et al. (2000). The proposed solution method performs well at low pressure ratios for permeate versus feed sides and high stage cuts where separation is dominated by partial pressure differences.

### 3.6 A new approximate method for predicting facilitated transport membrane separation factor and the permeate composition of a binary system

In the literature, exact and approximate solutions are proposed to solve the set of mass balance and flux equations describing membrane module performance (e.g., Shindo et al., 1985; Chen et al., 1994; Coker et al., 1998; Makaruk and Harasek, 2009). In the exact solution approach, the membrane module is divided into small incremental areas and then the set of equations are solved numerically. Predicting the permeate and retentate purities in each element of the membrane presents a challenge. This is because the permeate and retentate mole fractions are varied along the membrane and a large number of elements are usually required to predict accurately the membrane performance. In addition, nonlinear differential model equations might not converge to an exact solution, as illustrated in Section 3.3.3.

In the preliminary design stage, an approximate method would be appropriate for evaluation of membrane-assisted separation processes. An approximation method can rapidly predict the performance of a membrane module and this is useful for process design and optimisation. Approximate analytical solutions to the governing equations that describe the performance of membrane module for various flow patterns have been introduced by many researchers (e.g., Krovvidi et al., 1992; Naylor and Backer, 1955, cited in Seader and Henley, 1998). However, to my knowledge, an approximate method to describe the transport of ethane and ethylene across a facilitated transport membrane by a dual-mode transport model does not exist.

The advantages of using facilitated transport membranes for ethylene-ethane separation processes have attracted many researchers. The main advantage of facilitated transport membrane as compared to polymeric membrane is the higher
sorption selectivity of ethylene over ethane (Rungta et al., 2013). This intrinsic feature of facilitated transport membrane could enable a reduction in the capital costs and energy requirements of ethylene-ethane separation. This research aims to explore the potential for the application of facilitated transport membrane coupled with a distillation column for ethylene-ethane separation. An approximate method could result in fast screening of separation alternatives; therefore, an approximate solution is considered in this study.

3.6.1 Mathematical formulation

This section introduces an approximate solution method based on Naylor and Backer (1955), cited in Seader and Henley (1998).

For a given feed composition \( (x_{i,f}) \), Naylor and Backer (1955) develop an analytical solution to determine the permeate purity for a cross-flow module, as shown schematically in Figure 3.2 (a), wherein gas molecules sorb at one surface of the membrane, diffuse through the membrane under a pressure driving force, and then desorb from the surface. The transport flux for this membrane was described by Fick’s law (Seader and Henley, 1998).

The main assumptions, considered by Naylor and Backer (1955) for modelling cross-flow module, are:

- Binary mixture
- Negligible film mass-transfer coefficient on both sides of the membrane. The partial pressures adjacent to the membrane surface are described by Henry’s law.
- Constant separation factor \( (\alpha_{AB}) \). Separation factor is defined similarly to relative volatility in distillation, as shown in equation 3.32. However, unlike the distillation column, the permeate stream composition is not in equilibrium with the retentate stream composition (Seader and Henley, 1998)

\[
\alpha_{AB} = \sqrt[1.4142]{\left(\frac{y_{A,p}}{x_A}\right) \cdot \left(\frac{y_{B,p}}{x_B}\right) \cdot \left(\frac{1 - y_{A,p}}{1 - x_A}\right) + \frac{1}{\left(\frac{y_{A,p}}{x_A}\right) \cdot \left(\frac{y_{B,p}}{x_B}\right) \cdot \left(\frac{1 - y_{A,p}}{1 - x_A}\right)}}
\]  
(3.32)
• Constant pressure ratio ($\gamma$): the ratio of permeate pressure to feed pressure
• Plug-flow on the feed side of the membrane and cross-flow along the permeate side of the membrane (see Figure 3.2 (a)).

The permeate mole fraction may be determined by equation 3.33 (Naylor and Backer, 1955).

$$ y_{A,p} = \frac{\int_{x_f}^{x_r} y_A dF}{\int_{x_f}^{x_r} dF} = \frac{1}{\theta F_f} \int_{x_f}^{x_r} y_A dF $$

(3.33)

Where $y_{A,p}$ is the permeate mole fraction of component $A$, $F_f$ is the feed molar flow rate, $x_f$ and $x_r$ are the feed and retentate mole fraction, respectively.

Integration of equation 3.33 yields equation 3.34. Details of the derivation of equation 3.34 are available in Seader and Henley (1998).

$$ y_{A,p} = x_{A,r} \left( \frac{1}{1 - \frac{\alpha_{AB}}{\alpha_{AB}}} \left( 1 - x_{A,r} \right) \frac{\alpha_{AB}}{1 - \frac{\alpha_{AB}}{\alpha_{AB}}} \right) \left( x_{A,f} \frac{\alpha_{AB}}{1 - \frac{\alpha_{AB}}{\alpha_{AB}}} - x_{A,r} \frac{\alpha_{AB}}{1 - \frac{\alpha_{AB}}{\alpha_{AB}}} \right) $$

(3.34)

Component material balance yields the retentate composition:

$$ x_{A,r} = \frac{x_{A,f} - \theta y_{A,p}}{1 - \theta} $$

(3.35)

Solving equations 3.34 and 3.35 simultaneously makes it possible to determine $y_{A,p}$ and $x_{A,r}$ for a variable $\theta$. It can be seen that equation 3.34 is a function of stage cut, retentate mole fraction of component $A$ ($x_{A,r}$) and the separation factor ($\alpha_{AB}$). It should be mention that equation 3.34 can be applied for any type of membrane. However, the value of $\alpha_{AB}$ will depend on the mass transport phenomena within the membrane unit and the thermodynamic equilibria (Seader and Henley, 1998).

When the solution-diffusion mechanism is the controlling mechanism, and the flux is represented by Fick’s law, the separation factor can be determined as follow:

• If the pressure of the permeate stream is negligible compared with the feed stream pressure, such that $y_{A,P} << x_{A,F}$ and $y_{B,P} << x_{B,F}$ (Seader and Henley,
1998), the separation factor, $\alpha_{AB}$, will be equal to the ideal separation factor ($\alpha_{AB}^*$); this is the permeance ratio for the two components being separated.

$$\alpha_{AB}^* = \frac{\alpha_{AB}}{\frac{P_{MA}}{P_{MB}}}$$

(3.36)

Where $\frac{P_{MA}}{P_{MB}}$ are the permeance of components A and B, respectively.

- If the permeate stream pressure is not negligible, the separation factor is calculated by equation (3.37) as presented by Seader and Henley (1998).

$$\alpha_{AB} = \frac{P_{MA}}{P_{MB}} \left[ \frac{x_A(\alpha_{AB} - 1) + 1 - \gamma \alpha_{AB}}{x_A(\alpha_{AB} - 1) + 1 - \gamma} \right]$$

(3.37)

If it is the case that the mass transfer within the membrane module occurs by simple solution-diffusion and solute-carrier complex diffusion, a new correlation is derived to obtain the separation factor, as shown in equation 3.38. The membrane model in this case is based on the assumption that a thermodynamic equilibrium exists between the product and reactant species at the two fluid membrane interfaces. Furthermore, it is assumed that the diffusivity and solubility coefficients of each species are independent of pressure and that the temperature is the same at both membrane faces.

Section 2.2.1.1 introduces the flux equations that describe a dual-mode transport based on the preceding assumptions. Equation 3.38 is obtained by combining equation 3.32 and the mole balance equations with the flux ratio of equations 2.15 and 2.16. Appendix A illustrates the derivation of equation 3.38.
It can be seen that the separation factor in equation 3.38 is a function of the feed purity of component \( A \), \( x_A \), and the pressure ratio, \( \gamma \), permeate pressure, \( P_p \), feed pressure, \( P_f \), and membrane experimental data (permeance of each component, equilibrium constant, \( K_{eq} \), membrane thickness, \( \delta \), diffusion coefficient of the complex, \( D_C \), molar concentration of the carrier in the membrane, \( C^C \), and Henry’s coefficient of component \( A \), \( H_A \)). For a given feed composition and membrane data, the separation factor can be found by using iterative methods.

The significance of equations 3.34 and 3.38 is that they help to describe the extent of separation, and assist in predicting membrane performance, and thereafter the design and evaluation of process alternatives (e.g., hybrid membrane-distillation). The following section verifies the model’s prediction for ethylene-ethane separation.

### 3.6.2 Models assessment

In order to illustrate the robustness of the analytical solution method (approximate model), this section presents a comparison of the results of the analytical model with those from the exact model (model equations and solution methods are given in Section 3.2.2 and 3.3.1, respectively).

Consider a binary mixture to be separated by facilitated transport membranes; namely immobilized liquid membrane (Teramoto et al., 1986 and Hughes et al., 1986, cited in Al-Rabiah, 2001) and solid polymer electrolyte membrane (Pinnau and Toy, 2001). The feed compositions and permeability data are listed in Table 3.6. In immobilized liquid membrane, the diffusivity of ethylene silver complex is \( 1.66 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \), the equilibrium constant is \( 0.13 \text{ m}^3 \text{ mol}^{-1} \), the carrier concentration is \( 6 \text{ mol l}^{-1} \), and the membrane thickness is \( 1.7 \times 10^{-6} \text{ m} \). The permeate pressure is set at 1.01 bar and feed pressure at 19 bar. Representation values for stage cuts are taken as 0.01, 0.1, 0.2, 0.3, 0.4, and 0.5.

Table 3.6: Feed compositions and permeability data for approximate model performance evaluation

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Permeability(^a), m(^3) (STP) m(^{-2}) s(^{-1}) pa(^{-1})</th>
<th>Permeability(^b), m(^3) (STP) m(^{-2}) s(^{-1}) pa(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_4)</td>
<td>0.54</td>
<td>( 1.2 \times 10^{-11} )</td>
<td>( 1.8 \times 10^{-11} )</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>0.46</td>
<td>( 4.3 \times 10^{-13} )</td>
<td>( 1.5 \times 10^{-13} )</td>
</tr>
</tbody>
</table>

\(^a\)Immobilized liquid membrane; \(^b\) Solid polymer electrolyte membrane
In the exact solution method, the model equations given in Section 3.2.2 are solved simultaneously using the fourth/fifth order Runge-Kutta method with $\text{RelTol}$ of $10^{-3}$ and $\text{AbsTol}$ of $10^{-6}$. The results of the approximate analytical solution are obtained by solving equations 3.34, 3.35 and 3.38 for the immobilized liquid membrane, and by solving equations 3.34, 3.35 and 3.37 for solid polymer electrolyte membrane, using the ‘trust-region-dogleg Algorithm’ in MATLAB. $\sigma_{AB}$ is estimated by assuming $x_A = x_{A,f}$ in equations 3.34 and 3.38.

Figure 3.16 shows the ethylene purity in the permeate stream as a function of stage cut for the two types of facilitated transport membranes. Figure 3.16 shows the models to be in good agreement.

In terms of accuracy, the prediction of the membrane performance of the exact model is more accurate than the approximate model. The maximum absolute error between the approximate and exact models is 0.33\% for permeate mole fraction prediction. In terms of computational efficiency, the computational time of the exact solution approach is longer than for the approximate solution (e.g. at stage cut = 0.1, the algorithm takes about 0.08 sec to solve the nonlinear differential equations 3.16 and 3.17 along with equations 3.10, 3.13 to 3.15; and 0.01 sec to solve the algebraic equations 3.34 and 3.35).

![Figure 3.16: Variation in permeate purity as a function of stage cut for a cross-flow membrane module: (---) exact solution; (---) approximate solution](image)
3.6.3 Summary– Approximate model

In this section, a reasonably simple but approximate analytical solution method for a cross-flow facilitated transport membrane module is presented. The method assumes that $\alpha_{AB}$ is fixed. With this assumption, the derivation of equation 3.33 can be simplified to nonlinear algebraic equation 3.34, which can be solved simultaneously with equation 3.35 by an iterative method. The simulation results show that the analytical and exact solution methods are very similar in their predictive capability of permeate purity for stage cuts smaller than 0.3. Compared with the exact solution, which involves the numerical solution of highly nonlinear differential equations, the approximate solution is quicker at predicting the membrane performance. The shortcoming of the proposed approximate solution method is that it is only applicable to membrane separating binary mixtures and that the value of permeate purity could be underestimated at high stage cut values. Nevertheless, the method could be useful for predicting membrane performance in the preliminary stage of design and optimisation.

3.7 Conclusions

This chapter puts forward a simple membrane model together with an accurate and computationally efficient solution strategy. The model is able to consider multicomponent mixtures and various flow patterns. The permeate mole fractions have been bounded to avoid the need for user intervention during the simulation and to avoid obtaining unfeasible solutions. Also, the ode solver parameters have been adjusted. A suitable range for RelTol is $10^{-6}$ to $10^{-9}$ and for AbsTol is $10^{-8}$ to $10^{-10}$.

To predict the module model’s performance, exact (detailed) and approximate methods are used. The exact solution method based on Shindo et al. (1980) has been modified and new algorithms, especially for cross-flow and counter-current operation, are introduced. The modified exact solution approach avoids the drawbacks of Shindo et al. (1980) (e.g. initial estimates of permeate purities, stiffness and nonlinearity of differential equations, and the long computation time). The developed solution strategy for solving a cross-flow model in Section 3.3.1 and a counter-current flow model in Section 3.3.2 is shown to be stable and effective for
predicting the membrane performance even at high stage cuts and low pressure ratios, as demonstrated in Section 3.3.3.

A new approximate analytical method for predicting the performance of facilitated transport membranes is also introduced. The approximate method is based on the Naylor-Backer approximate method, modified to account for a dual-mode transport. The main advantage of the approximate solution method is that it can be used to perform a quick design evaluation. However, compared with the exact solution method, as shown in Section 3.6.2, the approximate solution method underestimates the permeate purity at high stage cut values. Error between the approximate and detailed models is less than 1% at low stage cut. Therefore, the modified exact solution methods will be used for solving the membrane models equations in this thesis.

To verify that the proposed solution method provides an accurate prediction of membrane performance, the membrane model is validated by comparison with published results and experimental data for various flow patterns and multicomponent systems. The membrane models are in good agreement with the experimental data over a range of stage cuts and separation cases.

The membrane models and the solution methods presented in this chapter are necessary for an analysis of the degrees of freedom and to evaluate the operating cost trade-offs in the hybrid membrane-distillation separation system, both of which are dealt with in the chapters that follow.
Chapter 4 Distillation Column Design

4.1 Introduction

Cryogenic distillation has been the dominant technology utilized for the separation of light olefins and paraffins for several decades (Zimmermann and Walzl, 2012). However, the demand for utility at sub-ambient temperatures and high pressures results in high operating costs, which make these separations energy intensive operations (Zimmermann and Walzl, 2012).

As presented in Chapter 1, there are many way to improve energy efficiency. The hybrid membrane-distillation process is one of them. A membrane separation unit reduces the energy consumption and operating cost of hybrid processes by breaking the column pinch and performing part of the separation work (Caballero et al., 2009). In order to ascertain the energy savings that can be achieved using a hybrid membrane-distillation, a column design model is required. The column design model should include important characteristics of the column for the hybrid schemes, such as a multiple feeds and/or multiple products.

A distillation column for hybrid distillation systems can be designed by using either rigorous models or shortcut models. The analysis and design of a complex column by rigorous simulation is a relatively tedious and time-consuming task (Rose, 1985). Rigorous simulation requires iteratively changing the design variables and repeating the simulation until the best economic performance is achieved. In the primary stage of process design, where several hybrid-membrane-distillation schemes and operating condition have to be evaluated, shortcut methods may be preferred. Shortcut methods are simple and they can be easily used to predict the number of stages if the reflux rate is selected, or to estimate the reflux ratio if the
Chapter 4 Distillation Column Design

Theoretical number of stages is known. A shortcut method can also be combined with a heat recovery model for improving the energy efficiency of the separation system.

As Chapter 2 points out, the shortcut design method of Nikolaides and Malone (1987) could be applied to the column design of a hybrid membrane-distillation system. The calculation method of Nikolaides and Malone (1987) is based on Underwood equations, which allow calculation of the minimum reflux ratio at an infinite number of stages. In this chapter, the approximate calculation method developed by Nikolaides and Malone (1987) is employed for a complex column design of hybrid processes and modified by including energy balance in the calculation of minimum reflux ratio. Illustrative examples are presented to show the application of the extended column design method; the model results are validated by comparing them against rigorous simulation results obtained using HYSYS.

4.2 Applying enthalpy correction to a simple column

The shortcut methods of Fenske (1932), Underwood (1948) and Gilliland (1940) can be used for preliminary design and optimisation of a conventional distillation column. However, the Underwood equations tend to underestimate the minimum reflux ratio because of the assumption of constant molar overflow (Suphanit, 1999; Smith, 2005).

![Figure 4.1: Material and energy balance envelopes for rectifying the pinch section at minimum reflux](image)
Suphanit (1999) proposed a modification to improve the performance of the Underwood equations. The modified procedure under the minimum reflux conditions is as follows: In the pinch zone, the vapour flow rate \( (V_\infty) \) is calculated from the Underwood equations. Then, energy balance around the top section of the column (envelope 2) is carried out to estimate the condenser duty \( (Q_C) \) and subsequently the vapour flow rate \( (V) \) at the top of the column, as shown in Figure 4.1.

The logic diagram in Appendix B outlines the computational procedure as it is programmed for a simple conventional column equipped with a total or partial condenser. Sometimes the distillate is needed in further production steps as a vapour; therefore, the type of the condenser (partial or total) is considered in the calculations method in this work.

Note that the calculations procedure for a simple column can be applied for the column design of the hybrid membrane-distillation system in Figure 5.4 (a).

### 4.3 Extension applying enthalpy correction to complex column

In this section, the approach proposed by Suphanit (1999) is extended to multiple feeds and/or multiple products column design for hybrid distillation processes.

First, the complex column is decomposed into the thermodynamically equivalent configuration of simple columns. Then, the modified Underwood method, as proposed by Nikolaides and Malone (1987), is used to estimate the minimum reflux ratios in the feed pinch zones. Although each feed is assumed to produce a pinch zone, only the control feed is important for the column design. The control feed can be targeted as the one that requires the largest minimum reflux ratio when the complex column is decomposed into \( n \) single-feed columns.

Energy balances around the controlling pinch section and the condenser are considered to determine the minimum reflux ratio and the minimum condenser duty. Section 4.3.1 will present the extended calculation procedure in detail for a two-feed column.

#### 4.3.1 Calculation procedure for a two feed column

The calculation method in this section can be applied to the design of the column for the hybrid distillation systems in Figures 2.4 (a) and 2.4(b). The calculation
procedure is based on known compositions, flow rates and thermal conditions of the whole column streams. Chapter 3 introduced the membrane modelling approach which can be implemented to predict the retentate and permeate purities for a given stage cut, pressure ratio, membrane feed composition and flow rate. However, for some hybrid systems schemes, such as the parallel hybrid configuration, the pressure ratio, the membrane feed composition and flow rate are design variables that must be optimised to determine the optimum reflux ratio in the column. Chapter 7 describes the optimisation procedure that is developed to optimise the operating conditions of the hybrid membrane distillation process.

The procedure used to design a double feed column is as follows: first, the column is decomposed into thermodynamically equivalent simple columns. The envelope in Figure 4.2 (a) shows a diagram of a distillation column with two feeds and two products, in addition to its thermodynamically equivalent arrangement (Figure 4.2 (b)). The column is decomposed into two hypothetical simple columns $I_1$ and $I_2$. Upper feed is the feed to column $I_1$, whose top product is the overall distillate flow rate, $D$, and its bottom product flow rate is a pseudo bottom product flow rate, $B_{I_1}$. The pseudo bottom molar flow rate is obtained by subtracting lower feed flow rate, $F_2$, from the overall bottom product flow rate ($B$). The lower feed flow rate, $F_2$, is the feed to column $I_2$, whose top product flow rate is a pseudo distillate flow rate, $D_{I_2}$, and bottom product flow rate is $B$. The pseudo distillate flow rate is calculated by subtracting upper feed flow rate from the overall distillate
product flow rate. The pseudo products flow rate is always in equal magnitude and opposite in direction (Nikolaides and Malone, 1987; Shah and Kokossis, 2002).

The modified Underwood equations are used to predict the minimum reflux (Nikolaides and Malone, 1987).

Equations 4.1 and 4.2 are used to determine $\varnothing$ values associated with both of the hypothetical simple columns (see equation 4.1 and 4.1).

\[
\sum_{i=1}^{n} \frac{x_{i,F1} \alpha_i}{\alpha_i - \varnothing_{I1}} = 1 - q_{I1} \tag{4.1}
\]

\[
\sum_{i=1}^{n} \frac{x_{i,F2} \alpha_i}{\alpha_i - \varnothing_{I2}} = 1 - q_{I2} \tag{4.2}
\]

Where $x_{i,F1}$ and $x_{i,F2}$ are the upper and lower feed mole fraction of component $i$, $\alpha_i$ is the relative volatility with respect to the heaviest component, in the mixture, $q_{I1}$ and $q_{I2}$ are the feed thermal conditions for the hypothetical columns I1 and I2 respectively and $\varnothing_{I1}$ and $\varnothing_{I2}$ are the Underwood roots. These roots depend only on the feed composition and relative volatilities.

For a binary separation, one root needs to be calculated: $\varnothing_{I1}$ for equation 4.1 and $\varnothing_{I2}$ for equation 4.2. The root lies between the relative volatility of the light and heavy key components $\alpha_1 = \alpha_{LH}$ and $\alpha_2 = \alpha_{HH} = 1$ so: $\alpha_1 > \varnothing_{I1} > \alpha_2$ and $\alpha_1 > \varnothing_{I2} > \alpha_2$.

A simple Bisection method can be used to obtain the root values. Once the roots are identified, equations 4.3 and 4.4 are used to calculate the minimum reflux ratios $R_{\text{min,I1}}$ and $R_{\text{min,I2}}$ in the two-feed column (Nikolaides and Malone, 1987).

\[
R_{\text{min,I1}} = \sum_{i=1}^{n} \frac{x_{i,D} \alpha_i}{\alpha_i - \varnothing_{I1}} - 1 \tag{4.3}
\]

Nikolaides and Malone (1987) calculated the minimum reflux ratio of the column when the lower feed is controlling using the minimum reflux ratio of the second hypothetical column and the liquid flow rate balance equation between the two hypothetical columns as shown in equation 4.4.
Then the minimum reflux ratio required for column operation and design is the maximum of the two minimum reflux ratios.

\[ R_{\text{min}} = \max \{ R_{\text{min},11}, R_{\text{min},12} \} \]  

(4.5)

To overcome the constant molar overflow rate assumption, the values of the minimum reflux ratios are adjusted as follow:

**If the first feed (upper feed) is controlling the column,** \( R_{\text{min}} = R_{\text{min},11} \)

In the pinch zone the compositions and temperatures are constant from stage to stage. This means the internal liquid and vapour compositions do not change in the pinch zone. Since the liquid and vapour streams in the pinch zone are in equilibrium, \( y_{i,\infty} \) is related to \( x_{i,\infty} \) by:

\[ y_{i,\infty} = K_{i,\infty} x_{i,\infty} \]  

(4.6)
\[ x_{i,\infty} = \frac{x_{i,D}}{L_{\infty}} \left( \frac{\alpha_i}{\emptyset} - 1 \right) \] 

\[ i = 1:n - 1; \emptyset = \emptyset_{II} \]  

\[ x_{n,\infty} = 1 - \sum_{i=1}^{n-1} x_{i,\infty} \] 

\[ i = n = 2 \]  

Where \( \emptyset \) is the root of the Underwood equation 4.3 which satisfies the inequality: \( 0 < \emptyset < 1 \).

For a binary mixture, equation 4.3 is rearranged to give:

\[ a_0 \emptyset_{II}^2 + a_1 \emptyset_{II} + a_2 = 0 \]  

(4.9)

Where

\[ a_0 = 1 \]  

(4.10)

\[ a_1 = \frac{\sum_{i=1}^{n=2} \alpha_i (x_{i,D}) - \sum_{i=1}^{n=2} \alpha_i}{R_{min} + 1} \]  

(4.11)

\[ a_2 = \alpha_1 \alpha_2 \left( 1 - \frac{1}{R_{min} + 1} \right) \]  

(4.12)

Then, an enthalpy balance over the top section (envelope 2 in Figure 4.3 (a)) is performed to ascertain the modified minimum reflux ratio and the minimum condenser duty (Seader, 1998).

\[ \frac{L}{D} = \frac{L_{\infty}}{D} \left( H_{V,\infty} - H_{L,\infty} \right) + \left( H_{V,\infty} - H_V \right) }{H_V - H_L} \]  

(4.13)

Where \( H_V, H_L \) = molar enthalpies of the vapour and liquid at the top of the column,

\( H_{V,\infty}, H_{L,\infty} \) = molar enthalpies of the vapour and liquid at the rectifying pinch,

\( D = \) distillate molar flow rate,

\( \frac{L}{D} = \) modified minimum reflux ratio (R)
Chapter 4  Distillation Column Design

Molar enthalpies for each stream are functions of compositions, pressure, and thermal state (i.e. stream vapour fraction)

\[ H = H(x, p, q) \]  \hspace{1cm} (4.14)

\[
 f(H) = \begin{cases} 
 H_{V_\infty}, & x = y_\infty \quad q = 1 \\
 H_{L_\infty}, & x = x_\infty \quad q = 0 \\
 H_V, & x = y_V \quad q = 1 \\
 H_L, & x = x_L \quad q = 0 \\
 H_{F1}, & x = x_{F1} \quad 0 \leq q \leq 1 \text{ or } q > 1
\end{cases}
\]  \hspace{1cm} (4.15)

Molar enthalpies of the vapour and liquid streams are evaluated using the Soave-Redlich-Kwong equation of state.

The liquid flowrate, \( L \), at the top of the column can be found simply by

\[ L = D \times R \]  \hspace{1cm} (4.16)

A total material balance around the condenser gives the total molar flow rate of the vapour leaving the top stage of the column.

\[ V = L + D \]  \hspace{1cm} (4.17)

Where \( D \) is the distillate molar flow rate and \( V \) is the vapour molar flow.

The condenser duty (\( Q_C \)) can be calculated from a heat balance around the condenser.

\[ Q_C = VH_v - (DH_D + LH_L) \]  \hspace{1cm} (4.18)

Finally, an overall enthalpy balance around the column is carried out to estimate the corresponding reboiler duty (\( Q_R \)).

\[ Q_R = DH_D + BH_B + Q_c - F_1H_{F1} \]  \hspace{1cm} (4.19)

Where \( H_B \) is the enthalpy of the bottom product.

**If the second feed (lower feed) is controlling the column, \( R_{min} = R_{min,l2} \)**

An overall material balance may be written around the rectifying-section pinch zone of Figure 4.3 (b) as
\[ V_\infty = L_\infty + D - F_1 \]  

(4.20)

Where \( V_\infty \) and \( L_\infty \) are the vapour and liquid flow rates at the pinch, respectively.

A component material balance around the rectifying-section pinch zone and the top of the column shown in Figure 4.3 (b) is

\[ V_\infty y_{i,\infty} = x_{i,\infty} L_\infty + D x_{i,D} - F_1 x_{i,F1} \]  

(4.21)

Where \( y_{i,\infty} \) and \( x_{i,\infty} \) are the vapour and liquid mole fraction of component \( i \) at the rectifying pinch zone, respectively.

Underwood (1948) showed that the liquid-vapour equilibrium relationship at the rectifying pinch zone can be obtained from:

\[ K_{i,\infty} = \frac{L_\infty \alpha_i}{V_\infty \varnothing} \]  

(4.22)

Substituting equations 4.6 and 4.22 into equation 4.21 and rearranging yields

\[ x_{i,\infty} = \frac{x_{i,D} - x_{i,F1} \left( \frac{F_1}{D} \right)}{L_\infty \left( \frac{\alpha_i}{\varnothing} - 1 \right)} \] \[ \varnothing = \varnothing_{12} \]  

(4.23)

Where \( \varnothing \) is the root of the modified Underwood equation 4.4. For a binary mixture, equation 4.4 is rearranged to give:

\[ a_0 \varnothing_{12}^2 + a_1 \varnothing_{12} + a_2 = 0 \]  

(4.24)

Where

\[ a_0 = 1 \]  

(4.25)

\[ a_1 = \frac{\sum_{i=1}^{n=2} \alpha_i \left( x_{i,D} - x_{i,F1} \frac{F_1}{D} \right)}{R_{min} + 1 - \frac{F_1}{D} (1 - q_1)} - \sum_{i=1}^{n=2} \alpha_i \]  

(4.26)
\[ a_2 = \alpha_1 \alpha_2 \left( \frac{1}{R_{\text{min}} + 1 - \frac{F_1}{D} (1 - q_1)} \right) + \frac{(F_1/D) \alpha_1 \alpha_2}{R_{\text{min}} + 1 - \frac{F_1}{D} (1 - q_1)} \] (4.27)

There are two values of \( \varphi_{I2} \) which satisfy equation 4.24, noted as \( \varphi_1 \) and \( \varphi_2 \). The appropriate root is the one associated with the heavy key, which is the one below \( \alpha_{\text{HK}} \) (Smith, 2005). This is given by \( 0 < \varphi_{I2} < \alpha_{\text{HK}} \). If the two values of \( \varphi_{I2} \) are above \( \alpha_{\text{HK}} \), the value of \( \varphi \) closest to \( \alpha_{\text{HK}} \) should be chosen. The value of \( \varphi_{I2} \) can then be substituted in equation 4.23 to obtain the liquid pinch composition.

The vapour pinch composition, \( y_{\infty} \), can be determined from the equilibrium relationship or from equations 4.28 and 4.29.

\[
y_{i,\infty} = \left( \frac{x_{1,\infty} \frac{L_{\infty}}{D} + x_{i,D} - x_{i,F1} \left( \frac{F_1}{D} \right)}{\frac{L_{\infty}}{D} + 1} \right) \quad i = 1:n-1 \quad (4.28)
\]

\[
y_{n,\infty} = 1 - \sum_{i=1}^{n-1} y_{i,\infty} \quad i = n \quad (4.29)
\]

An energy balance around the top pinch of the column shown in Figure 4.3(b) gives

\[ Q_c = V_{\infty} H_{V,\infty} - L_{\infty} H_{L,\infty} - D H_D + F_1 H_{F1} \] (4.30)

Combining equations 4.17, 4.18, 4.20 and 4.30 and rearranging gives

\[
\frac{L}{D} = \frac{\frac{L_{\infty}}{D} (H_{V,\infty} - H_{L,\infty}) + (H_{V,\infty} - H_V) - \frac{F_1}{D} (H_{V,\infty} - H_{F1})}{H_V - H_L} \] (4.31)

The minimum condenser duty can be calculated from equation 4.30. The corresponding reboiler duty can be calculated by an overall enthalpy balance around the column.

\[ Q_R = DH_D + BH_B + Q_c - (F_1 H_{F1} + F_2 H_{F2}) \] (4.32)
4.3.2 Calculation procedure for three feeds and one side-stream distillation column

This section proposes a modified shortcut method for a column design for a parallel hybrid distillation system, as shown in Figure 4.4 (a). The envelope in Figure 4.4 (a) shows a schematic of a distillation column with three feeds (permeate stream, column feed stream and retentate stream), one side draw (feed stream to the membrane) and two products, together with its thermodynamic equivalent Figure 4.4 (b). The column is decomposed into three simple columns I1, I2 and I3. The upper feed flow rate to column I1 is the recycled permeate, \( P \). The top product flow rate of column I1 is the overall distillate, \( D \). The middle feed, \( F \), is the feed flow rate to column I2. The lower feed flow rate to column I3 is the recycled retentate, \( R \). The bottom product flow rate of column I3 is \( B \).

![Figure 4.4](image)

Figure 4.4: Schematic of a parallel hybrid scheme (a) and the corresponding column equivalent arrangements (b) for minimum reflux ratio.

The first Underwood equations 4.33 to 4.35 are used to determine \( \phi_{I1}, \phi_{I2} \) and \( \phi_{I3} \) values. The relative volatility values are based on the feed conditions and the Underwood roots lie between the volatilities of the key components.

\[
\sum_{i=1}^{n} \frac{x_{i,P} \alpha_i}{\alpha_i - \phi_{I1}} = 1 - q_P
\]

(4.33)
\[
\sum_{i=1}^{n} \frac{x_{i,f} \alpha_i}{\alpha_i - \varphi_{I_2}} = 1 - q_F 
\] (4.34)

\[
\sum_{i=1}^{n} \frac{x_{i,R} \alpha_i}{\alpha_i - \varphi_{I_3}} = 1 - q_R 
\] (4.35)

Where \(x_{i,p}, x_{i,f}\) and \(x_{i,R}\) are the upper, middle and lower feed mole fraction of component \(i\), and \(q_p, q_f\) and \(q_R\) are the feed thermal conditions for sections I1, I2 and I3 respectively.

To calculate the minimum reflux ratios \(R_{\text{min},I_1}\), \(R_{\text{min},I_2}\) and \(R_{\text{min},I_3}\) for the complex column, the approximate expressions of Nikolaides and Malone (1987) are used, as in equations 4.36, 4.37 and 4.38. Note that these equations are obtained by incorporating the minimum reflux ratio of the hypothetical columns and the internal liquid flow rate balance equations.

\[
R_{\text{min},I_1} = \sum_{i=1}^{n} \frac{x_{i,D}}{\alpha_i - \varphi_{I_1}} - 1 
\] (4.36)

\[
R_{\text{min},I_2} = \left( \sum_{i=1}^{n} \frac{\alpha_i (x_{i,D} - \frac{P}{D} x_{i,P})}{\alpha_i - \varphi_{I_2}} \right) + \frac{P}{D} (1 - q_p) - 1 
\] (4.37)

\[
R_{\text{min},I_3} = \left( \sum_{i=1}^{n} \frac{\alpha_i (x_{i,D} - \frac{P}{D} x_{i,P} + \frac{M}{D} x_{i,M} - \frac{F}{D} x_{i,f})}{\alpha_i - \varphi_{I_3}} \right) + \frac{P}{D} (1 - q_p) \right)
- \frac{M}{D} (1 - q_M) + \frac{F}{D} (1 - q_F) - 1 
\] (4.38)

The minimum reflux ratio required in the column is the maximum of the three minimum reflux ratios.

\[
R_{\text{min}} = \max \{ R_{\text{min},I_1}, R_{\text{min},I_2}, R_{\text{min},I_3} \} 
\] (4.39)

As discussed in Chapter 2, the minimum reflux ratio calculated at the pinch zone may be different from the one calculated at the top of the column. In this section, an
energy balance is considered in the column design model to provide more accurate prediction to the column minimum external reflux ratio.

When the upper feed (Permeate stream) is controlling the column, $R_{\text{min}} = R_{\text{min,11}}$, equations 4.6 to 4.8 and 4.13 are used. Where $\emptyset$ is the root of the Underwood equation 4.36.

When the middle feed (column feed stream) is controlling the column, $R_{\text{min}} = R_{\text{min,12}}$, equations 4.40 and 4.41 are used to calculate the liquid pinch compositions (Figure 4.5 (b)) and the external minimum reflux ratio.

![Figure 4.5: Minimum reflux calculation procedure for a complex column. (a) Permeate stream is controlling the column; (b) Feed stream is controlling the column; (c) Retentate stream is controlling the column](image)

For a binary separation, equation 4.38 is rearranged to give

$$x_{i,\infty} = \frac{x_{i,D} - x_{i,P}}{L_{\infty} \left( \frac{\alpha_i}{\emptyset} - 1 \right)}$$  \hspace{1cm} (4.40)

Where $x_{i,P}$ is the mole fraction of component $i$ in the permeate stream, $P$ is the permeate flow rate, and $L_{\infty}$ is the liquid flow rate at the pinch.

$$\frac{L}{D} = \frac{L_{\infty} \left( H_{V,\infty} - H_{L,\infty} \right) + \left( H_{V,\infty} - H_V \right) - P \left( H_{V,\infty} - H_P \right)}{H_V - H_L}$$  \hspace{1cm} (4.41)

When the lower feed (retentate stream) is controlling the column, $R_{\text{min}} = R_{\text{min,13}}$, equations 4.42 to 4.44 are used to estimate the root in equation 4.45.

For a binary separation, equation 4.38 is rearranged to give
\[ \phi^2 + a_1 \phi + a_2 = 0 \]  

(4.42)

Where

\[ a_1 = \frac{\sum_{i=1}^{n} \alpha_i \left( x_{i,D} - x_{i,P} \frac{P}{D} - x_{i,f} \frac{F}{D} + x_{i,M} \frac{M}{D} \right)}{R_{min} + 1 - \frac{P}{D} (1 - q_p) - \frac{F}{D} (1 - q_f) + \frac{M}{D} (1 - q_M)} - \sum_{i=1}^{n} \alpha_i \]  

(4.43)

\[ a_2 = \alpha_1 \alpha_2 \left( 1 - \frac{1}{R_{min} + 1 - \frac{P}{D} (1 - q_p) - \frac{F}{D} (1 - q_f) + \frac{M}{D} (1 - q_M)} \right) \]  

(4.44)

\[ + \frac{\left( \frac{P}{D} + \frac{F}{D} - \frac{M}{D} \right) \alpha_1 \alpha_2}{R_{min} + 1 - \frac{P}{D} (1 - q_p) - \frac{F}{D} (1 - q_f) + \frac{M}{D} (1 - q_M)} \]

Considering envelope 4 in Figure 4.5 (c), the liquid compositions at the pinch point are estimated as follows:

\[ x_{i,\infty} = \frac{x_{i,D} - x_{i,P} \frac{P}{D} - x_{i,f} \frac{F}{D} + x_{i,M} \frac{M}{D}}{L_{\infty} \left( \frac{\alpha_i}{\phi} - 1 \right)} \]  

(4.45)

Where \( x_{i,M} \) is the mole fraction of component \( i \) in the membrane stream, \( M \) is the membrane flow rate, \( x_{i,f} \) is the mole fraction of component \( i \) in the feed stream, \( F \) is the column feed flow rate, and \( L_{\infty} \) is the liquid flow rate at the pinch.

To calculate the external minimum reflux ratio, an enthalpy balance around the pinch and top sections of the column (shown in Figure 4.5 (c)) are carried out.

An energy balance around envelope 4 in Figure 4.5 gives:

\[ H_{V,\infty}V_{\infty} = H_{L,\infty}L_{\infty} + H_p D - H_F F - H_p P + H_M M + Q_c \]  

(4.46)

A material balance around envelope 4 gives:

\[ V_{\infty} = L_{\infty} + D - F - P + M \]  

(4.47)
Incorporating the condenser enthalpy balance 4.18 into the envelope 4 enthalpy balance 4.46 and combining with condenser, envelope 1, and envelope 4 mass balances 4.17 and 4.47 yields:

\[
\frac{L}{D} = \frac{L_{\infty}}{D}(H_{V_{\infty}} - H_{L_{\infty}}) + \frac{H_{V_{\infty}} - H_{V}}{H_{V} - H_{L}} \left( \frac{P}{D}(H_{V_{\infty}} - H_{P}) + \frac{F}{D}(H_{V_{\infty}} - H_{F}) + \frac{M}{D}(H_{V_{\infty}} - H_{M}) \right)
\]

(4.48)

Where \( H_{V} \) and \( H_{L} \) represent the molar enthalpies of the vapour and liquid, respectively, at the top of the complex column, \( H_{M} \) is the molar enthalpy of the membrane stream, \( H_{P} \) is the molar enthalpy of the permeate, \( H_{F} \) is the molar enthalpy of the feed stream, \( H_{V_{\infty}} \) and \( H_{L_{\infty}} \) are the molar enthalpies of the vapour and liquid, respectively, at the pinch (Figure 4.5 (c)).

### 4.4 Illustrative examples: Applying enthalpy correction to the prediction of minimum reflux ratio

The purpose of this section is to illustrate the application of the extended column design method based on those of Nikolaides and Malone (1987) and Suphanit (1999) to the design of simple column (single feed and two products, distillate and bottom product) and complex column (three feed streams and one side draw stream). To validate the extended shortcut model, it is compared with a more rigorous model. HYSYS is used for rigorous steady-state modelling of the ethane-ethylene separation, while Soave-Redlich-Kwong is the fluid package used to calculate the physical properties.

#### 4.4.1 Example 1: Effect of variations in relative volatility on simple column performance

90 kmol/h of a binary mixture of ethylene and ethane is to be separated by distillation at a top pressure of 2.7 bar and a bottom pressure of 3.7 bar. The feed contains a 0.5542 mole fraction of ethylene and has a temperature of 99.4°C at 3.7 bar. The overhead product purity is 99.9 mol% of ethylene and the bottom product
purity of the ethane is 99.5 mol%. It is necessary to determine the influence of the
relative volatility on the calculation of the minimum reflux ratio.

![Diagram](image1)

Figure 4.6: Comparison between a rigorous model and the Underwood method with
and without enthalpy correction at minimum reflux ratio; calculation of relative
volatility is based on feed stage conditions (a) shortcut model; (b) modified shortcut
model of FUG; (c) rigorous model

![Diagram](image2)

Figure 4.7: Comparison between the Underwood method with and without enthalpy
correction and a rigorous model at minimum reflux ratio; calculation is based on
average relative volatility. (a) Shortcut model; (b) modified shortcut model of FUG;
(c) rigorous model

It can be seen that the minimum vapour flow rate is overestimated in Figure 4.7
(b) when the relative volatilities are determined as an average between the top and
bottom. However, there is good agreement between the modified Underwood
method and rigorous simulation when the relative volatilities are based on the feed
stage, as shown in Figures 4.6 (b) and 4.6 (c). This is because the location of the
pinches is often close to the feed (Smith, 2005).
4.4.2 Example 2: The modified shortcut model’s prediction for simple and complex column

This section focuses on an examination of a binary mixture (ethane-ethylene) with feed compositions and column specifications as shown in Tables 4.1 and 4.2. In this example, the vapour leaving the top of the column is partially condensed and the column operating pressure is assumed to be constant (pressure drop in the distillation column is zero). All the column streams of the complex column are saturated vapour and they have an operating pressure equal to the column pressure.

Table 4.1: Input data for simple column

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed mole fraction %</th>
<th>Product purity (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>55.42</td>
<td>99.9</td>
</tr>
<tr>
<td>Ethane</td>
<td>44.58</td>
<td>99.5</td>
</tr>
</tbody>
</table>

Feed condition and column specifications

<table>
<thead>
<tr>
<th>Molar flow rate, kmol/h</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column pressure, bar</td>
<td>7.3</td>
</tr>
<tr>
<td>Feed state</td>
<td>Saturated vapour</td>
</tr>
</tbody>
</table>

Table 4.2: Input data for complex column

<table>
<thead>
<tr>
<th>Streams name</th>
<th>Mole fraction%</th>
<th>Molar flow rate, Kmol/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethylene</td>
<td>Ethane</td>
</tr>
<tr>
<td>Feed 1 (P)</td>
<td>0.963</td>
<td>0.037</td>
</tr>
<tr>
<td>Feed 2 (F)</td>
<td>0.540</td>
<td>0.460</td>
</tr>
<tr>
<td>Side draw (M)</td>
<td>0.540</td>
<td>0.460</td>
</tr>
<tr>
<td>Feed 3 (R)</td>
<td>0.117</td>
<td>0.883</td>
</tr>
</tbody>
</table>

The Underwood equations 2.28 and 2.29 calculate the minimum vapour flow rate at the pinch composition of the simple column. The calculation procedure presented in Section 4.3.1 is used to calculate the minimum reflux ratio and the corresponding column duties of the complex column. In the Underwood equations, the relative volatilities are based on the feed condition.
To validate the extended calculation procedure, a shortcut model at minimum reflux (i.e., an infinite number of stages) for both a simple and a complex distillation column is compared with HYSYS. To perform rigorous simulation of the distillation column at minimum reflux ratio, a large number of stages are needed. The maximum number of stages is obtained when the reflux ratio becomes constant, i.e., the reflux ratio does not change as the number of stages increases, and a constant zone of composition (pinches) appears, as shown in Figure 4.8.

![Figure 4.8: Vapour composition profile using HYSYS simulator for a complex column](image)

From Table 4.3, it is obvious that the Underwood equations underestimate the minimum reflux ratio. However, the modified shortcut distillation model (with enthalpy correction) gives much better predictions than the model without enthalpy correction (FUG). Including energy balance makes it possible to compensate for the variation in molar overflow and as a result obtain a more accurate prediction of the minimum reflux ratio. As Table 4.3 demonstrates, the minimum vapour flow rate at the pinch is 224.3 kmol h\(^{-1}\) and the minimum vapour flow rate at the top is 235.5 kmol h\(^{-1}\).
Table 4.3: Enthalpy correction for predicting minimum reflux ratio

<table>
<thead>
<tr>
<th></th>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>Rigorous model (HYSYS)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Simple column</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>3.17</td>
<td>3.38</td>
<td>3.38</td>
</tr>
<tr>
<td>$V_{\text{min, top}, \text{kmol/h}}$</td>
<td>224.3</td>
<td>235.5</td>
<td>235.5</td>
</tr>
<tr>
<td>$Q_{\text{c,min}, \text{kW}}$</td>
<td>550.1</td>
<td>586.2</td>
<td>586.2</td>
</tr>
<tr>
<td>$Q_{\text{r,min}, \text{kW}}$</td>
<td>387.5</td>
<td>423.6</td>
<td>423.5</td>
</tr>
<tr>
<td>$N_{\text{min}}$</td>
<td>21</td>
<td>21</td>
<td>22</td>
</tr>
<tr>
<td><strong>Complex column</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>1.93</td>
<td>2.10</td>
<td>2.10</td>
</tr>
<tr>
<td>$V_{\text{min, top}, \text{kmol/h}}$</td>
<td>157.7</td>
<td>166.9</td>
<td>167.0</td>
</tr>
<tr>
<td>$Q_{\text{c,min}, \text{kW}}$</td>
<td>335.1</td>
<td>365.0</td>
<td>365.1</td>
</tr>
<tr>
<td>$Q_{\text{r,min}, \text{kW}}$</td>
<td>172.5</td>
<td>202.3</td>
<td>202.5</td>
</tr>
<tr>
<td>$N_{\text{min}}$</td>
<td>21</td>
<td>21</td>
<td>20</td>
</tr>
</tbody>
</table>

FUG: Fenske Underwood Gilliland; MFUG: Modified Fenske Underwood Gilliland

The minimum number of stages for a simple column can be calculated by using the Fenske equation. Average relative volatility is used for estimating the minimum number of stages.

The methodology proposed by Joyner et al. (1962) is used to determine the total minimum number of theoretical stages required in the complex column. The calculation method of Joyner et al (1962) calculates the minimum number of stages in each section of the column; therefore, the streams’ locations in the column can be defined, as shown in Figure 4.10. The feed stage locations obtained via the shortcut method can be used to initiate the column design in HYSYS. The optimum locations of the column streams are the points where the stream composition matches the stage composition, as shown in Figure 4.9. It can be seen that the results of calculations from shortcut methods are in good agreement with the results obtained from the rigorous simulation. The result of the shortcut methods is found to be less than 5% of the value obtained from the rigorous calculation using HYSYS, which is adequate for screening purposes of process alternatives.
Chapter 4  Distillation Column Design

Figure 4.9: Rigorous simulation results: (a) calculation of the minimum number of theoretical stages at total reflux; (b) calculation of the minimum reflux ratio at an infinite number of stages

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</thead>
<tbody>
<tr>
<td>F</td>
<td>R</td>
<td>Condenser</td>
<td>D</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td>Condenser</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>Molar Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60.29°C</td>
<td>730.0 kPa</td>
<td>27.5 kgmole/h</td>
</tr>
<tr>
<td>-51.70°C</td>
<td>730.0 kPa</td>
<td>100.0 kgmole/h</td>
</tr>
</tbody>
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<tbody>
<tr>
<td>F</td>
<td>R</td>
<td>Condenser</td>
<td>D</td>
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<td>P</td>
<td></td>
<td></td>
<td>Condenser</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>Molar Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>-44.06°C</td>
<td>730.0 kPa</td>
<td>27.0 kgmole/h</td>
</tr>
</tbody>
</table>

Figure 4.10: Shortcut results: calculation of the minimum number of theoretical stages at total reflux in a complex column.

<table>
<thead>
<tr>
<th></th>
<th>Reflux</th>
<th>To Condenser</th>
<th>Boulup</th>
<th>To Reboiler</th>
<th>D</th>
<th>F</th>
<th>B</th>
<th>P</th>
<th>R</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp. Mole Frac. (Ethylene)</td>
<td>0.9988</td>
<td>0.9990</td>
<td>0.0002</td>
<td>0.0073</td>
<td>0.9993</td>
<td>0.5400</td>
<td>0.0053</td>
<td>0.9628</td>
<td>0.1167</td>
<td>0.5400</td>
</tr>
<tr>
<td>Comp. Mole Frac. (Ethane)</td>
<td>0.0012</td>
<td>0.0010</td>
<td>0.9906</td>
<td>0.9927</td>
<td>0.3007</td>
<td>0.4600</td>
<td>0.9903</td>
<td>0.0372</td>
<td>0.8833</td>
<td>0.4600</td>
</tr>
</tbody>
</table>

\[
N_{\min S1} = 7.46 \\
N_{\min S2} = 5.57 \\
N_{\min S3} = 3.61 \\
N_{\min S4} = 4.36
\]
4.5 Conclusions

This chapter details the development in the shortcut modelling of the distillation column for hybrid membrane-distillation processes design. The novel work in this chapter is that a new design models in Sections 4.3.1 and 4.3.2 for complex columns (multiple feeds and/or multiple products) is introduced. These models are based on the approximate design method of Nikolaides and Malone (1987). However, energy balance is included in the calculation of minimum reflux ratio to overcome the assumption of constant molar overflow. This can help adjusting the minimum reflux ratio and also satisfying the overall enthalpy balance in complex columns.

Two illustrative examples are presented to show the application of the methodology to a binary, close-boiling mixture and to a range of column configurations (i.e., a simple column and a three feed and one side draw column). Applying energy balance around the top rectifying section improves the accuracy of the minimum reflux ratio calculation method of Nikolaides and Malone (1987); consequently, good predictions of the column duties can be obtained. The results are in very much good agreement with the rigorous model carried out using HYSYS. The differences of the minimum reflux ratio between shortcut without enthalpy correction and the modified shortcut method are 6% for a simple column and 8% for a complex column design. No deviations in the minimum reflux ratio and the column duties predications are observed between the modified shortcut method and the simulation results from HYSYS.

The calculation procedure can be used for quick screening of process alternatives at a preliminary stage of design. Also, the method can be easily used for synthesis and optimisation purposes. The extended column design method will be incorporated in the design and optimisation framework in the next chapters to systematically explore, evaluate and optimise various hybrid membrane-distillation schemes. The combination of the membrane model in Chapter 3 and the modelling approach of the distillation column in this chapter and the heat recovery model in Chapter 6 will make it possible to improve the energy efficiency of the hybrid separation system as Chapter 5 will show.
5.1 Introduction

Hybrid separation flow sheets may be regarded as a network composed of streams and equipment that include membranes, distillation columns, coolers, heaters, valves, and compressors. This equipment can be configured in numerous different arrangements. The challenge is to develop a general framework that is able to explore various separation alternatives and capture interactions between the membrane and distillation units for a range of potential hybrid designs. In practice, the separation units are connected to other units, such as coolers, heaters and compressors, as well as to the refrigeration system that provides sub-ambient cooling to the separation system. Together, these units form the system of interest. Interactions between these units affect the economic performance of the whole system. To develop a cost-effective design, opportunities for heat recovery within the system should also be taken into account during the screening and evaluation procedure. However, system modelling and design is complicated, so a reliable and robust hybrid membrane-distillation modelling framework is required.

This chapter introduces a new systematic approach to designing and evaluating various hybrid separation options, both with and without consideration of heat integration within the system. A case study is presented to illustrate the implementation of the approach developed. The performance of the separation flowsheets is assessed with respect to energy efficiency. A conventional distillation column is used as the base case for comparison of the hybrid schemes. The model results are validated by comparing them with results of a rigorous simulation using HYSYS.
5.2 Systematic separation process design approach

Feasible process technologies and design alternatives need to be systematically explored. This section proposes a process synthesis approach, as illustrated in Figure 5.1. The approach uses optimization and shortcut models to simultaneously determine the optimal structure and operating conditions of a hybrid separation flowsheet.

![Figure 5.1: A systematic approach to hybrid separation process design](image)

5.2.1 Identifying separation process alternative (Step 1)

Three separation technologies will be examined for their use in separating low-boiling low-volatility mixtures; namely, distillation, membrane gas separation process and hybrid membrane-distillation separation processes. Distillation is currently the main separation technology; therefore, it has been selected as the base case for the analysis.

In Section 5.4.2, two types of highly selective membranes are examined for separation of ethylene-ethane mixtures. The results reveal that selective membranes with a single membrane unit cannot both produce high product purity and achieve a high recovery. Therefore, a single membrane unit can be eliminated. Nevertheless, if a set of membrane units are connected in parallel or in series, the desired product purity and recovery may be achievable. However, investigation of such an approach is not an aim of this work.

Combining the membrane with distillation could result in more energy-efficient separation processes, but there are many hybrid system configurations that can be generated. If all of these were included in one superstructure representation, it would
be difficult to solve the resulting mathematical problem. Therefore, it is better to eliminate unfeasible hybrid processes from the evaluation at an early stage of the design, as will be described in Step 2.

5.2.2 Screening of separation process options (Step 2)

Multiple hybrid configurations can be generated by integrating a membrane unit with a distillation column. In this work, the ‘parallel’ hybrid membrane-distillation scheme is categorized according to the way in which a membrane is integrated with the distillation column – the membrane may be connected either across the conventional column feed or not across it (i.e., above it or below it). The combination of a membrane with the distillation above the feed is illustrated in Figure 5.2(b). In this arrangement, the membrane is in the rectifying section; therefore, the flows of the rectifying section change. Between the column feed and the top product, the operating line will not have the same equation and form as the corresponding operating line for a simple column. In this configuration, the membrane assists the separation process by introducing two fractionated feeds of different compositions at different points in the column, which might make the distillation column work more efficiently than introducing one feed at a single point. As a result of the separation carried out by the membrane, the condenser duty and the number of stages might be reduced.

Another configuration, where the membrane is placed below the column feed, is illustrated in Figure 5.2(c). This arrangement works for changing the flows of the stripping section, where the column is rich in the less volatile component and the membrane feed stream is leaner in the more volatile component than the column feed. Carrying out extensive runs of the simulation show that the ‘bottom parallel’ hybrid membrane-distillation scheme is not a feasible option when the permeate stream has a purity that is less than the column feed purity for the fast-permeating component. An illustrative example to demonstrate this finding is presented in Appendix D.

If the retentate stream has a mole fraction that is more than the column feed mole fraction for the fast-permeating component, a lower membrane area is needed. The lower membrane area and the relatively low permeate flow rate are correlated with
small and less expensive process equipment and low demand for utilities, where there is a low demand for power to recompress the permeate stream to the column pressure and to chill the permeate stream to its dew point. In addition, it is probable that the condenser duty will change. Therefore, the ‘top parallel’ hybrid membrane-distillation scheme (Figure 5.2b), which would probably require a lower membrane area, is investigated in this work.

![Diagram of parallel hybrid configurations](image)

Figure 5.2: Parallel hybrid configurations. (a) Membrane placed across the feed stage; (b) Membrane placed above the feed stage; (c) Membrane placed below the feed stage.

There are three ways in which a membrane may be placed across the feed of a distillation column, as shown in Figure 5.2(a). In practice the side stream may be either above or below the column pinch. In this scheme, a saturated vapour stream is withdrawn from the column and permeate and retentate streams are recycled back to the column. A high purity separation in the membrane is not required; therefore, the product recoveries of the membrane module are likely to be acceptable. Thus, neither a high stage cut (resulting in high recompression power demand) nor a large membrane area (with high capital cost) will be required (Stephan et al., 1995). Since these two arrangements could bring energy savings, they are chosen for screening and evaluation in this work.
The ‘bottom series’ schemes, as shown in Figure 2.5(c), carry out further separation on the bottom products. It is expected that there would be no benefit to using a membrane to separate the bottom product further, as the membrane feed stream would be rich with the slow-permeating component. If the permeate stream is returned to the column below the feed stage, the condenser duty and refrigeration power demand will hardly be affected. In this case, although a small permeate-to-feed flow ratio is required, the recycle permeate purity is less than the column feed purity for the fast-permeating component, and this leads to a minor effect on the column reflux ratio. For higher membrane feed flow rates, where the permeate mole fraction becomes richer in the fast-permeating component, the condenser duty could be reduced at the expense of a large membrane area and high permeate recompression and cooling duties (see Appendix D). Therefore, this configuration is also eliminated from the analysis.

5.2.3 Evaluations of separation options (Step 3)

This work employs shortcut simulation/design methods to evaluate process alternatives and to select the most energy-effective configurations. The evaluation of different process alternatives is better accomplished by means of shortcut methods than by rigorous process simulators or superstructure presentation, especially for complex process arrangements with recyclers, so as to reduce computation time and the complexity of the model. Shortcut methods for both simple and complex column designs can compromise between accuracy and simplicity, as discussed in Chapter 2. Shortcut methods provide reliable predictions of column performance with minimal complexity in modelling. Complex columns can be decomposed into simple columns and then solved by simple approximated calculation methods. This leads to a significant reduction in model size, and avoids the numerical problem of solving large numbers of linear and nonlinear equations simultaneously. The methodology used here to simulate and evaluate various hybrid schemes will be described in detail in Section 5.3. Since heat recovery impacts significantly on process performance, it is also included in the evaluation.

5.2.4 Identifying the optimal separation process (Step 4)

In Step 4, a sensitivity analysis is carried out in order to explore important process interactions and their impact on the overall process performance. The focus will be
on energy requirements, and in particular the total compression work required by the process for refrigeration and permeate recompression. This is because it is expected that power costs will dominate the process economics. Cases studies in Chapter 7 show that the cost of refrigeration power represents more than 75% of total operating costs. After the key decision design variables are identified, optimisation will be performed to determine the optimal set of operating conditions. An optimisation framework is introduced to optimise the candidate separation flowsheets. A superstructure representation is proposed to synthesise the hybrid flowsheet that includes various possible configurations, such as the parallel schemes. A global optimisation tool in MATLAB is used to simultaneously determine the optimal heat-integrated hybrid flowsheet and its operating conditions. Step 4 will be described in detail in Chapter 7.

5.3 A novel approach to the design of hybrid membrane-distillation schemes

This section presents a systematic synthesis methodology for simulating and evaluating various separation process options, while taking into account opportunities for heat recovery. Each step in Figure 5.3 will be described and discussed in detail below.

![Figure 5.3: Hybrid membrane-distillation synthesis and simulation framework](image)

5.3.1 Process specifications

In separation process design, it is necessary to identify key degrees of freedom for design before simulating the process. Process “variables” are classified as ‘parameters’ (fixed) and ‘variables’ (varying).
Process parameters are the input parameters which remain fixed during the design, such as the feed compositions, pressure, temperature or thermal state of the main feed stream, product purities or recoveries, utility temperatures and the associated utility costs.

The selectivity is sensitive to changes in temperature because both diffusivity and solubility are temperature dependent. For simplicity, the membrane permeability is assumed to be constant (i.e. does not change with temperature, pressure or concentration) for a specific type of membrane (Baldus and Tillman, 1986).

Design degrees of freedom are those variables that could have an impact on the separation process performance; these include the distillation design variables (column pressure, number of stages or actual reflux ratio, column side draw location and flow rate) and membrane design variables, permeate and retentate conditions, stage cut or membrane area, and membrane module configuration. Any changes in these design variables impact the overall separation process. Consequently, simulation and economic evaluation of the whole flowsheet need to be repeated every time a new variable is considered.

The column operating pressure is an important degree of freedom that impacts significantly on energy cost and capital cost. For a given separation, the impact of changing the column operating pressure on the separation performance can be summarised as follows:

- Increasing the column pressure increases the temperature in the reboiler and condenser. Where expensive low-temperature refrigeration is required, there may be advantages in operating at higher pressures to reduce the power consumption of the refrigeration system (which rejects its heat to cooling water). In addition, substantial energy savings can be achieved if the refrigeration cycle rejects its heat to low-temperature heat sinks. However, there is a trade-off, as increasing the column pressure usually increases reboiler and condenser duties. Increasing pressure also increases the number of stages required and reflux requirements, thus increasing the capital cost of the column and heat exchangers.
• Changing column pressure indirectly affects the performance of an integrated membrane unit, and consequently the overall separation system. For example, for some hybrid arrangements, a vapour-phase column side draw is a membrane feed stream. Since the column pressure determines the temperature profile within the column, it controls the side stream temperature, and consequently the membrane operating conditions. The membrane feed should be at a temperature equal to or greater than the dew point temperature of the feed in order to avoid condensing the membrane vapour product streams (Ahmad et al., 2012) or to prevent freezing the carrier solution in the membrane (Al Rabiah, 2001). The condensation might arise from the change of vapour temperature across the membrane. The change of temperature across the membrane is a function of the pressure drop across the membrane, feed composition and stage cut (Clancy, 1996; Ohlrogge and Sturken, 2005). If the side draw pressure is within the working range of the membrane and at a temperature below the freezing point of the carrier solution inside the membrane, the solution will freeze; therefore, to achieve separation, the feed must be heated before it enters the membrane unit. For this work, an immobilized liquid membrane with a carrier solution of 6 M silver nitrate aqueous solution was selected for investigation. In this case, the temperature in the distillation column decreases from –7 to about –30°C at a column pressure of 20 bar; as the carrier freezing point at this concentration is –30.41°C, freezing should not take place (Al Rabiah, 2001).

Moreover, when the permeate stream is recycled to the column, its pressure should to be equal to the column pressure. Increasing the permeate pressure affects the driving force across the membrane. A small driving force requires a large membrane area but relatively low compression power requirements for both recompression and refrigeration.

Stage cut and membrane area are also important variables. To predict the technical performance of the hybrid system, one of these variables should be specified and the other is calculated. With pre-set values of membrane compositions, \( x_M \), feed pressure, \( P_F \), permeate pressure, \( P_p \), given selectivity, stage cut and desired permeate purities, \( y_p \), the result is a specific membrane area, \( A \), needed for the separation. Regardless of the type of flow, as the stage cut increases the membrane
area increases and membrane separation factor reduces because the permeate purity reduces. A stage cut of one indicates that the membrane feed is equal (in terms of both purity and flow rate) to the permeate; that is, the membrane does not perform any separation. As the stage cut decreases, the compression duty also decreases, but the condenser duty increases significantly (see Section 5.4.3).

The flow pattern of the gas streams on the two sides of the membrane is another important variable that affects the unit performance. Figure 2.2 shows different flow patterns that conceptualized for membranes. In the cross-flow, the high-pressure stream flows parallel to the membrane, whereas the low-pressure stream (permeate) flows perpendicular to the membrane. In the case of counter-current flow, the permeate stream flows in parallel to the feed stream but in the opposite direction. For a given degree of separation, a counter-current arrangement requires a lower membrane area compared to other types of flow pattern (Shindo et al., 1985; Makaruk and Harasek, 2009) because it provides the best driving force for permeation (Motelica et al., 2012). Solving the counter-current model is more complex and so is more time-consuming—particularly when various hybrid system schemes are to be screened and optimized—than using the cross-flow model; therefore, for simplicity, the cross-flow model will be used.

5.3.2 MATLAB–HYSYS interface for process design

As illustrated in Figure 5.3, this work applies to models implemented in MATLAB for the distillation column, membrane and heat recovery arrangements of the hybrid scheme, and employs HYSYS simulation software to predict the physical and thermal properties of the process streams. This framework lends itself to preliminary process design and also facilitates parametric studies to understand the impact of design variables and configurations on the performance of the overall separation process. In addition, the integration HYSYS with MATLAB allows heat integration opportunities to be explored simultaneously during separation process optimisation. This interface allows some thermodynamic and physical properties to be predicted with ease.

An interface written in MATLAB can link MATLAB to the HYSYS simulation environment to allow variables to be imported and exported. Appendix C provides
an example of the interface code for the calculation of thermo-physical properties. Once these properties are obtained, the unit operations (distillation column, membrane module, coolers, heaters and compressors) can be simulated in MATLAB and the heat recovery models can be applied to the resulting streams.

5.3.3 Hybrid design procedure for fixed configuration

This section introduces the methodology used to design the various hybrid systems illustrated in Figure 5.4. The design of the hybrid processes starts with modelling a single-stage membrane unit for a given membrane feed composition and feed flow where the membrane performance characteristics (selectivity or permeability of each component) are known. The model predicts the membrane area required and product purities.

![Figure 5.4: Hybrid configurations](image)

As discussed in Section 3.2.1, the membrane model equations are independent of the feed stream temperature. However, usually, the permeate stream temperature is
colder than the feed temperature because the permeate stream has a lower pressure and is richer in the most permeable component. Since the membrane unit is assumed to operate at a constant temperature, the permeate stream temperature, $T_P$, is equal to the retentate stream temperature, $T_R$.

After carrying out a material balance on a membrane unit, an energy balance is carried out to determine the product enthalpies. The energy balance is given by equation 5.2.

$$T_R = T_P$$  \hspace{1cm} (5.1)

$$H_M = H_p + H_R$$  \hspace{1cm} (5.2)

Where $H_M$, $H_p$ and $H_R$ are the stream enthalpy in kJ h$^{-1}$ for the membrane feed, permeate and retentate respectively.

The permeate stream pressure is below the column pressure, so it needs to be recompressed to the column pressure and cooled to the desired condition. To calculate the outlet pressure and temperature of the compressor, as well as the compression power demand, a compressor model (see Section 6.3) and cooler model are developed. Cooling water and the compression refrigeration cycle may be used to provide cooling. If the permeate stream after recompression is a superheated vapour and it is required to be a saturated vapour, it must be cooled, first using cooling water and then using a refrigerant. Power consumption in the refrigeration system is evaluated by developing a simple refrigeration model rather than applying a complex model. Chapter 6 presents a detailed description of how the refrigeration model is derived and implemented.

At this point, the column is ready to be designed (i.e. to decide on the number of stages and reflux requirements). The methodology needs to permit evaluation of both the parallel scheme and the sequential scheme (double-feed column). The difference between the two configurations is that the side draw rate and its composition are design variables in the parallel scheme, while the membrane feed stream is specified in the sequential scheme. The parallel configuration has more design degrees of freedom and it is more complex to design than the other hybrid schemes. Figure 5.5
presents the design flowchart for the parallel and sequential (double-feed column) hybrid flowsheet.

Figure 5.5: Design flowchart for the parallel and sequential (double-feed column) hybrid system shown in Figures 5.4(b) and 5.4(c)

For the sequential scheme (single-feed column) shown in Figure 5.4(a), the retentate stream and the bottom column stream are mixed. The ‘minimum retentate purity’ of the slow permeating component needs to be determined. This purity corresponds to the minimum stage cut that allows the bottom product specifications to be met. However, the minimum retentate purity corresponding to minimum stage cut value will yield high bottom product purity, so the column will require a very large number of trays to produce the desired product purity, and hence the capital cost will be high. However, the operating cost will be low because the condenser duty is small. Figure 5.6 shows the design flowchart for the sequential (single-feed column) hybrid scheme.
In the case of the ‘top’ hybrid scheme shown in Figure 5.4(d), the permeate flow rate and composition are determined by the product specifications. For each initially assumed membrane feed purity \(x_{i,M}\), there is a unique stage cut value that produces the given permeate stream purity and flow rate. This value needs to be estimated in order to determine the distillate flow rate and then design the column. Also, there is a minimum membrane feed purity that meets the product purity specifications. The membrane simulation can start with feed purity \(x_{i,M}\) that is lower than that of the permeate. The minimum value of the feed purity, \(x_{i,M}\), can be approximately calculated by solving equation 3.32. However, \(x_M\) is a design variable that can be optimised within the range \(x_{i,M(\text{min})}\) to \(y_{i,p}\). In this ‘top’ scheme, the cooler and compressor model might be required to recompress and cool the permeate stream to the desired pressure and temperature. Figure 5.7 demonstrates the design flowchart for the top hybrid scheme.
Once the column feeds and side stream conditions are identified, the column is designed as shown in Figure 5.8. To design the column, the modified shortcut models described in Chapter 4 are employed. Shortcut calculations allow column duties at minimum reflux ratio to be estimated. To predict the actual column performance, either the theoretical number of stages ($N$) or a multiple of the minimum reflux ratio ($R/R_{\text{min}}$) needs to be specified. If the ratio of the minimum reflux ratio is specified, the number of stages is determined from solving equations 2.30, 2.32 to 2.34, and consequently the condenser and reboiler duties are determined from energy balance equations. Both of these techniques have been used for evaluation of hybrid systems (e.g. Pettersen et al., 1996; Al Rabiah, 2001; Caballero et al., 2009). Temperatures and heat capacities in the condenser, reboiler, heater and coolers are estimated and will be used within the heat recovery algorithm.
Figure 5.8: Column design flowchart. Two approaches can be used for the column design: either by fixing the number of stages \( N \) or fixing the ratio of the actual reflux ratio \( R \) to the minimum reflux ratio \( R_{\text{min}} \).

### 5.3.4 Opportunity for heat integration within the separation process

To facilitate a comparison of heat-integrated conventional technologies with non-heat-integrated and heat-integrated hybrid schemes, various options are considered. In option 1, the heat integration model determines the opportunities for heat recovery between the column and the refrigeration system only. In this case, the refrigerant condenser serves as the heat source for the reboiler. In option 2, the heat integration model identifies opportunities for heat recovery between various “Feed and product” streams and the refrigeration cycle. In the non-heat integrated option, the heating and cooling demands of the separation processes are dealt with by external utilities. Chapter 6 describes the proposed mathematical programming approach implemented for modelling and evaluating heat integration opportunities.

### 5.3.5 Performance indicator

The performance indicator to be considered when evaluating alternative designs for any given product specifications (pressure, temperature, and product purity and component recovery) are: operating cost, capital cost or total annualised cost of the
system, including both the capital and operating costs. The choice between these objective functions is the designer’s decision.

If the cost of energy dominates the process economics, then operating cost can be selected for screening and evaluation of different classes of separation processes. The operating cost includes the cost of both cold and hot utilities and the compressor power costs. For sub-ambient separation processes, the cost of the power consumed is a major contributor to the operating cost (Motelica et al., 2012); therefore, minimizing shaft power consumption in the separation and refrigeration systems is set as the objective function for the comparison of hybrid membrane-distillation designs with conventional distillation designs. The shaft power consumption can mainly be reduced by reducing the column cooling requirement and temperature at which cooling is required. If the cooling duty for the distillation condenser is reduced, the refrigerant flow rate will decrease, which then reduces compression power demand in the refrigeration system. The power demand is related not only to the refrigerant flow rate but also to column pressure. If the column pressure increases, the temperature in the reboiler and condenser increases; and, consequently, the refrigeration power is reduced.

The operating costs of a process are influenced by its operating conditions and there are many degrees of freedom that can be examined. In this work, only key decision variables which are expected to be crucial to the economic performance are investigated. Here, ‘key’ decision variable is identified by sensitivity studies (see Section 7.2).

5.4 Case study

One case study and three types of separation technologies are presented to illustrate the application of the proposed methodology to the design of a conventional column, membrane unit and a hybrid membrane-distillation flowsheet, in various configurations. Performance evaluation, in terms of total power demand, is carried out to decide which separation technologies are likely to be more cost-effective for a given degree of separation. The membrane data and the feed conditions used in the case studies are based on the study by Pinnau and Toy (2001).
5.4.1 Option 1: Distillation column design (Base case)

This case study considers the separation of a binary mixture of ethylene and ethane. It is assumed that there is no pressure drop within the column, reboiler or condenser, where the column pressure is considered constant at 7.3 bar. A constant reflux ratio of 1.05 times the minimum value is used for the column design. A conventional column for separating a saturated vapour feed that contains 54 mol% ethylene and 46% ethane is carried out. The feed rate is 100 kmol h\(^{-1}\). The required distillate and bottom purity are 99.9 mol% ethylene and 99.5% ethane respectively. The distillate product is a saturated vapour. Soave-Redlich-Kwong is the equation of state that is used to determine vapour-liquid equilibrium behaviour and thermophysical properties such as enthalpies.

The cooling requirement for the column condenser is supplied by the refrigeration system. The ambient temperature at which the condensing heat may be rejected from the refrigeration cycle is set at 20°C. The minimum temperature approach is assumed to be 5°C. To calculate the refrigeration operating costs, the power consumption (compression shaft work) of the refrigeration cycle needs to be estimated. The cost of electricity is assumed to be 330 £ kW\(^{-1}\) a\(^{-1}\) and the cost of cooling water is 33 £ kW\(^{-1}\) a\(^{-1}\) (Farrokhpanah, 2009). The utility cost data provided by Farrokhpanah (2009) are similar to those reported by EIA (2012) for electricity costs and to Motelica et al. (2012) for cooling water costs, in an ethylene-ethane separation system.

For the purposes of comparison and evaluation of alternatives, a conventional single-feed distillation column (the base case) is designed using the modified shortcut models described in Section 4.2 in MATLAB and simulated rigorously in HYSYS.

Table 5.1 presents the results. It may be seen that the results of the modified shortcut model, which includes enthalpy balances, are very similar to the rigorous simulation results. However, the modified shortcut model predicts a higher number of stages than the number that corresponds to the same reflux ratio in rigorous simulations using HYSYS, with a difference in the theoretical number of stages of 13%. This difference may be attributed to the limited accuracy of the analytical
representations of the Gilliland correlation. Figure 5.9 shows that there is disagreement between the Rusch correlation (Smith, 2005), the Eduljee correlation (Kister, 1992) and HYSYS over the whole range of reflux ratios. However, the difference in the theoretical number of stages predicted by HYSYS and the Gilliland correlation increases at low reflux ratios, e.g., less than 1.1 $R_{\text{min}}$.

Table 5.1: Comparison of simulation results from HYSYS and shortcut design results for C$_2$-splitter conventional column

<table>
<thead>
<tr>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{min}}$</td>
<td>3.168</td>
<td>3.376</td>
</tr>
<tr>
<td>$R_{\text{act}}$</td>
<td>3.33</td>
<td>3.54</td>
</tr>
<tr>
<td>$Q_{C}$, kW</td>
<td>577.5</td>
<td>616.5</td>
</tr>
<tr>
<td>$Q_{R}$, kW</td>
<td>414.9</td>
<td>452.9</td>
</tr>
<tr>
<td>$N$</td>
<td>59</td>
<td>59</td>
</tr>
</tbody>
</table>

FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; $R_{\text{min}}$: minimum reflux ratio; $R_{\text{act}}$: actual reflux ratio; $Q_{C}$: condenser duty; $Q_{R}$: reboiler duty; $N$: theoretical number of stages

Figure 5.9: Number of theoretical stages vs. ratio of reflux ratio to minimum reflux ratio for C$_2$- splitter in the case of saturated vapour feed state at 2.7 bar
5.4.2 Option 2: Membrane module design

In this case, the design obtained using the proposed design method introduced in Chapter 3 for the separation of the same binary mixture of ethylene and ethane through facilitated transport membranes, where \( \text{C}_2\text{H}_4 \) is the fast permeating component. This class of membranes has shown good selectivity and permeability compared to other conventional polymer membranes (Pinnau and Toy, 2001). The performance of these membranes has been investigated experimentally but no commercial industrial application for them is known to exist, primarily because of chemical instability issues and changing membrane structure over time (Merkel et al., 2007; Rungta et al., 2013). The molar composition of the feed mixture is 0.54 \( \text{C}_2\text{H}_4 \) and 0.46 \( \text{C}_2\text{H}_6 \). The membrane feed flow rate is 100 kmol h\(^{-1}\). The feed pressure is 7.3 bar and temperature is 23\( ^\circ \)C (Pinnau and Toy, 2001). The calculation is performed for various permeate pressures and stage cuts, as shown in Figure 5.13. The purity of ethylene in the permeate, the membrane area and the fraction of ethylene recovery are determined for a single membrane unit with a cross-flow pattern. For the sake of simplicity, the membrane behaviour is described with a cross-flow model, which is sufficiently precise for the assessment of asymmetric membrane-based separation processes (Kohl and Nielsen, 1997).

Permeability data are taken from Pinnau and Toy (2001) and Al Rabiah (2001) for solid polymer electrolyte membrane, SPEM, and immobilized liquid membrane (ILM), respectively. Immobilized liquid membrane is a microporous membrane impregnated with an aqueous solution carrier of silver nitrate (Faiz and Li, 2012). The separation in this membrane is based on the fact that only ethylene can react with the silver ion, thus enhancing its transport across a barrier. Section 2.2.1 discusses the transport mechanism through this type of membrane. Solid polymer electrolyte composite membrane is made from polyethylene oxide loaded with silver tetra fluoroborate (Pinnau and Toy, 2001). The transport of ethylene across the membrane occurs by movement of ethylene across fixed silver sites by a hopping mechanism (Pinnau and Toy, 2001; Rungta et al., 2013).

In the experiments of Pinnau and Toy (2001) the stage cut was less than 1% in order to guarantee retentate purity equal to the feed purity. However, higher yields are investigated here. In addition, the membrane permeability is not assumed to be
constant with respect to feed pressure to allow for estimation of the area of the membrane for more realistic application.

When considering the design of the membrane separation unit, the feed and permeate pressures are important degrees of freedom. Therefore, it is important to have permeance data for a range of operating pressures. According to Pinnau and Toy (2001) and Merkel et al. (2007), permeability decreases with increasing feed pressure for polymeric and facilitated transport membranes. In the binary mixture of ethylene and ethane, the ethylene permeance decreases by a factor of about 2 with an increase in feed pressure from 50 to 100 psig (Pinnau and Toy, 2001). For the same pressure change, the permeance of ethane increases by less than 1%. This information has been used to generate permeance data outside the range of the experimental data of Pinnau and Toy (2001). It is important to mention that the extrapolation data carried out in this section is based on the assumption that the observed trend (exponential relationship) for pure mixture can be applied for binary mixture. However, this may not be the case, and that would significantly change the extrapolation. Even if this is the case, extrapolation is still useful for exploring the potential advantages of the hybrid membrane-distillation at high operating pressure.

In this work, the membrane selectivity at a high feed pressure is estimated as follows: First, the ethylene and ethane permeance are estimated by extrapolation of the data of Pinnau and Toy (2001) for the range of feed pressure shown in Figure 5.10. Then, the best fit for the set of data is calculated. Following this, the membrane selectivity is calculated by the ethylene-ethane permeance ratio. Finally, the selectivity data is regressed to obtain a correlation that relates solid electrolyte membrane selectivity to the feed pressure. Figure 5.11 shows the derived membrane selectivity equation as a function of feed pressure. This equation makes it possible to determine the membrane selectivity at various feed pressures. In the membrane model, the dimensionless permeance ratio (i.e., the ratio between the permeance of component \(i\) and the permeance of the most permeable component) can be described in terms of selectivity. For example, in a case of ethylene-ethane separation, the dimensionless permeance ratio for ethane is the inverse of selectivity and for ethylene it is one.
Figure 5.10: Extrapolation ethylene and ethane permeance for solid electrolyte membrane for a range of feed pressure. Permeate pressure: 1.01 bar; temperature: 23°C; carrier concentration: 80 wt% AgBF₄.

Figure 5.11: Solid electrolyte membrane selectivity versus membrane feed pressure. Permeate pressure: 1 bar; temperature: 23°C; carrier concentration: 80 wt% AgBF₄.

Figures 5.13 and 5.14 show the influence of permeate pressure and stage cut on the performance (i.e., recovery and product purity as well as area requirement) of the solid electrolyte membrane (Pinnau and Toy, 2001). As the permeate pressure decreases, the permeate purity increases because the pressure driving force increases. It can be seen that the stage-cut has a significant effect: at a low stage cut, the permeate flow rate is low and the permeate purity is higher than that at a high stage-
cut. That is, there is a trade-off between the permeate purity and the recovery of the more permeating species.

Figure 5.12: Simulation results of a cross flow module: Effect of permeate pressure on SPEM performance for ethylene-ethane separation.

Figure 5.13: Simulation results of a cross flow module: Dimensionless SPEM area as a function of permeate pressure, $P_p$, and stage cut

Figure 5.13 presents the corresponding dimensionless area of the solid electrolyte membrane required to accomplish the separation. The dimensionless membrane area is estimated as described in equation 3.22. As the permeate pressure increases, the membrane area increases because the rate of gas permeation across the membrane decreases.
Figures 5.15 and 5.16 indicate that the same relationships hold for the immobilized liquid membrane, ILM (Al Rabiah, 2001). The permeate pressure affects the permeate purity and ethylene recovery significantly. Also, membrane area requirements appear to be more sensitive to permeate pressure or pressure ratio for a permeate recovery containing over 80 mol% ethylene. However, the membrane area required by the SPEM is larger than that of the ILM because the SPEM has a
lower permeability and it is thicker than ILM. A thicker membrane material and low permeability will increase the capital cost.

In this case; however, as shown in Figures 5.12 and 5.14, a single membrane unit cannot achieve the same purity and recovery of ethylene as in option 1. Figures 5.12 and 5.14 show that the maximum purity of the ethylene in the permeate stream is 98.9 mol % and 99.6 mol % for SPEM and ILM, respectively, at a stage cut of 0.1 and with the permeate at atmospheric pressure. If the membrane feed is rich in ethylene, the desired purity could be achieved using the ILM. However, there is a trade-off between product purity and recovery; capital and operating costs where the permeate stream needs to be recompressed and cooled using both cooling water and refrigerant. The cost of recompression and cooling will be extremely expensive in terms of both capital and operating costs. Therefore, the membrane on its own is not a useful design option. However, combining the membrane with distillation could result in more energy-efficient separation processes. Section 5.4.3 assesses various hybrid flowsheets for the ethylene-ethane separation system.

5.4.3 Option 3: Hybrid membrane-distillation design

To evaluate the performance of the hybrid membrane-distillation system for producing the specified overhead and bottom products, as in Option 1, various hybrid membrane-distillation configurations are considered. In this section, options with and without heat recovery will be explored. The permeate stream is introduced into the column as a saturated vapour at its dew point after being compressed from atmospheric pressure to the operating pressure of the column and cooled to dew point temperature. The utility system provides cooling, both above and below ambient conditions, to the permeate cooler for non-heat-integrated scenarios.

A solid polymer electrolyte membrane is considered for the assessment of various hybrid schemes because it is more stable than immobilized liquid membrane (Pinnau and Toy, 2001; Merkel et al., 2007; Rungta et al., 2013). Although the permeate pressure, membrane feed flow rate and membrane feed composition are design variables, they were assumed to be constant during the simulation during the initial comparison. Chapter 7 presents an optimization procedure that is applied to optimise key design variables for various hybrid configurations.
5.4.4 Option 3.1: Sequential hybrid membrane-distillation

In this case, the membrane module is placed before the distillation column, as shown in Figures 5.16(a) and (b). Three options are explored. In the first option, Figure 5.16(b), both the permeate stream and retentate stream feed the distillation column. In the second option, the permeate stream is mixed with the overhead product of the distillation column, while the retentate feeds the column. In the third option, Figure 5.16(a), the retentate is mixed with the bottom product of the distillation column and the permeate feeds the column. The second option is eliminated because the membrane cannot produce sufficiently high ethylene purity with this feed specification. Also, a disadvantage of this scheme is the high compression duty to recompress the permeate stream to the distillate operating pressure.

When the permeate stream is a feed stream of the distillation column, as in Figure 5.16(a), the purity of the bottom column product is no longer fixed. Since the purity
of the ethane product is specified to be 99.5 mol%, the purity of the bottom column product can be determined by a material balance around the mixer.

The mixer connects the membrane and distillation with the overall product of the process. The key to finding feasible solutions is to recognize that the mole fractions in the bottom product of the column need to be in the range 0 to 1.

There are two design variables that need to be specified in the design of the sequential hybrid flowsheet (single-feed column): the stage cut and permeate pressure. For a fixed permeate pressure, the stage cut value determines the permeate and retentate stream purities and the product flow rates, and consequently the bottom column purities and the bottom flowrate. In order to eliminate solutions that lie outside of the physically meaningful solution space, e.g., negative mole fractions, the minimum feasible stage cut $\theta_{\text{min}}$ needs to be determined. It is advantageous to identify $\theta_{\text{min}}$, as this allows one to specify the feasible working range of design parameters and thus reduce calculation time during optimization.

$\theta_{\text{min}}$ can be predicted from the intersection between the retentate purity profile produced from the membrane model calculation and the component material balance line of ethane (equation 5.3). In equation 5.3, the column bottom product purity of ethane ($x_{\text{C2H6,B}}$) is set to maximum (i.e. $x_{\text{C2H6,B}} = 1$).

Equation 5.3 is a new relationship derived from mass balance equations around the membrane, column and mixer. The derivation of equation 5.3 is illustrated in Appendix E. At the intersection point, the retentate purity calculated from equation 5.3 is equal to that estimated from the membrane model. Figure 5.17 shows that values of stage cut below $\theta_{\text{min}}$ will produce infeasible bottom column purity ($\theta_{\text{min}} \leq \theta \leq 1$).

$$x_{\text{C2H6,R}} = \frac{\theta x_{\text{C2H6,B}} - D \frac{x_{\text{C2H6,B}}}{M} - b_{\text{C2H6}}}{(\theta - 1)}$$ (5.3)

Where $\theta$ is the stage cut, $M$ is the membrane feed molar flow rate, $D$ is the distillate flow rate, $b_{\text{C2H6}}$ is the mixer output molar flow rate of ethane, $x_{\text{C2H6,R}}$ is the retentate mole fraction of ethane and $x_{B_{\text{C2H6}}}$ is the bottom column purity of ethane.
Figure 5.17: Simulation results for the sequential hybrid system (Fig. 5.16a). The minimum stage cut is determined by drawing equation 5.3 at a maximum column bottom purity of ethane and plotting the membrane model results.

Figure 5.18: Determination of the minimum stage cut and the corresponding ethane retentate purity for sequential hybrid system shown in Figure 5.16(a).

Figure 5.18 shows that the feasible area of design is above the mass balance equation 5.3 at various permeate pressures. A stage cut of 0.6 and permeate pressure of 1 bar produces an unfeasible design because the column bottom purity of ethane is above one ($x_{\text{C}_2\text{H}_6, \text{bc}} = 1.184$). However, at a stage cut of 0.7 and permeate pressure of
1 bar, the column bottom molar purity of ethane is 0.997. Therefore, for this configuration, a stage cut value of 0.7 is applied to simulate and design the hybrid system shown in Figure 5.16 (a). Cross-flow membrane model is used in MATLAB to predict the separation performance of solid polymer electrolyte membrane (Pinnau and Toy, 2001).

Table 5.2 shows the numerical results of the shortcut method implemented in MATLAB and the simulation results carried out in HYSYS for the sequential hybrid system (Fig. 5.16a). The membrane is represented in HYSYS using the component splitter unit. The output data to the component splitter is specified from the MATLAB membrane modelling results. Good agreement between the shortcut model and HYSYS is seen for predicting the column duties. The condenser duty was 32.5% less compared with conventional column.

Table 5.2: Simulation results from HYSYS and the shortcut method for the sequential hybrid system shown in Figure 5.16(a): permeate fed to the column and retentate stream mixed with the bottom column product

<table>
<thead>
<tr>
<th></th>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{min}} )</td>
<td>2.059</td>
<td>2.138</td>
<td>2.138</td>
</tr>
<tr>
<td>( R_{\text{act}} )</td>
<td>2.162</td>
<td>2.244</td>
<td>2.246</td>
</tr>
<tr>
<td>( Q_{C, \text{kW}} )</td>
<td>375.45</td>
<td>389.76</td>
<td>389.98</td>
</tr>
<tr>
<td>( Q_{R, \text{kW}} )</td>
<td>318.52</td>
<td>332.83</td>
<td>333.06</td>
</tr>
<tr>
<td>( N )</td>
<td>68</td>
<td>68</td>
<td>67</td>
</tr>
</tbody>
</table>

FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; \( R_{\text{min}} \): minimum reflux ratio; \( R_{\text{act}} \): actual reflux ratio; \( Q_{C} \): condenser duty; \( Q_{R} \): reboiler duty; \( N \): theoretical number of stages

The stage cut in the hybrid system is an optimization variable that impacts on total power demand. It also affects the membrane and the distillation performance (the membrane product flow rates and the component purities, as well as the column duties). As the stage cut varies between 0 and 1, there is a trade-off between power for recompression of the permeate stream, power demand for permeate cooling and
the column condenser duty. The trade-off illustrated in Figure 5.19 can be handled by estimating the net power consumption of the separation process. Section 5.4.7 presents the economic evaluation for various hybrid schemes.

![Figure 5.19: Power consumption for the sequential hybrid system shown in Figure 5.16(b): permeate and retentate streams are feed streams to the column](image)

Table 5.3: Simulation results from HYSYS and the shortcut method for the sequential hybrid system shown in Figure 5.16(b): permeate and retentate streams feed the column

<table>
<thead>
<tr>
<th></th>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{\text{min}})</td>
<td>1.806</td>
<td>1.97</td>
<td>1.830</td>
</tr>
<tr>
<td>(R_{\text{act}})</td>
<td>1.896</td>
<td>2.068</td>
<td>2.075</td>
</tr>
<tr>
<td>(Q_{C, \text{kW}})</td>
<td>329</td>
<td>359</td>
<td>360</td>
</tr>
<tr>
<td>(R/R_{\text{min}})</td>
<td>1.05^*</td>
<td>1.05^*</td>
<td>1.13</td>
</tr>
<tr>
<td>(Q_{R, \text{kW}})</td>
<td>157</td>
<td>187</td>
<td>188</td>
</tr>
<tr>
<td>N</td>
<td>65</td>
<td>65^*</td>
<td>65^*</td>
</tr>
</tbody>
</table>

^Indicates specified values; FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; \(R_{\text{min}}\): minimum reflux ratio; \(R_{\text{act}}\): actual reflux ratio; \(Q_{C}\): condenser duty; \(Q_{R}\): reboiler duty; \(N\): theoretical number of stages

Table 5.3 summarises the simulation results for the ‘sequential’ hybrid configuration, as shown in Figure 5.16(b), for a constant stage cut of 0.6 and
atmospheric permeate pressure. The modified Underwood Equations are applied to estimate the minimum reflux ratio. In this case, the distillation column has two feed streams, namely the permeate and retentate streams. The retentate stream is the feed that controls the column design because the pinch point is located on its tray feed composition, as discussed in Section 4.3.1. The retentate stream is a superheated vapour. By applying an enthalpy correction, the minimum reflux ratio is overestimated. As discussed in Section 4.4, the enthalpy correction to the Underwood Equations is most accurate when the feed thermal state, $q$, is between saturation conditions (i.e. $0 \leq q \leq 1$).

Figure 5.20: McCabe-Thiele diagram of the ethane/ethylene separation design problem (Option 3). This diagram also compares the conventional column and the other hybrid arrangements shown in Figure 5.16.

It can be seen that there is good agreement between the results of the HYSYS simulation and the modified shortcut model. The condenser duty is reduced by 43%, compared to the conventional column, for which results are presented in Table 5.1, but the number of stages required increases from 52 to 85 because the operating line becomes close to the vapour-liquid equilibrium curve, as shown in Figure 5.20, the McCabe-Thiele diagram for the C_2-spliter. It can be seen in Figure 5.20 that the distillation operating lines shift when the membrane is used together with the
distillation column. It is also apparent that the ‘top hybrid’ shown in Figure 5.16(d) requires the least number of stages compared with the conventional column and the other hybrid schemes because the operating line lies furthest from the equilibrium curve \(x_D = 0.98\) compared to \(x_D = 0.999\) in the conventional column.

The results obtained imply that the ‘sequential’ hybrid configurations could be competitive with the conventional column. Therefore, is considered for further evaluation in Chapter 7.

5.4.5 Option 3.2: Top hybrid membrane-distillation design

In this option, the membrane is located at the top of the distillation column and performs the final purification of the product. Ethylene of the required purity and flow rate is withdrawn as permeate. The retentate stream is recycled back to the distillation column at an appropriate location in the column. The permeate stream is cooled and recompressed to the required pressure. To keep the operating temperature of the membrane unit above –30°C, the top vapour is also heated to 23°C. Section 5.3.1 discusses the reasons for increasing the membrane feed temperature.

In this scheme, the distillate purity (membrane feed purity) is an independent design variable. The membrane feed flow rate is a dependent design variable because the permeate flow rate and its purity are known. For each membrane feed purity there is a unique stage cut that gives the desired permeate purities and the permeate flow rate.

To simulate this configuration, the distillate purity, which is equal to the membrane feed purity, needs to be determined. The minimum value for the membrane feed purity can be estimated from equations 3.32 and 3.36 assuming a perfect cross flow membrane with constant membrane selectivity (Caballero et al., 2009).

Figure 5.21 shows the influence of membrane feed flow rate on the membrane performance. It can be seen that a minimum mole fraction of ethylene in membrane feed can be obtained at a very large membrane feed flow rate. Obtaining a minimum flow rate necessitates a relatively pure membrane feed. At low feed flow rate, the stage cut is very close to one and the membrane feed purity is equal to the permeate
purity (Pettersen et al., 1996). However, reducing distillate purity or the distillate flow rate are impractical design options because the large membrane feed flow rate requires a high refrigerant flow rate and a large compression duty. On the other hand, the small membrane flow rate means that the membrane does not perform any separation. The membrane feed flow rate, membrane feed composition and the corresponding membrane area are therefore important optimization variables.

Figure 5.21 shows the influence of membrane molar flow rate on the condenser duty and the number of stages. It can be seen that a significant reduction in the number of stages may be obtained as the membrane flow rate increases. However, the minimum value for the condenser duty can be obtained at a low membrane molar flow rate value.

![Figure 5.21](image)

Figure 5.21: Performance of the ‘top’ scheme for the ethylene-ethane separation shown in Figure 5.16(d) at \( P_f = 1 \) bar, \( R/R_{\text{min}} = 1.05 \): (a) Influence of membrane feed flow rate on the column performance; (b) Influence of membrane feed flow rate on membrane performance
In this case, the ‘top’ hybrid scheme shown in Figure 5.16 (d) is investigated for the ethylene-ethane separation. Feed and product specifications and the column operating conditions are given in Section 5.4.1. The aim in this case is to design a column and membrane that meet the product specifications while evaluating the power demand for compression and cooling.

Table 5.4 compares the simulation results using HYSYS and the shortcut distillation method for a “membrane top hybrid system” at a stage cut value of 0.6 that corresponds to a membrane feed of 94 mol% ethylene and a dimensionless membrane area of 0.778, given the specifications of ethylene purity in the permeate of 99.9%, and the permeate molar flow rate of 53.82 kmol h⁻¹. It should be noted that the permeate purity is determined by the product specifications presented in Section 5.4.1. And the permeate flow rate is determined from the overall mass balance around the hybrid scheme shown in Figure 5.16(d). Although there is a significant reduction in the number of stages compared to the conventional distillation column (the results for which are presented in Table 5.1), the condenser duty increases.

Table 5.4: Simulation results using HYSYS and the shortcut method for the top hybrid system shown in Figure 5.16 (d). The stage cut (0.6) corresponds to a membrane ethylene feed purity of 0.94, dimensionless membrane area of 0.778 and permeate ethylene purity of 0.999

<table>
<thead>
<tr>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{min}</td>
<td>1.95</td>
<td>2.11</td>
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<tr>
<td>R_{act}</td>
<td>2.047</td>
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<td>Q_{C}, kW</td>
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<tr>
<td>Q_{R}, kW</td>
<td>422</td>
<td>472</td>
</tr>
<tr>
<td>N</td>
<td>39</td>
<td>40</td>
</tr>
</tbody>
</table>

FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; R_{min}: minimum reflux ratio; R_{act}: actual reflux ratio; Q_{C}: condenser duty; Q_{R}: reboiler duty; N: theoretical number of stages

Table 5.5, however, shows that with a stage cut of 0.975 and an ethylene membrane feed purity of 0.98, the condenser duty decreases by 3% compared to a conventional column design (see Table 5.1). The results presented in Table 5.5
indicate that the ‘top’ hybrid system is not competitive with a conventional column. Although the capital cost of the column can be reduced because the number of stages is reduced, the net capital cost of the separation process is likely to increase due to the need for auxiliary equipment (heater, cooler and compressor, plus the membrane itself). The economic evaluation in Section 5.4.7 will further support this conclusion.

Table 5.5: Simulation results using HYSYS and the shortcut method for the top hybrid system. The stage cut (0.975) corresponds to a membrane feed composition of 0.98 for ethylene, dimensionless membrane area of 1.28 and permeate ethylene purity of 0.999.

<table>
<thead>
<tr>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(\text{min})</td>
<td>3.036</td>
<td>3.225</td>
</tr>
<tr>
<td>R(\text{act})</td>
<td>3.188</td>
<td>3.386</td>
</tr>
<tr>
<td>(Q_{\text{C},\text{kW}})</td>
<td>570</td>
<td>605</td>
</tr>
<tr>
<td>(Q_{\text{R},\text{kW}})</td>
<td>407</td>
<td>442</td>
</tr>
<tr>
<td>(N)</td>
<td>44</td>
<td>45</td>
</tr>
</tbody>
</table>

FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; \(R_{\text{min}}\): minimum reflux ratio; \(R_{\text{act}}\): actual reflux ratio; \(Q_{\text{C}}\): condenser duty; \(Q_{\text{R}}\): reboiler duty; \(N\): theoretical number of stages

Caballero et al (2009) point out; further evaluation under other operating conditions will not bring about a significant reduction in the energy cost. Therefore, this option is dismissed from the process optimisation in Chapter 7.

5.4.6 Option 3.3: Parallel hybrid membrane-distillation

A parallel hybrid scheme for the ethylene-ethane separation system is shown in Figure 5.16(c). In this configuration, the membrane is placed in parallel to the distillation column to assist the distillation column in separating the desired mixture where the column is least effective (i.e. close to the column pinch tray).

In this case, the membrane feed is assumed to have a similar molar flow rate and purity to the column feed stream. The column side draw is the feed stream to the membrane unit. The permeate and retentate streams leaving the membrane unit are
recycled back to the distillation column (at appropriate stages, where the stream composition matches the tray composition).

Table 5.6 illustrates the simulation results of the parallel hybrid system. It can be seen that comparable results to the ‘sequential’ hybrid scheme are obtained. This is because the \( q \) line of the column feed stream and the side draw stream are matched for a given stage cut value of 0.6, membrane feed purity of 0.54 for ethylene and a membrane molar feed flow rate of 100, as shown in Figure 5.20. In this case, the operating line in the rectifying section moves closer to the equilibrium curve, which leads to a 22% increase in the number of stages in the column and a 46% reduction in the reflux ratio (\( R = 1.89 \)) compared to the reflux ratio of 3.54 in the conventional distillation column.

Table 5.6: Simulation results using HYSYS and the shortcut method for the parallel hybrid system shown in Figure 5.16(C)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{min}} )</td>
<td>1.806</td>
<td>1.807</td>
<td>1.830</td>
</tr>
<tr>
<td>( R_{\text{act}} )</td>
<td>1.896</td>
<td>1.897</td>
<td>1.922</td>
</tr>
<tr>
<td>( Q_{\text{C,kW}} )</td>
<td>329</td>
<td>330</td>
<td>334</td>
</tr>
<tr>
<td>( Q_{\text{R,kW}} )</td>
<td>157</td>
<td>154</td>
<td>162</td>
</tr>
<tr>
<td>( N )</td>
<td>65</td>
<td>65</td>
<td>85</td>
</tr>
</tbody>
</table>

FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; \( R_{\text{min}} \): minimum reflux ratio; \( R_{\text{act}} \): actual reflux ratio; \( Q_{\text{C}} \): condenser duty; \( Q_{\text{R}} \): reboiler duty; \( N \): theoretical number of stages

Table 5.6 illustrates the results for the parallel hybrid scheme, which are simulated using FUG shortcut method and the modified FUG shortcut method (MFUG). Table 5.6 shows that the modified shortcut method gives good predictions for the reflux ratio and energy requirement compared to rigorous simulation carried out using HYSYS for a fixed reflux ratio (RR) of 1.05.

It is clear that the performance of the distillation column changes when a membrane unit is placed on top, in series or parallel to the column. Economic trade-
off between the cost of distillation versus the cost of membrane separation as well as the cost of compression of the compressor and the refrigeration system should be considered when screening the separation process design alternatives. Section 5.4.7 introduces the criterion used for the evaluation.

5.4.7 Economic evaluations

There is a trade-off of energy consumption between the distillation column and the membrane unit (recompression and cooling requirement). The economic evaluation in terms of the net power consumption is used to determine the optimal design option for the given separation process. Heat integration between the separation process and the refrigeration system is accounted for in order to find the most promising separation alternatives that use the least amount of utility. Chapter 6 describes the methodology of heat integration implemented in this work.

For the purposes of comparison, non-heat integrated scenario is also considered. It is important to remember that the optimum configuration and the operating conditions should be identified simultaneously for any given separation problem. Chapter 7 illustrates the methodology used for the synthesis of separation processes. The conventional column is selected to be the base case design. The power consumption of the hybrid systems is then compared with the base case design. Below is the evaluation of the investigated configurations.

Option 1: Conventional column (base case)

In the conventional case, 616 kW cooling is required at –61°C. For the non-heat integration scenario, heat is rejected to an external heat sink that is set as cooling water, which accepts heat from 20°C. To meet the cooling requirement, the cascaded ethylene-propylene cycle is used. The total shaft power requirement is found to be 0.61 MW.

The economic evaluation of the base case shows that a considerable energy saving may be achieved by integrating heat into the process. In the heat-integrated scenario, the total shaft power requirement is reduced to 0.32 MW. A 47% power saving is obtained when the separation process is heat integrated with the
refrigeration system. The refrigeration cycle rejects part of its heat to the reboiler and the remainder to the cooling water.

**Option 2: Membrane separation process**

The simulation results of the membrane demonstrate that a single membrane unit is not competitive with the conventional column because the specified flow rate and the extremely pure vapour product requirement cannot both be achieved. However, a membrane system with a permeate recycle stream or a complex arrangement of membrane units that is placed in series, parallel or a combination of both could meet the high purity and recovery requirement. It should be noted that these design alternatives need recompression and cooling, which may dominate the system costs. It is recommended that these complex design alternatives, which are not considered here, be addressed in the future.

**Option 3: Hybrid configurations**

**Option 3.1: Sequential hybrid configuration**

The sequential hybrid membrane-distillation design shown in Figure 5.17(a) contains three sources and two streams that require cooling and heating, respectively. In this configuration, the recompression power requirement to recompress the permeate stream to the column pressure is 0.131 MW.

In case of the non-heat-integrated scenario, the net power consumption is 0.5876 MW from which 0.3863 and 0.0703 MW refrigeration power are needed to cool the overhead column product and permeate stream, respectively. A comparison between the non-heat-integrated base case and the hybrid case shows that a saving of about 4% in the total shaft work can be obtained for the non-heat-integrated hybrid system.

When both the permeate stream and retentate stream feed the distillation column, as shown in Figure 5.16(b), more energy saving is achieved. In this configuration, the net power demand is reduced by 13% compared to the conventional base case. This reduction results from reducing the condenser duty to 0.356 MW and the recompression duty of the permeate stream to 0.111 MW. The permeate stream exits from the compressor at 120°C. To cool this stream to a saturation vapour
temperature, it is first cooled to 30°C using cooling water. Then, it is cooled by a refrigerant where the required compression power is found to be 0.0631 MW.

Note that the recompressing and cooling the permeate stream reduce the energy efficiency of the hybrid system. About 31% of the net power demand is consumed before processing the permeate stream to the column.

A further reduction of energy is accomplished by heat integration of the hybrid separation process with the refrigeration system, as net power demand is reduced to 0.3624 MW. The column reboiler accepts heat pumped from the column condenser. The rest of cooling required by the column condenser is supplied by refrigeration, which rejects heat to cooling water.

**Option 3.2: Top hybrid configuration**

In the non-heat-integrated top hybrid case, the column condensing power is reduced to 0.596 MW and the number of stages is significantly reduced, thereby decreasing the capital cost for the distillation column. However, in contrast to the previous configurations, the top hybrid system provides no saving compared to the conventional base case design when the ratio of the reflux ratio is assumed to be constant at 1.05. This is because the permeate stream needs to be recompressed and cooled. The compression duty of the permeate stream is 0.0991 MW, which represents 13% of the net power demand, and the cooler refrigeration power requirement represents 9% of the net power demand. It should be mentioned that the cost of cooling by using cooling water after the compression stage is insignificant compared with the cost of power. This is will be demonstrated when the minimum utility cost is estimated in Chapter 7.

**Option 3.3: Parallel hybrid configuration**

It should be emphasized that the settings for the stage cut, membrane feed molar flow rate and membrane feed purity in the parallel hybrid configuration are similar to those of the sequential hybrid system with two feed column. Therefore, the economic evaluation results of the parallel hybrid configuration are the same as those for the sequential hybrid scheme design. Table 5.7 summarizes the net power demand of the processes design investigated.
Table 5.7: Summary of the net power consumption (NPC) & total operating costs (TOC) for case study

<table>
<thead>
<tr>
<th>Separation scheme</th>
<th>Without heat integration</th>
<th>With heat integration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NPC, MW</td>
<td>TOC, £/1000 y</td>
</tr>
<tr>
<td>Conventional column</td>
<td>0.6100</td>
<td>255</td>
</tr>
<tr>
<td>Sequential hybrid system:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>double-feed column</td>
<td>0.5306</td>
<td>212</td>
</tr>
<tr>
<td>Sequential hybrid system:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>single-feed column</td>
<td>0.5876</td>
<td>238</td>
</tr>
<tr>
<td>Parallel hybrid system</td>
<td>0.5306</td>
<td>212</td>
</tr>
<tr>
<td>Top hybrid system</td>
<td>0.7661</td>
<td>313</td>
</tr>
</tbody>
</table>

5.4.8 Summary– Case study

This section presents a case study as an illustration of the application of the design method to a range of hybrid configurations. This involves two different sequential hybrid systems; a membrane top hybrid and a parallel hybrid scheme. The performance of these configurations is compared with that of a conventional column and two types of facilitated transport membranes. The total power demand is used for assessing the performance of the separation flowsheets because this dominates the total operating costs.

For separation problem in question, high purity and recovery cannot both be achieved using a single unit of highly selective facilitated transport membrane. Therefore, replacing a conventional distillation with facilitated transport membranes is not a feasible solution. Even if the membrane system is able to produce the required purity and recovery there is still an issue with the high recompression and cooling costs. Added to this is a number of other factors relating to the membrane materials and the operating conditions.

The economic evaluations of the hybrid systems demonstrate that the parallel hybrid system and the sequential membrane-distillation (double-feed column) give the best energy performance. These schemes reduce the condenser duty requirement by 46% compared to the conventional distillation (base case).
The heat integrated parallel hybrid system and the sequential hybrid membrane-distillation (double-feed column) reduce the net power demand by 41% compared with the non-heat integrated base case. Unfortunately, it was found that hybrid processes are not competitive with the conventional distillation column if this is heat integrated.

Note that, in the cases studied, the column pressure is set to 7.3 bar. The overhead column temperature at this pressure is –61°C; therefore, a refrigeration cycle along with an ethylene-propylene system is needed. To allow condensation of the overhead stream with a less expensive refrigerant, it is worth considering a high column pressure operation. The influence of the column pressure on system performance is addressed in the optimization calculation in Chapter 7.

5.5 Conclusions

In this chapter, a new framework relates hybrid membrane-distillation flowsheet, refrigeration system and heat recovery system is presented and illustrated by the separation of a binary mixture. The main features of the developed approach are:

1. A set of models for membrane, compressor and cooler as well as for a simple and complex column is implemented in MATLAB. These models are used to design, screen and evaluate various separation flowsheets.
2. The influence of many design parameters on the separation process performance can be examined. The basis of evaluation can be either the total power demand or the total operating costs of the separation flowsheets.
3. In this work, MATLAB and HYSYS are integrated by an automation method to determine thermo-physical properties. Therefore, the challenges associated with modelling equations of state to determine streams properties are overcome.
4. Heat integration between the separation process and the refrigeration system is taken into consideration. Therefore, it is possible to take advantage of interactions within the separation process and interactions between the separation process and its associated refrigeration system. Chapter 6 discusses the methodology of heat recovery.
A systematic methodology for the simulation and design of various hybrid membrane-distillation systems is also introduced. The developed methodology gives good predictions compared to rigorous simulation results obtained from HYSYS. It should be mentioned here that the shortcut model for hybrid membrane-distillation system takes 1.4 seconds to solve while the HYSYS simulation for column model requires a large number of individual computer runs to locate the optimum stage locations and determine the minimum reflux ratio; a couple of hours are usually required depending on the column features.

A case study results show that the parallel hybrid scheme (Figure 5.16 (c)) can reduce the condenser duty by about 46%. The total operating cost of the parallel hybrid scheme is reduced by 17%, compared to the non-heat-integrated conventional column. However, the number of stages is increased by 22%.

The sequential hybrid scheme (single-feed column, Figure 5.16 (a)) can also reduce the column cooling duty by 46% but the reduction in the condenser duty is offset by the increase of compression duty and the refrigerant cooling duty. Maximum energy saving is achieved at a minimum stage cut value (approximately 0.7). To find the minimum stage cut value, a new relationship derived from mass balance equations around the membrane, column and mixer in Section 5.4.4.

Top hybrid scheme shown in Figure 5.16 (d) was not competitive with a conventional column although the number of stages is reduced by 23% and the condenser duty is decreased by 3%. This is because of the high compression and cooling costs which are required to recompress and cool the permeate product stream to the column operating pressure and the desired temperature.

A bottom parallel hybrid shown in Figure 5.2(c) is found not to be a feasible design because the membrane product purities are inconsistent with the hybrid constraints. Also, simulation results show that there is no benefit to place the membrane at the bottom product where membrane feed stream is rich with the slow permeating component. Large compression and cooling duty will be required. In this work, unfeasible hybrid configurations as well as the hybrid schemes which do not provide a significant energy saving will be disregarded from the process optimisation in Chapter 7.
Chapter 6 Modelling of Heat-Integrated Hybrid Membrane-Distillation Systems

6.1 Introduction

Although considerable research has been devoted to investigating the design and simulation of hybrid membrane-distillation processes, rather less attention has been paid to studying opportunities for heat integration in these processes. If heat integration is considered, operating costs can be reduced. In the hybrid membrane-distillation process, heat can be exchanged between ‘cold’ streams that need heating and ‘hot’ streams that need cooling, either directly or indirectly, through the refrigeration cycle. Refrigeration cycles can exchange heat with process source streams and reject the absorbed heat to a cold heat sink within the process and/or to an external cooling utility.

To explore the advantages of heat integration, a heat recovery model and a refrigeration model for determining the total shaft work requirement are needed. The refrigeration model should be applicable over a wide range of temperatures to accommodate the needs of diverse separation processes most efficiently. Moreover, the refrigeration model should be easy to implement, as in the hybrid membrane-distillation design and optimisation framework introduced in Chapter 7.

In this chapter, a novel strategy for synthesis and design of heat-integrated hybrid membrane-distillation processes is introduced. The heat integration methodology presented here considers heat pumping to process heat sinks, rather than just to an ambient heat sink, such as air or cooling water. The shaft work requirement for low-temperature process design is estimated using a simple model to represent the refrigeration cycle; this approach removes the need to design the refrigeration cycle. The model estimates the actual coefficient of performance (COP\text{act}) of the
refrigeration cycle, taking into account the effects of key design parameters on the overall performance of vapour compression refrigeration systems. The implementation of the refrigeration model and the heat integration approach together for prediction of the net power demand of a hybrid separation process is illustrated by studying a sub-ambient separation system.

6.2 A brief review of heat integration approaches

In the literature, systematic design approaches to process heat integration have been developed to maximise heat recovery, minimise energy costs or minimise the total annualised cost, which includes both operating and annualised capital costs. These approaches include ‘pinch analysis’ methods, and mathematical optimisation methods.

6.2.1 Pinch method

‘Pinch analysis’, which is based on insights from the first and second laws of thermodynamics, allows energy ‘targets’ to be established (i.e., determination of the minimum utility requirements). Pinch technology establishes a pinch, which is the point where the lowest driving forces between hot and cold streams are located. This divides the overall process into two parts: a high-temperature heat sink above the pinch requiring heating and a low-temperature heat source below the pinch requiring cooling. Linnhoff and Hindmarsh (1983) developed a ‘pinch design method’ to allow the energy targets to be achieved, given a set of ‘hot’ and ‘cold’ streams and a selected minimum approach temperature. In this methodology, heat should not be transferred across the pinch and cold utilities are only placed below the pinch and hot utilities above the pinch. Although the ‘pinch design method’ is useful, as it allows the calculation of the minimum hot and cold utility demand—independent of the heat exchanger network design—it is difficult to implement at industrial scales, where there are a large number of streams need to be heat integrated, and, consequently, a large number of ‘matching’ options (Smith et al., 2010). In addition, pinch analysis is based on heuristics rules that can contradict each other, possibly resulting in sub-optimal solutions (Ahmad, 2009). Therefore, instead of heuristics, mathematical modelling approaches for heat exchanger network design were developed.
Mathematical programming approaches for heat recovery

Mathematical techniques use deterministic or stochastic optimisation methods for heat integration, designing heat exchanger networks and establishing the heat loads of each exchanger. Studies that have explored the synthesis of heat-integrated sub-ambient separation processes include the work of Shah (1999), Wang (2004) and Farrokhpanah (2009). These identified a number of challenges associated with sub-ambient separation systems. One of the main challenges for synthesis of sub-ambient separation processes is the complex interaction between the separation and the refrigeration system.

Shah (1999) developed a systematic approach that screens simple and complex distillation options, optimizes the operating pressures of the columns and provides targets for the important parameters applied to two case studies on sub-ambient processes (LNG separation train and ethylene cold-end separation). Shah’s work was based on task superstructure representation and mixed integer linear programming (MILP) was used to find the optimum separation sequence. Shah did not consider heat integration between process streams but used the shortcut model for a refrigeration system developed in Shelton and Grossman (1985). The developed model was used to predict the coefficient of performance (COP) of simple vapour-compression cycles for pure refrigerants under the assumption of isentropic compression. The shortcut model of Shelton and Grossman (1985) predicted the COP by using system temperatures and thermodynamic data of refrigerant (i.e., specific heat capacity and molar latent heat of vaporization). This model is easy to use but it is restricted to simple cycles and pure refrigerant. In the work of Shah (1999), the power consumption in the refrigeration compressor is calculated by dividing the evaporator duty by the cycle COP, which reduces the computation burden and complexity of the optimisation. However, heat is rejected to external utility rather than process streams, so the opportunities of matching refrigeration system with process streams—which can provide significant energy savings—are missed.

Wang (2004) used a genetic algorithm for synthesis and optimisation of low-temperature gas separation processes. A superstructure representation involving both simple and complex distillation columns is employed to generate heat-integrated
separation sequences. However, other separation technologies, such as hybrid membrane-distillation, were not considered. In addition, process streams in the heat integration algorithm are assumed to be isothermal (e.g., the inlet and outlet temperatures of the streams that undergo phase change in coolers and reboilers in distillation columns are taken as constant) and two heuristics are considered for a heat-integrated refrigeration system with separation processes: 1) It is favourable to reject heat with minimum temperature differences between evaporating and condensing temperatures. 2) It is desirable to provide a refrigerant to satisfy a heat source at a lower temperature prior to that of a higher temperature. These rules of thumb are useful at the preliminary design stage: The lower the temperature differences between the source and sink the lower will be the pressure ratio in the compressor, and, consequently, the lower the power consumption of the refrigeration system. However, the assumption of an ‘isothermal’ stream in the heat integration approach limits opportunities for more heat recovery between the process stream that releases or gains heat over a temperature range (non-isothermal).

More recently, Farrokhpanah (2009) developed a systematic methodology to design a heat-integrated separation distillation sequence and an associated refrigeration system in the context of low-temperature separation processes. In this methodology, each process source stream (cold end stream temperature), exchanges heat with any process sink stream (hot end stream temperature), either directly or through a heat pump system (i.e., the refrigeration system) where any heating or cooling not satisfied by the exchange among process streams is provided by external utilities. The problem of heat exchanger network synthesis is formulated as a linear optimisation to determine the minimum utility cost. The optimisation variable is the load on each match. If there is no match between a source and a sink, the associated load will be zero and therefore the need to introduce integer variables is eliminated. In the work of Farrokhpanah (2009), a refrigeration database including the power demand at various operating conditions is generated and used for estimating the cost of indirect heat exchange (i.e., the cost of the refrigeration system that transfers heat in the matches between the sources and sinks). To generate the refrigeration database, refrigeration system designs are performed.
The main advantages of her approach are: i) the opportunity to absorb heat from source stream and reject it to sink stream through the use of refrigeration system is considered; ii) non-isothermal streams are not considered to be isothermal; and iii) process streams that exchange sensible and latent heats are decomposed into sub-streams for the superheated and saturated parts. The limitation of the approach is that the trade-offs between the operational and capital costs of the network are not considered.

In this work, the optimisation-based approach of Farrokhpanah (2009) is implemented and modified for heat-integrated hybrid membrane-distillation processes to determine the net power consumption. The compression work, which is required to recompress the permeate stream from permeate pressure to the column pressure and consumed in the compressors of refrigeration cycles to lift refrigerant from evaporating pressure to condensing pressure, is the primary energy ‘power’ input to the hybrid process, so only shaft work needs to be evaluated.

Section 6.3 illustrates the new heat integration approach used in this work. The approach considers the heat integration options between the process streams of the hybrid separation process and the refrigeration system as well as opportunities for process-to-process heat recovery.

### 6.3 New approach for heat integration

The heat integration approach used in this work is a modification to that described by Farrokhpanah (2009) in Section 6.2.2. First, the heat exchanger network is formulated as a linear optimisation problem to optimise the heat load and determine the refrigeration power demand. Then, a nonlinear optimisation algorithm is used to calculate total power requirement for a specified range of constraints. In contrast to Farrokhpanah (2009), a simple refrigeration model to predict the actual coefficient of performance and evaluate the required shaft power of the refrigeration system is developed in this work (see Section 6.5).

Figure 6.1 shows the proposed heat integration approach. The heat integration algorithm uses outputs of simulation models and only process streams that require heating and cooling are used. In the approach, process streams might be segmented if they exist in more than one interval. The proposed linear model uses a ‘matching
matrix’ (M) to generate a ‘costing matrix’ that evaluates the cost of each match per unit of heat. The matching matrix simply shows how heat can be exchanged between sources and sinks. Each hot stream can potentially be matched against any cold stream either directly ($M_{ij} = 1$) or indirectly ($M_{ij} = -1$) through a heat pump. The value of $M_{ij}$ is decided based on temperature constraints. In steps 6, to cost the indirect match, a simple linear refrigeration model is developed. The refrigeration model has been used in step 8 to calculate the total shaft power for optimal heat duties optimised in step 7. Steps which are modified in the heat integration approach of Farrokhpanah are steps 6 and 8 in Figure 6.1. Section 6.3 describes in detail each step of the heat integration approach.

**Figure 6.1: Heat integration approach to evaluate process power demand**

- Step 1: Extract process data from simulation results
  - Specify:
    - Minimum approach temperature
    - Utility data

- Step 2: Classify process streams
  - Calculate duties and determine total heat capacity

- Step 3: Generate temperature intervals based on problem table algorithm proposed by Linnhoff and Flower (1978)

- Step 4: Partition process streams and obtain a set of segmented source and sink streams data

- Step 5: Generate matching matrix based on temperature difference rule

- Step 6 (Modified): Apply refrigeration model
  - Determine cost matrix based on matching matrix

- Step 7: Apply LP optimisation to minimise heat loads
  \[ \min f(Q) = \Sigma_i \Sigma_j Q_{ij} C_{ij} \]

- Step 8 (New): Calculate total shaft power for optimal heat duties
Step 1:

The first step is to specify the process streams supply (inlet) and target (outlet) temperatures and their associated heat duties. It is also necessary to identify the process utilities and their temperature ranges, their annual costs per unit of heat and the minimum approach temperature. For above-ambient separation systems, typical values range from 10°C to 20°C. For sub-ambient separation systems, a lower temperature range can be used; for example, the range of 3°C to 5°C would be suitable (Turton et al., 1998).

Step 2:

Classify the process streams into sets of hot ($H$) and cold ($C$) streams. Cold streams include the process sinks. Hot streams include the process sources. Generate a temperature matrix for the hot streams, $T_{\text{source}}$, and cold streams, $T_{\text{sink}}$, and a vector of heat sinks ($Q_{\text{sink}}$) and sources ($Q_{\text{source}}$). A cold temperature matrix includes sink streams supply ($T_{\text{in}}$) and target temperatures ($T_{\text{out}}$). The hot temperature matrix includes source streams supply ($T_{\text{j,in}}$) and target temperatures ($T_{\text{j,out}}$).

Cold streams

$$C = \begin{bmatrix} C_j \\ \vdots \\ C_{n_{\text{sink}}} \end{bmatrix}$$

$$T_{\text{sink}} = \begin{bmatrix} T_{j,\text{in}} & T_{j,\text{out}} \\ \vdots & \vdots \\ T_{n_{\text{sink}},\text{in}} & T_{n_{\text{sink}},\text{out}} \end{bmatrix}; Q_{\text{sink}} = \begin{bmatrix} Q_j \\ \vdots \\ Q_{n_{\text{sink}}} \end{bmatrix}$$ (6.1)

Hot streams

$$H = \begin{bmatrix} H_i \\ \vdots \\ H_{n_{\text{source}}} \end{bmatrix}$$
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\[ T_{\text{source}} = \begin{bmatrix} T_{i,\text{in}} & T_{i,\text{out}} \\ \vdots & \vdots \\ T_{n_{\text{source}},\text{in}} & T_{n_{\text{source}},\text{out}} \end{bmatrix}; Q_{\text{source}} = \begin{bmatrix} Q_i \\ \vdots \\ Q_{n_{\text{source}}} \end{bmatrix} \]

The total heat capacity \((CP)\), which is the product of mass flow rate and specific heat capacity \((mC_p)\), is evaluated by equation 6.2.

\[
CP = \frac{Q}{T_{\text{out}} - T_{\text{in}}} \tag{6.2}
\]

Where \(Q\) is the heating or cooling demand of the stream \(T_{\text{out}}\) and \(T_{\text{in}}\) are the outlet and inlet stream temperatures, respectively.

**Step 3:**

The next step is to generate temperature intervals based on the problem table algorithm (Linnhoff and Flower, 1978). A vector of temperature intervals is generated by arranging the inlet and outlet shifted temperatures of the source and sink streams in descending order.

**Step 4:**

In this step the process streams are partitioned based on the temperature intervals to set of partitioned source process streams \((H')\) and sink process streams, \(C'\). Process streams are partitioned and divided into several streams if the process stream exists in more than one interval. Dividing the process stream into a number of segments has some advantages. For instance, consider a source process stream that has a supply temperature above ambient temperature and a target temperature below ambient temperature. If this stream is partitioned into two segments—one segment above ambient temperature and the second segment below ambient temperature—the refrigeration load at sub-ambient temperature will be reduced, resulting in lower power consumption compared to a non-segmented stream. A cheaper utility, e.g., cooling water, can be used to provide the cooling requirement for the first segment.

The heat load \((Q^i)\) of segment \(k\) belonging to source \(i\) or sink \(j\) is calculated by the following relationship (Farrokhpanah, 2009)
\[ Q^k = CP\left(T_{k+1}^*-T_k^*\right) \] (6.3)

Where \( CP \) is the stream heat capacity, \( T_{k+1}^* \) and \( T_k^* \) are the shifted outlet and inlet temperatures of segment \( k \) belonging to the process stream \( j \) or \( i \). The shifted temperature for a hot stream \( i \) and a cold stream \( j \) is calculated from equations 6.4 and 6.5, respectively.

For a hot stream \( i \):

\[ T_i^* = T_i + \frac{\Delta T_{\text{min}}}{2} \] (6.4)

For a cold stream \( j \):

\[ T_j^* = T_j - \frac{\Delta T_{\text{min}}}{2} \] (6.5)

It should be emphasized that shifting temperature will guarantee an adequate driving force of \( \Delta T_{\text{min}} \) between the source and sink streams for feasible heat transfer within each interval (Smith, 2005).

**Step 5:**

Once the sets of partitioned source process streams \( H' \) and sink process streams \( C' \) are defined along with their supply and target temperatures and heat loads \( (Q^k_j \text{ and } Q^k_i) \), each source stream is allowed to exchange heat with any sink stream or utility streams. Utility is supplying residual heating and cooling after any heat integration.

A ‘match matrix’ \( M \), as shown in Figure 6.2, is generated, where the rows are source streams (partitioned process streams plus hot utility streams) and columns are sink streams, including both partitioned process streams and cold utility streams. For example, \( H^1_1 \) and \( H^2_1 \) are two segments of stream \( H_1 \). The matrix element \( M_{ij} \) is set to 1 if direct heat exchange is feasible, to -1 if heat pumping is required and to 0 if heat exchange is forbidden (Farrokhpanah, 2009). The application of a matrix approach provides a convenient framework for systematic representation of heat exchange between source stream \( i \) and cold stream \( j \). The representation of the matrix approach allows for series and parallel heat exchange as well as stream splitting options to be represented. For example, stream segment \( C^6_3 \) is split; the exchangers d and f in Figures 6.2(b) and 6.2(c) receive heat from streams \( H_2 \) and \( H_3 \).
respectively. Also, series heat exchange between the exchanger d and h can be achieved as shown in Figure 6.2(c).

\[
\begin{align*}
M_i^j &= \begin{cases}
1 & \text{if } T_{\text{in},i} - T_{\text{out},j} \geq \Delta T_{\text{min}} \\
1 & \text{and } T_{\text{out},i} - T_{\text{in},j} \geq \Delta T_{\text{min}}
\end{cases}
\end{align*}
\]

For process-to-process (or process-to-utility) indirect heat exchange, a heat pump system is required for rejecting heat from the source to the sink (Farrokhpanah, 2009). The elements of the matching matrix have a value of -1 if the hot and cold side supply and exit temperatures of a heat exchanger satisfy the following conditions:
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\[
M_{ij} = \begin{cases} 
1 & \text{if } \left( \frac{T_{\text{in},i} - T_{\text{out},j}}{\Delta T_{\text{in}}} \right) \leq 0 \\
-1 & \text{if } \left( \frac{T_{\text{out},i} - T_{\text{in},j}}{\Delta T_{\text{min}}} \right) \leq 0 
\end{cases}
\]

Other cells (match between hot and cold utility) might also have zero value \((M_{ij} = 0)\).

**Step 6:**

To find the optimum load between each source stream \(i\) and sink stream \(j\) in the ‘match matrix’, a ‘cost matrix’ needs to be estimated. The ‘cost matrix’ is generated according to the ‘match matrix’ determined in Step 5. The cost associated with each match in the matrix is calculated as follows

1. Direct heat exchange \((M_{ij} = 1)\)
   - Process-to-process heat exchange
     
     If a source and a sink directly exchange heat, the utility cost is zero.
   - Process-to-utility heat transfer
     
     If a source (or a sink) uses a utility to reach the target temperature, the unit cost will be the cost of the cold (or hot) utility:

\[
C_{ij} = C_{ij}^{\text{utility}} \quad (6.6)
\]

2. Indirect heat exchange \((M_{ij} = -1)\)
   
   This part relates to calculating the cost if a refrigeration system is used. In the refrigeration cycle, the absorbed heat from source \(i\) can be rejected to external sink utility \(j\) (cooling water) or to a process heat sink \(j\).
   
   - For process-to-process heat exchange
     
     If a source process stream and a sink process stream indirectly exchange heat through a heat pump system, as shown in Figure 6.3, the cost associated with this match is
$C_{ij} = \left( \frac{1}{COP_{act,ij}} \right) C_{ij}^{power}$

(6.7)

Where $C_{ij}^{power}$ is the cost of power per unit of heat absorbed and $COP_{act}$ is an actual coefficient of performance. The coefficient of performance is defined as the ratio of the cooling duty (evaporator heat load) to the shaft work required (Elliott and Lira, 1999).

Figure 6.3: Simple schematic of heat transfer between the process stream and refrigeration system

To estimate the actual coefficient of performance, a refrigeration model is developed which will be discussed in Section 6.5. In the refrigeration model, the actual coefficient of performance is a function of the temperatures of a sink stream $j$ and a source stream $i$. For the set of temperatures of sources and sinks, a coefficient of the performance matrix is formed, in which a refrigeration coefficient of performance $COP_{ij}$ is determined. The refrigeration cycle absorbs heat from a source stream $i$ with a supply temperature of $T_{in, source}$ and target temperature of $T_{out, source}$ and rejects heat to a sink $j$ with the target temperature of $T_{out, sink}$. For heat transfer between the process and the refrigeration system to be feasible, the process source stream must be colder than the process sink stream. Also, the evaporating and condensing temperatures of the refrigeration system must satisfy the following conditions:

$$
T_{evap,i} \leq T_{out,i} - \Delta T_{min}
$$

$$
T_{cond,j} \geq T_{out,j} + \Delta T_{min}
$$

(6.8)
Where $\Delta T_{\text{min}}$ is the minimum approach temperature, $T_{\text{evap},i}$ is the evaporating temperature (K) of a source stream $i$, $T_{\text{cond},j}$ is the condensing temperature (K) of a sink stream $j$, $T_{\text{out},i}$ is the target supply temperature of a source stream $i$ and $T_{\text{out},j}$ is the target supply temperature of a sink stream $j$.

- Process-to-utility heat transfer

In the event that a heat pump rejects heat absorbed from a source process stream $i$ to a sink stream $j$, which is a utility stream, the cooling cost needs to be added to the power cost.

$$C_{ij} = \left( \frac{1}{\text{COP}_{\text{act},ij}} \right) C_{ij}^{\text{power}} + \left( 1 + \frac{1}{\text{COP}_{\text{act},ij}} \right) C_{ij}^{\text{utility\text{-}CW}}$$  \hspace{1cm} (6.9)

Where $C_{ij}^{\text{utility\text{-}CW}}$ is the cost per unit of heat rejected (load of a cold utility); in this work, the utility is taken to be cooling water.

To apply a heat pump, the source temperature should be below ambient, and the sink temperature should be higher than that of the source. If the temperature of a source stream $i$ is above ambient, and heat pump is assigned to do the match forbidden between source $i$ and sink $j$, a hypothetical heat pump will be used (Haselden, 1971). To evaluate the cost that prevents such a match, very low cycle efficiency ($\eta$) is used in equation 6.10. This will eliminate the match through the optimisation process because the cost is very high.

$$C_{ij} = \left( \frac{1}{\eta \text{COP}_{\text{ideal},ij}} \right) C_{ij}^{\text{power}} + \left( 1 + \frac{1}{\eta \text{COP}_{\text{ideal},ij}} \right) C_{ij}^{\text{utility\text{-}CW}}$$  \hspace{1cm} (6.10)

Where $\text{COP}_{\text{ideal},ij} = \frac{T_{\text{out},i}}{T_{\text{out},j} - T_{\text{out},i}}$  \hspace{1cm} (6.11)

3. Utility-to-utility heat transfer ($M_{ij} = 0$)

A source utility stream $j$ and a sink utility stream $i$ cannot be matched, as such a match is prohibited. Thus, the cost associated with this match should be zero. It should be noted that, the heat exchanged load between a source utility stream $j$ and a sink utility stream $i$ is also zero.
Step 7:

Since utilities are costly, utility loads need to be minimised. Minimisation can be accomplished by optimisation. The Simplex method is the method used for solving linear programming problems (Lewin et al., 1998). The Simplex method is very efficient at solving linear systems, is easy to use and does not need a derivative function. It is also appropriate for complex problems involving many variables. However, all the variables must be nonnegative.

The objective function is to minimise the utility cost:

\[
\min f(Q) = \sum_{i=1}^{n_{\text{source}}} \sum_{j=1}^{n_{\text{sink}}} Q_{ij} C_{ij}
\]

(6.12)

Where \( Q \) is the load on the match between source \( i \) (in stream set \( H' \)) and sink \( j \) (in stream set \( C' \)), \( C_{ij} \) is the utility cost of the match between source \( i \) and sink \( j \) per unit of heat load, \( n_{\text{source}} \) is the number of source streams and \( n_{\text{sink}} \) is the number of sink streams.

Equality Constraints

In this formulation, energy balances are the equality constraints of the objective function. These equality constraints specify that heat transferred to (or from) each cold (or hot) stream must be equal to the sum of the heat exchanged with the cold (or hot) streams.

- Energy balance constraint for each partitioned source stream \( k \) belonging to source stream \( i \) is determined by:

\[
Q^k_i = \sum_{j=1}^{n_{\text{sink}}} Q_{ij}
\]

(6.13)

- Energy balance constraint for each partitioned sink stream \( k \) belonging to sink process stream \( j \) is estimated by:

\[
Q^k_j = \sum_{i=1}^{n_{\text{source}}} Q_{ij}
\]

(6.14)
Where $Q^k_i$ is the duty of the partitioned source stream $k$ which belongs to source process stream $i$, $Q^k_j$ is the duty of the partitioned sink stream $k$ belonging to sink process stream $j$.

- At sub-ambient temperatures, a heat pump is used as a cooler to cool a source stream. If a heat pump is employed, the following relation is used:

$$Q^k_j = \sum_{i=1}^{n_{source}} Q_{ij} \left( 1 + \frac{1}{COP_{act,ij}} \right)$$

(6.15)

This constraint (equation 6.15) was not reported by Farrokhpanah (2009).

**Upper and Lower Bounds**

Energy balances are also employed for determining the upper and lower bounds for the variable $Q_{ij}$ (heat load exchanged between source stream $i$ and sink stream $j$).

- Upper bound for process-to-process heat exchange

For the source process stream $i$ and the sink process stream $j$, the upper bound for the match is the minimum load of $i$ and $j$:

$$Q_{ij} \leq \min (Q^k_i, Q^k_j)$$

(6.16)

- Upper bound for process-to-utility heat transfer

For the process source stream $i$ matched against utility $j$ the upper bound in this case is equal to the process source load:

$$Q_{ij} \leq Q^k_j$$

(6.17)

For the process sink stream $j$ matched against utility $i$ the upper bound is equal to the process sink load:

$$Q_{ij} \leq Q^k_i$$

(6.18)

- Upper bound utility-to-utility heat transfer

No heat exchange is allowed between a hot utility $i$ and a cold utility $j$ therefore the upper bound for the match between the cold and hot utility is 0:
\[ Q_{ij} \leq 0 \]  
(6.19)

The lower bound for each match is also 0.

\[ Q_{ij} \geq 0 \]  
(6.20)

These bounds form constraints in the optimisation problem.

**Step 8:**

In order to determine the total power demand of a separation process, both the power consumption in the refrigeration system and the recompression power demand for the permeate stream, as well as any work required to compress the distillate product to the final conditions, have to be considered.

The power requirement of the heat pump is determined by

\[ W_{HP,ij} = \frac{Q_{ij}^{source}}{COP_{act,ij}} \]  
(6.21)

For a centrifugal compressor, shaft work can be calculated from a simplified formula derived from energy balance around the compressor (Smith, 2005):

\[ W_{comp} = \frac{P_{in}}{\zeta_p} \left( \frac{\Omega}{\Omega - 1} \right) r \frac{\Omega}{\Omega - 1} \]  
(6.22)

\[ \Omega = \frac{\Psi \eta_p}{\Psi \eta_p - \Psi + 1} \]  
(6.23)

\[ \Psi = \frac{C_p}{C_p - R} \]  
(6.24)

\[ r = \frac{P_{out}}{P_{in}} \]  
(6.25)

Where

\[ \zeta_p \]: is polytropic efficiency, i.e., ratio of polytropic power to actual power; in this work it is assumed to be 76%, as recommended by Turton et al. (2009)
\( \Omega \): Polytropic coefficient

\( P_{\text{in}}, P_{\text{out}} \): inlet and outlet pressures, bar; ‘inlet’ = in and ‘outlet’ = out

\( F_n \): inlet volumetric flow rate

\( \Psi \): inlet heat capacity ratio

\( C_P \): inlet stream heat capacity

\( r \): pressure ratio (outlet pressure divided by inlet pressure)

\( W_{\text{comp}} \): work required for each gas stream compression

Total process shaft work (\( W_{\text{total}} \)) consumption is thus:

\[
W_{\text{total}} = \sum_{1}^{n_{\text{c}}} W_{\text{comp,nc}} + \sum_{i=1}^{n_{\text{source}}} \sum_{j=1}^{n_{\text{sink}}} W_{\text{HP,ij}} \tag{6.26}
\]

Where \( n_{\text{c}} \) is the number of compressors in the flowsheet

In the heat integration algorithm, equation 6.26 can be used to evaluate the net power demand (heat loads are the only variable in the formulation). For variable pressures, the optimisation problem is no longer linear; therefore, a nonlinear optimisation algorithm is used to optimise the net power demand in Chapter 7.

In summary, in this work the approach developed by Farrokhpahan (2009) for heat integration is modified by developing a simple refrigeration model in Section 6.5. This model is used to calculate the COP of the refrigeration system. A new energy balance constraint for indirect heat exchange is introduced. A simplex algorithm to optimise the load on each ‘match’ between the sinks and the sources can be used. The algorithm applies a linear model which can be applied at above-ambient and sub-ambient conditions. Stream splitting and series heat exchange are allowed in the model, which facilitates a maximum heat recovery among the process streams but complicates the heat exchanger network design.

A major advantage of the algorithm is its ability to minimise the utility and power requirements even for a large number of streams within a very short time. A disadvantage of the heat integration approach is that a heat exchanger network design with a minimum number of heat exchangers cannot be guaranteed. This is because the intermediate temperatures of the heat exchangers in series are restricted to the temperature intervals, i.e., temperatures are limited to the inlet and outlet
temperatures of the existing process streams and utilities.

The implementation of the modified heat integration approach for matching heat sinks and sources through a refrigeration cycle and evaluating the vapour compression cycle performance is demonstrated in Section 6.3.1.

6.3.1 Illustrative example: Implementation of a heat integration approach for refrigeration integration with sub-ambient process streams

For systems working at sub-ambient temperatures, the power demand can be very high; the lower the source temperature, the larger the amount of energy consumed. However, there is a great chance to reduce of the energy consumption in these processes if process heat integration is considered. In this example, multiple process streams at sub-ambient temperature that require both heating and cooling are investigated. The objective is to calculate the minimum total shaft power consumption in the refrigeration system for two scenarios.

Scenario 1:

In the first scenario, utilities are used to satisfy the heat sinks and sources; the refrigeration pumps the extracted heat source to the external utility that is, cooling water. Heat sources are provided by external hot utilities such as steam. The specification of the process streams and utility data for this system are given in Tables 6.1 and 6.2, respectively. A uniform minimum temperature approach of 3°C, a 0.1°C drop in the source temperatures and a 0.1°C increase in the sink temperature of the isothermal streams are assumed for this example. The data given in Table 6.1 are taken from Wang (2004) for the optimum simple distillation sequence of gas mixture separation of an ethylene plant.

Table 6.1: Process hot and cold stream data (Wang, 2004)

<table>
<thead>
<tr>
<th>Streams</th>
<th>Isothermal Temperature, °C</th>
<th>Load, kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>-5</td>
<td>16530</td>
</tr>
<tr>
<td>H₂</td>
<td>-14</td>
<td>70280</td>
</tr>
<tr>
<td>H₃</td>
<td>-100</td>
<td>3310</td>
</tr>
<tr>
<td>C₁</td>
<td>86</td>
<td>21810</td>
</tr>
<tr>
<td>C₂</td>
<td>11.9</td>
<td>78890</td>
</tr>
<tr>
<td>C₃</td>
<td>-25</td>
<td>5220</td>
</tr>
</tbody>
</table>
Table 6.2: Utility data

<table>
<thead>
<tr>
<th>Supply</th>
<th>Target</th>
<th>Cost, £/kW.y</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Steam</td>
<td>150</td>
<td>149</td>
</tr>
<tr>
<td>Electric power</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The first step is to construct a vector of temperature intervals, in which shifted temperatures of sink and source are merged and then sorted in descending order, omitting temperatures common to both sink and source streams. The next step is to obtain a set of sink and source stream temperatures and their duties. The column matrix of $T_i \ (\degree \text{C})$ includes the inlet and outlet temperature of source streams. The column vector $Q_i \ (\text{kW})$ is their corresponding duties. The column matrix of $T_j$ includes the inlet and outlet temperature of sink streams. The column vector $Q_j$ in kW is their corresponding duties. It can be seen that the sources and sinks are not partitioned, as each stream only exists in one interval.

Sources:

$$T_j = \begin{bmatrix} -5 & -5.1 \\ -14 & -14.1 \\ -100 & -100.1 \end{bmatrix} \quad Q_i = \begin{bmatrix} 16530 \\ 70280 \\ 3310 \end{bmatrix}$$

Sinks:

$$T_j = \begin{bmatrix} 86 & 86.1 \\ 11.9 & 12 \\ -25 & -24.9 \end{bmatrix} \quad Q_j = \begin{bmatrix} 21810 \\ 78890 \\ 5220 \end{bmatrix}$$

After that the ‘matching matrix’ $M$ for the sets of source $i$ and sink $j$ temperatures is generated, as described in Section 6.3 step 5. The matching matrix for the example presented is:

$$M = \begin{bmatrix} C_1^1 & C_2^2 & C_3^3 & C_4^4 \\ H_1^1 & -1 & -1 & 1 & -1 \\ H_2^2 & -1 & -1 & 1 & -1 \\ H_3^3 & -1 & -1 & -1 & -1 \\ H_4^4 & 1 & 1 & 1 & 0 \end{bmatrix}$$

Where $C_4$ and $H_4$ are the cold and hot utility, respectively.
When refrigeration systems reject their heat to cooling water utilities, the total shaft work required for cooling the source streams is 40.38 MW. Individual shaft work on each match is determined by equation 6.21. The total operating cost matrix given below shows that the total utility costs for Scenario 1 is about 40 M£/y.

\[
\text{Q}^{\text{source}} (\text{kW}) = \begin{bmatrix}
H_1^1 & 0 & 0 & 0 & 16530 \\
H_2^1 & 0 & 0 & 0 & 70280 \\
H_3^1 & 0 & 0 & 0 & 3310 \\
H_4^1 & 21810 & 78890 & 5220 & 0
\end{bmatrix}
\]

\[
\text{Q}^{\text{sink}} (\text{kW}) = \begin{bmatrix}
H_1^1 & 0 & 0 & 0 & 21721 \\
H_2^1 & 0 & 0 & 0 & 98591 \\
H_3^1 & 0 & 0 & 0 & 10196 \\
H_4^1 & 21810 & 78890 & 5220 & 0
\end{bmatrix}
\]

Total operating cost (M£/y) =

\[
\begin{bmatrix}
H_1^1 & 0 & 0 & 0 & 3.925 \\
H_2^1 & 0 & 0 & 0 & 20.67 \\
H_3^1 & 0 & 0 & 0 & 4.521 \\
H_4^1 & 2.181 & 7.889 & 0.522 & 0
\end{bmatrix}
\]

**Scenario 2:**

In the second scenario, sink and source streams at sub-ambient temperatures are integrated via heat pumps. Heat rejected from a condenser is pumped to a sink stream and/or to an external utility. Linear optimisation is carried out to minimise the objective function (equation 6.12), which is subject to the constraints presented in equations 6.13 to 6.20. In order to cost the indirect match, the optimisation uses \(\text{COP}_{\text{act}}\) matrix. The detailed description of the developed methodology used to evaluate \(\text{COP}_{\text{act}}\) is illustrated in Section 6.4.

\[
\text{COP}_{\text{act}} = \begin{bmatrix}
H_1^1 & 3.185 \\
H_2^1 & 5.299 & 2.482 \\
H_3^1 & 0.645 & 1.035 \\
H_4^1 &
\end{bmatrix}
\]
The optimised results are the optimal load of each match, which are displayed in the heat sink and the heat source matrices and the shaft work need to provide the cooling requirement.

\[
Q_{\text{source}} \text{ (kW)} = \begin{bmatrix}
C_1^1 & C_2^2 & C_3^3 & C_4^4 \\
H_1^1 & 0 & 0 & 0 & 16530 \\
H_2^2 & 0 & 0 & 64961 & 5319 \\
H_3^3 & 0 & 655 & 2655 & 0 \\
H_4^4 & 21810 & 0 & 0 & 0
\end{bmatrix}
\]

\[
Q_{\text{sink}} \text{ (kW)} = \begin{bmatrix}
C_1^1 & C_2^2 & C_3^3 & C_4^4 \\
H_1^1 & 0 & 0 & 0 & 21721 \\
H_2^2 & 0 & 77220 & 0 & 7461 \\
H_3^3 & 0 & 1670 & 5220 & 0 \\
H_4^4 & 21810 & 0 & 0 & 0
\end{bmatrix}
\]

It should be pointed out that summing the elements in each column of \(Q_{\text{Sink}}\) yields the cooling duty of each sink stream, while summing the elements in each row of \(Q_{\text{Source}}\) gives the heating duty requirement for each source stream.

The total utility cost for Scenario 2 is about 20 M£/y. By applying heat integration between the process streams and refrigeration system, the total shaft power consumed in the refrigeration system is reduced to 23 MW, a 42% saving compared with Scenario 1. The above optimal results (Scenario 2) can be presented more clearly in the following layout

\[
\text{Total operating cost (M£/y)} = \begin{bmatrix}
C_1^1 & C_2^2 & C_3^3 & C_4^4 \\
H_1^1 & 0 & 0 & 0 & 3.925 \\
H_2^2 & 0 & 1.564 & 0 & 10.22 \\
H_3^3 & 0 & 0.672 & 1.736 & 0 \\
H_4^4 & 2.181 & 0 & 0 & 0
\end{bmatrix}
\]
Figure 6.4: The optimised hot and cold utilities load and electricity demand for the illustrative Example 6.3.1. Dotted lines represent refrigeration shaft power in kW. Solid lines represent the amount of energy absorbed in kW.

The boxes in Figure 6.4 represent the energy in the hot and cold process streams, cold and hot utilities and the shaft work requirement. The amount of energy transferred and the shaft work requirements are listed above the line in black and red, respectively. Figure 6.4 shows that the energy balances are satisfied, e.g., the duty of C3 (5220) is fully covered by indirect heat exchange with H3 (2655) and refrigeration power demand (2565). Generally, Figure 6.4 shows that all the heat in the hot streams and utilities are transferred to the cold streams and cold utilities. Heat is transferred from the source streams to cold streams and/or cold utility through a heat pump, in addition to the heat transferred directly between sink stream C1 and external hot utility H4, steam.

**Summary– Illustrative Example**

In this section an illustrative example is presented to illustrate the implementation of the modified heat integration approach for minimising the utility cost when heat integration is considered. The approach generates a COP matrix that is used to calculate the shaft work and the total operating cost matrices in a non-heat-integrated case.

It is clear from the results that the shaft work is reduced from 40 MW to 23 MW. This reduction in power consumption for the refrigeration system is due to integrating heat sources and heat sinks with the refrigeration cycles. The refrigeration system rejects some of its heat process load to process sink streams at a lower temperature level than cooling water instead of rejecting heat only to cooling water.
It has been shown that the modified approach for heat integration developed in this work can optimise the heat load and evaluate the refrigeration shaft work in the absence of a detailed refrigeration system design. The methods developed in this work can allow for optimising the power demand or the utility costs of hybrid separation system working at above or below sub-ambient temperatures.

### 6.4 Refrigeration cycle model

A refrigeration model is required to determine the impact of the distillation operating conditions on the energy requirements of the refrigeration system. A relatively complex refrigeration system is required. Rather than applying a complex model for the refrigeration system, a simplified model, which relates the actual performance of the refrigeration cycle to the ideal performance (i.e. the Carnot cycle), is proposed to be used in the modified heat recovery approach to predict the actual performance of the refrigeration cycle.

The actual coefficient of performance (COP) of the refrigeration system can be calculated from:

\[
COP_{act} = \frac{Q_{evap}}{W_{act}} \tag{6.27}
\]

An ideal coefficient of performance was defined by (Smith, 2005):

\[
COP_{ideal} = \frac{T_{evap}}{T_{cond} - T_{evap}} = \frac{Q_{evap}}{W_{ideal}} \tag{6.28}
\]

Where \(Q_{evap}\) is the heat absorbed (kW), \(W\) is the shaft work (kW), \(T_{evap}\) is the evaporating temperature (K) and \(T_{cond}\) is the condensing temperature (K).

The net power requirement predicted by equation 6.28 is always lower than that calculated by equation 6.27. In order to estimate the actual COP, equation 6.29 can be used with a coefficient of performance ratio, \(\eta\), typically equal to 0.6 (Smith, 2005).

\[
COP_{act} = \eta \frac{T_{evap}}{T_{cond} - T_{evap}} \tag{6.29}
\]

Section 6.4.3 examines the possibility of using the typical value for \(\eta\) (0.6) to calculate the actual performance and the power requirement of a refrigeration cycle.
Results from Section 6.4.3 are used to find a new correlation between $\text{COP}_{\text{act}}$ and $\text{COP}_{\text{ideal}}$. Section 6.5 explains the model development in detail, while Sections 6.4.1 and 6.4.2 outline the principles on which the model is based.

### 6.4.1 Refrigeration cycle configurations

#### 6.4.1.1 Simple cycles

Figure 6.5 illustrates a simple vapour compression refrigeration cycle. Process cooling, i.e., heat, is absorbed from a process stream provided through evaporation of a liquid refrigerant in an evaporator. The amount of heat transferred to the refrigerant in the evaporator is called the refrigeration load, $Q_{\text{evap}}$. The refrigerant at point 1 enters the evaporator as a mixture of vapour and liquid and leaves the evaporator as saturated vapour. At point 2, the refrigerant enters a compressor to be compressed. As the refrigerant is compressed, the pressure and temperature of the refrigerant increase from the evaporating pressure and evaporator temperature $T_{\text{evap}}$ to the condensing pressure and superheated temperature (point 3). After the compressor, the superheated vapour refrigerant at high pressure passes through the condenser where it is cooled and condensed to a saturated liquid $T_{\text{cond}}$ (point 4). During this process, the refrigerant rejects most of its energy to external heat sinks. Next, the refrigerant passes through the expansion valve causing the temperature and pressure to decrease from the condensing pressure to the evaporating pressure. On expansion, the liquid refrigerant is partially vaporised. The liquid passes through the evaporator and produces a cooling effect to provide the refrigeration. Figure 6.5(b) illustrates the cycle on a pressure-enthalpy diagram.

![Simple refrigeration system](image)

Figure 6.5: Simple refrigeration system (Smith, 2005). (a) Simple refrigeration cycle; (b) Pressure-enthalpy diagram for a simple refrigeration cycle.
Simple cycles are typically used to provide cooling for evaporating temperatures as low as \(-40^\circ\text{C}\) (Smith, 2005). For lower evaporating temperatures and for a large temperature range between evaporation and condensation, in which one refrigerant cannot cover the whole temperature range, more complex configuration, such as cascade cycles are employed.

### 6.4.1.2 Cascaded Cycles

Cascaded cycles are composed of two or more refrigeration cycles, where each cycle employs a different refrigerant. The lower temperature cycle and a higher temperature cycle, as shown in Figure 6.6, are connected to each other through a heat exchanger, which acts as an evaporator for the high temperature cycle and a condenser for the lower temperature cycle. In this arrangement, the lower temperature cycle absorbs heat at temperature \(T_{\text{evap}}\) and lifts it to the upper cycle at temperature \(T_{\text{cond1}}\). The upper cycle accepts the heat at temperature \(T_{\text{evap1}}\) and pumps it to an external heat sink at temperature \(T_{\text{cond}}\).

![Figure 6.6: Cascaded refrigeration system (Smith, 2005). (a) Cascaded refrigeration cycle; (b) Pressure-enthalpy diagram for a cascaded refrigeration cycle.](image)

### 6.4.2 Selection of refrigerant

Generally, there are several factors which need to be considered when selecting the refrigerant for compression refrigeration.
• The refrigerant should, as far as possible, be nontoxic, non-flammable, noncorrosive, chemically stable and have low ozone depletion and a low global warming potential (Smith, 2005).

• The refrigerant should have good thermal properties. It is desirable to have a refrigerant with a high heat of vaporization and low specific heat. The higher the heat of vaporization and the lower the specific heat, the lower the flow rate of refrigerant that is circulated and the lower the power consumption. In addition, the working refrigerant should have a temperature above its freezing point temperature and pressure above atmospheric pressure to avoid air ingress, i.e., the selected refrigerant should have a normal boiling temperature below the required evaporating temperature, (Smith, 2005).

• Ideally, the selection should be made from refrigerants that are already available in the plant. For example, in an ethylene plant, methane, propylene and ethylene are product streams produced in the plant. Therefore, these products could supply the refrigerant. Pure refrigerants can be used in certain operating temperature ranges, as shown in Figure 6.7 (Smith, 2005).

![Operating ranges of refrigerants](image)

Figure 6.7: Operating ranges of refrigerants (Smith, 2005)

### 6.4.3 Illustrative example for COP estimation

An example is shown to illustrate the influence of key design parameters on COP and power demand of the refrigeration cycle. In this example, three options are explored: 1) The influence of condensing temperature on cascaded cycle performance for various refrigerants, 2) The influence of condensing temperature on
propylene simple cycle performance, 3) The influence of evaporation temperature on cascaded cycle performance for various refrigerants.

In option 1, 523 kW cooling is required at a temperature of -77°C. The heat sink is assumed to be available at 40, 30, or 20°C. In option 2, 523 kW cooling is required at a temperature of -30°C. In option 3, the condensing temperature is assumed to be 40°C. In the cascaded refrigeration cycle, as shown in Figure 6.6, ethane/propylene, ethylene/propylene, ethylene/propane or ethane/propane can be used to provide cooling at or below -77°C. Ethylene or ethane refrigeration is used in the lower cycle and propylene or propane is used in the upper cycle.

Aspen HYSYS is applied for simulation of the cycles with physical properties calculated by choosing Soave-Redlich-Kwong as the fluid package. In the HYSYS simulation, the partition temperature ($T_{\text{part}}$) between the two cycles is optimised to minimise the total shaft work of the cascaded cycle. In the simulation of the refrigeration system, $T_{\text{part}}$ is allowed to change between the lowest temperature that the upper cycle can operate at, which is the normal boiling point for the refrigerant of the upper cycle, and the maximum temperature at which the lower cycle can reject the heat. At each partition temperature, the total shaft work of the cascaded cycles is calculated by adding the shaft work consumption of the upper cycle and of the lower cycle. Then, an optimal partition temperature is identified by optimising the shaft work as shown in Figure 6.8.

![Figure 6.8: Influence of partition temperature on the net power demand of a cascaded cycle (Ethylene/propylene). $T_{\text{evap}} = -82^\circ\text{C}$, $T_{\text{cond}} = 40^\circ\text{C}$ and $Q_{\text{evap}} = 523$ kW.](image-url)
In this work, it has been found that the optimum partition temperature is closest to the first evaporation level of the upper cycle rather than the last evaporation level of the lower cycle; a similar conclusion has been reported by Lee (2001).

Table 6.3 The effect of condensing temperature on COP

<table>
<thead>
<tr>
<th>Q_{evap}</th>
<th>T_{evap}</th>
<th>T_{cond}</th>
<th>T_{part}</th>
<th>HYSYS shaft work, kW</th>
<th>η</th>
<th>COP_{act}</th>
<th>COP_{ideal}</th>
<th>COP_{act} (η=0.6)</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>-82</td>
<td>40</td>
<td>-40</td>
<td>333</td>
<td>0.43</td>
<td>0.67</td>
<td>1.57</td>
<td>0.94</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>-44</td>
<td>306</td>
<td>0.46</td>
<td>0.79</td>
<td>1.71</td>
<td>1.03</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>-47</td>
<td>279</td>
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<td>0.92</td>
<td>1.88</td>
<td>1.13</td>
<td>23</td>
</tr>
</tbody>
</table>

Ethylene/propylene (Cascaded cycle)

<table>
<thead>
<tr>
<th>Q_{evap}</th>
<th>T_{evap}</th>
<th>T_{cond}</th>
<th>T_{part}</th>
<th>HYSYS shaft work, kW</th>
<th>η</th>
<th>COP_{act}</th>
<th>COP_{ideal}</th>
<th>COP_{act} (η=0.6)</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>-82</td>
<td>40</td>
<td>-32</td>
<td>333</td>
<td>0.45</td>
<td>0.70</td>
<td>1.57</td>
<td>0.94</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>-37</td>
<td>306</td>
<td>0.48</td>
<td>0.82</td>
<td>1.71</td>
<td>1.03</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>-42</td>
<td>279</td>
<td>0.5</td>
<td>0.95</td>
<td>1.88</td>
<td>1.13</td>
<td>19</td>
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Ethane/propylene (Cascaded cycle)

<table>
<thead>
<tr>
<th>Q_{evap}</th>
<th>T_{evap}</th>
<th>T_{cond}</th>
<th>T_{part}</th>
<th>HYSYS shaft work, kW</th>
<th>η</th>
<th>COP_{act}</th>
<th>COP_{ideal}</th>
<th>COP_{act} (η=0.6)</th>
<th>%Error</th>
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</thead>
<tbody>
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<td>523</td>
<td>-35</td>
<td>40</td>
<td>165</td>
<td>336</td>
<td>0.49</td>
<td>1.56</td>
<td>3.18</td>
<td>1.91</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>143</td>
<td>265</td>
<td>0.54</td>
<td>1.97</td>
<td>3.66</td>
<td>2.20</td>
<td>11</td>
</tr>
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<td></td>
<td></td>
<td>20</td>
<td>121</td>
<td>208</td>
<td>0.58</td>
<td>2.51</td>
<td>4.33</td>
<td>2.60</td>
<td>3</td>
</tr>
</tbody>
</table>

Propylene (Simple cycle)

In Table 6.3, equations 6.27 and 6.28 are used to calculate the actual (HYSYS) and the ideal \( COP \), respectively. \( \eta \) is calculated by dividing the actual coefficient performance on the ideal coefficient performance. The actual coefficient of performance of the refrigeration cycles is also compared with 0.6 of the ideal coefficient of performance.

\[
\% Error = \frac{COP_{act} (\text{HYSYS}) - COP_{act} (\eta = 0.6)}{COP_{act} (\text{HYSYS})} \times 100
\]

In Table 6.3, it may be seen that the coefficient of performance ratio (\( \eta \)) is below 0.6, which is the typical value for \( \eta \) (Smith, 2005). If a constant value of 0.6 is used in equation 6.28, the \( COP_{act} \) for most of the simulated cases will be over-estimated, and the compression shaft work will be under-estimated. However, for a simple propylene cycle, the typical coefficient of performance ratio gives a relatively good
prediction (within 9%) of the $COP_{act}$ when the evaporation temperature is as low as -35°C and the condensing temperature is below 40°C.

In addition to the choice of refrigerant, the influence of evaporation temperature on cascaded cycle performance is also examined. The cascaded refrigeration cycle with propylene (or propane) and ethylene (or ethane) is simulated for an ambient temperature of 40°C. The simulation results of the cascaded cycles are listed in Table 6.4.

Table 6.4: The influence of evaporation temperature on COP of cascaded cycle

<table>
<thead>
<tr>
<th>$Q_{evap}$, kW</th>
<th>$T_{evap}$, °C</th>
<th>$T_{cond}$, °C</th>
<th>$T_{part}$, °C</th>
<th>Ideal shaft work, kW</th>
<th>HYSYS shaft work, kW</th>
<th>$\eta$</th>
<th>$COP_{act}$</th>
<th>$COP_{ideal}$</th>
<th>$COP_{act}$ ($\eta=0.6$)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane/propylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>523</td>
<td>-82</td>
<td>40</td>
<td>-32</td>
<td>333</td>
<td>770</td>
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<td>0.68</td>
<td>1.57</td>
<td>0.94</td>
<td>39</td>
</tr>
<tr>
<td>527</td>
<td>-79</td>
<td>40</td>
<td>-31</td>
<td>324</td>
<td>743</td>
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<td>0.71</td>
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</tr>
<tr>
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<td>-28</td>
<td>311</td>
<td>70</td>
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<td>0.78</td>
<td>1.76</td>
<td>1.06</td>
<td>35</td>
</tr>
<tr>
<td>564</td>
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<td>-25</td>
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<td>627</td>
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<td>0.9</td>
<td>1.95</td>
<td>1.17</td>
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<td>2.3</td>
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<td>Ethylene/propylene</td>
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<td>1.38</td>
<td>33</td>
</tr>
<tr>
<td>Ethylene/propane</td>
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<td></td>
<td></td>
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<tr>
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<tr>
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<td>2.3</td>
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<tr>
<td>Ethane/propane</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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<td>-30</td>
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<td>0.67</td>
<td>1.57</td>
<td>0.94</td>
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<tr>
<td>527</td>
<td>-79</td>
<td>40</td>
<td>-29</td>
<td>324</td>
<td>725</td>
<td>0.44</td>
<td>0.71</td>
<td>1.63</td>
<td>0.98</td>
<td>38</td>
</tr>
<tr>
<td>547</td>
<td>-73</td>
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<td>-27</td>
<td>311</td>
<td>701</td>
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<td>0.78</td>
<td>1.76</td>
<td>1.06</td>
<td>35</td>
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<tr>
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<td>1.95</td>
<td>1.17</td>
<td>33</td>
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<td>590</td>
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<td>40</td>
<td>-20</td>
<td>257</td>
<td>536</td>
<td>0.48</td>
<td>1.1</td>
<td>2.3</td>
<td>1.38</td>
<td>25</td>
</tr>
</tbody>
</table>
Table 6.4 presents refrigeration system performance results for various cascaded cycles. It may be seen that the COP ratio ($\eta$) is below 0.6 in these cases. Table 6.4 shows that in the lower cycle it is better to use ethane than ethylene, while in the upper cycle it is better in terms of energy efficiency to use propylene than propane. These findings are in agreement with those of Smith (2005), which stated that ethane requires less shaft power than ethylene in the cascaded cycle. Although ethane/propylene provides higher $COP_{act}$ than ethylene/propylene, ethylene/propylene will be the refrigerant chosen here. Ethylene/propylene cascaded refrigeration is preferred in this work because it is readily available in the ethylene plant. Additionally, ethylene has a lower normal boiling point (-104°C) than ethane (-88°C), which facilitates its implementation at a very low process source temperature (e.g., $T_{\text{evap}} < -40^\circ$C).

In summary, the illustrative example demonstrates that using a single value for the efficiency factor $\eta$ is not the correct way to evaluate the refrigeration system performance. Results in Tables 6.3 and 6.4 show that the error is significantly large if the ‘typical’ ratio of 0.6 is used to predict the actual COP. Therefore, a new shortcut approximation of $COP_{act}$ is needed.

This section also demonstrates the influence of important design variables (e.g., evaporating and condensing temperatures, refrigeration configuration and refrigerants) on the power consumption of the refrigeration cycles. These design variables are used in Section 6.5 to establish a shortcut model to quickly predict the performance of refrigeration cycles for a range of refrigerants and refrigeration cycle arrangements.

### 6.5 Refrigeration model development

The aim of this section is to develop a shortcut model for evaluating refrigeration cycle performance. Figure 6.9 illustrates the steps that are used to develop a refrigeration model. The results of a rigorous simulation (HYSYS) of a range of cycles are used to develop a shortcut model for the refrigeration cycle COP in terms of $T_{\text{evap}}$ and $T_{\text{cond}}$. Model parameters are regressed by fitting the model to the simulation results.
6.5.1 Rigorous simulation of the refrigeration system

The first step in building the refrigeration model is to set specifications for rigorous simulation using the HYSYS simulation package. Inputs to the simulator include: evaporation temperature, $T_{\text{evap}}$, cooling duty, $Q_{\text{evap}}$, and condensing temperature, $T_{\text{cond}}$. The refrigeration cycle is simulated for a specified refrigerant and refrigeration configuration. In the refrigeration cycle, the refrigerant flow rate does not need to be specified because the refrigerant flow rate depends on $Q_{\text{evap}}$.

Rigorous simulations of refrigeration cycles are carried out with the following assumptions:

1. Steady state.
2. The Soave-Redlich-Kwong (SRK) is used to calculate thermodynamic and physical properties.
3. Centrifugal compressor.
4. 75% adiabatic efficiency.
5. The valves are adiabatic.
7. The outlet state of the condenser is saturated liquid and that of the evaporator is saturated vapour.
8. In a cascaded system, the temperature difference between the condensing temperature of the lower cycle and the evaporating temperature of upper cycle is $5^\circ$C.

9. The temperature difference between the process source stream temperature and the evaporating temperature is $5^\circ$C.

10. For the condenser, different options are evaluated using cooling water, seawater or process stream.

The outputs of the refrigeration system simulation in HYSYS include the compressor power demand and the refrigerant condenser duty.

To generate a set of output data, the simulations are repeated for an appropriate range of operating conditions. The input and output data will be used in Section 6.5.2 to find relationships between them.

6.5.2 Analysis of refrigeration data

This section describes the methodology used to analyse the input data and output data of the simple and cascaded refrigeration cycles simulated in Section 6.5.1. The steps in the analysis can be summarized as follows: 1) Specify independent and dependent variables. 2) Estimate relationships among variables. 3) Assess the difference between the actual (HYSYS) and the predicted (model).

Step 1: After the simulation, the set of input data ($T_{\text{cond}}$, $T_{\text{evap}}$ and $Q_{\text{evap}}$) and the set of output data ($W_{\text{act}}$) are collected and exported to a Microsoft excel spreadsheet. Then, $COP_{\text{act}}$ (dependent variable) and $COP_{\text{ideal}}$ (independent variable) are determined using equations 6.27 and 6.28 respectively.

Step 2: An initial examination prior to modelling is carried out by plotting $COP_{\text{ideal}}$ against $COP_{\text{act}}$. These plots demonstrate a linear relationship between $COP_{\text{act}}$ and $COP_{\text{ideal}}$. Therefore, a linear relationship between $COP_{\text{act}}$ and $COP_{\text{ideal}}$, of the form is proposed. The proposed linear model that expresses $COP_{\text{act}}$ as function of $COP_{\text{ideal}}$ is shown in equation 6.30.

\[
COP_{\text{act}} = \omega COP_{\text{ideal}} + \beta
\]  

(6.30)
Where $\omega$ and $\beta$ are parameters of the model, $COP_{\text{ideal}}$ is defined in equation 6.28, and $COP_{\text{act,i}}$ is defined in equation 6.27.

The model parameters are obtained by regression. Regression attempts to fit this mathematical model to the simulation results by minimising the sum of squared errors, SSE, between the value of $COP_{\text{act}}$, determined by HYSYS and the approximate value $COP_{\text{act}}$ predicted by the linear model.

Figure 6.10 shows the linear relationship between $COP_{\text{ideal}}$ and $COP_{\text{act}}$ for a cascaded refrigeration system. Ethylene refrigeration is used in the lower cycle and propylene is used in the upper cycle. The comparison between the simulated results and the computed values of $COP_{\text{act}}$ yields a coefficient of determination, $R^2$ of 99.5% for the cascaded cycle.

\[ Y = 0.596x - 0.213 \]
\[ R^2 = 0.995 \]

Figure 6.10: A linear model for a cascaded cycle using ethylene/propylene as refrigerant.

Table 6.5 presents linear models of $COP_{\text{ideal}}$ versus $COP_{\text{act}}$ for cascaded and simple configurations. These linear models can be applied within a different range of evaporating and condensing temperatures, which makes it possible to overcome the limitations imposed by using a value of 0.6 for $\eta$ in equation 6.29. If there is an overlap in the refrigeration temperature working range, the biggest value of $COP_{\text{act}}$ (calculated from equations 6.31, 6.32 and 6.33) that gives the minimum shaft work will be chosen. For example, if the temperature of the heat sink is -10°C and the temperature of the heat source is -81°C, a simple refrigeration cycle using ethylene may be used for this temperature range; or, alternatively, the cascaded refrigeration cycle using ethylene/propylene can be used. The actual coefficient of performance of
the refrigeration cycle using ethylene is 1.2 and that using of ethylene/propylene is 1.4. In this case, the highest \( \text{COP}_{\text{act}} \) will be selected, which is 1.4.

Table 6.5: Model coefficients and the coefficients of determination of regressed refrigeration models \( (\text{COP}_{\text{act}} = \omega \text{COP}_{\text{ideal}} + \beta) \)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Refrigerants</th>
<th>Working range, °C</th>
<th>( \omega )</th>
<th>( \beta )</th>
<th>( R^2 )</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cascade cycle</td>
<td>Ethylene/propylene</td>
<td>(-104 \leq T_{\text{evap}} \leq -9)</td>
<td>0.596</td>
<td>-0.213</td>
<td>0.995</td>
<td>(6.31)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-47 \leq T_{\text{cond}} \leq 46)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simple cycle</td>
<td>Propylene</td>
<td>(-47 \leq T_{\text{evap}} \leq T_{\text{amb}})</td>
<td>0.758</td>
<td>-0.747</td>
<td>0.999</td>
<td>(6.32)</td>
</tr>
<tr>
<td></td>
<td>Ethylene</td>
<td>(-104 \leq T_{\text{evap}} \leq -9)</td>
<td>0.741</td>
<td>-0.810</td>
<td>0.993</td>
<td>(6.33)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( T_{\text{evap}} &lt; T_{\text{cond}} \leq -9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Step 3: To illustrate the predictive accuracy of the linear model, a confidence level—a relative measure of error—is computed by dividing the difference between the \( \text{COP}_{\text{act}} \) (HYSYS) and the \( \text{COP}_{\text{act}} \) (model) by the \( \text{COP}_{\text{act}} \) (HYSYS). For 85% of the sample, the error was less than or equal to 5%, which is acceptable for the preliminary design of heat-integrated hybrid separation processes. Further statistical tests are used in the next section to validate the linear models.

6.5.3 Model validation

The adequacy of the model developed compared with HYSYS simulation is demonstrated by a parity plot and a residuals plot. For example, for the cascaded cycle, as shown in Figure 6.11 (a), the model matches the simulation results nearly perfectly. When the model results are plotted versus the simulation results, the predicted values lie on a line with a slope close to one and an intercept very close to zero. Also, as shown in Figure 6.11 (b) there is no systematic variation in the difference between the simulation results and the results predicted by the model is found.

Overall, the model coefficient, parity plot and residual plot all indicate that the linear model offers a good representation of the simulated data. The potential benefit
of the linear model is that it is easy to implement in a synthesis framework for evaluating refrigeration power demand. Further, the refrigeration model is computationally efficient for process design and optimization.

Figure 6.11: (a) Parity and (b) Residuals plots of the model for ethylene/propylene cascaded cycle.

6.5.4 Summary: Refrigeration model development

To sum up, linear refrigeration models, which are based on rigorous simulation, are presented here. These models can predict the shaft work without the need for refrigeration design and they are only a function of condensing and evaporating temperatures. These models can be applied over a wide temperature range between which the specific source and sink operate (see Table 6.5) and, therefore, can accommodate diverse separation processes effectively. The advantage use of the refrigeration models developed here in the heat integration approach is illustrated in Section 6.6

6.6 Case study: Distillation column and sequential hybrid membrane-distillation separation system

This is a case study by Motelica et al. (2012) on the separation of an ethylene-ethane mixture (Figure 6.12). To reduce the energy consumption of the conventional column, Motelica et al. integrated a membrane pre-separation stage, as shown in Figure 6.13. The membrane module has a selectivity of 50, stage cut of 0.5, ethane permeance of $1.6 \times 10^{-9}$ mol m$^{-2}$ Pa$^{-1}$ s$^{-1}$, ethylene permeance of $8 \times 10^{-8}$ mol m$^{-2}$ Pa$^{-1}$ s$^{-1}$ and retentate to permeate pressure ratio of 4. Feed data and product specifications of the separation process and utility costs are given in Tables 6.6 and 6.7 respectively.
For the simulation of the separation process, Motelica et al. (2012) used Aspen Plus. An SRK fluid package was used to calculate the physical and thermodynamic properties.

Motelica et al. (2012) did not consider heat integration between the separation process, the permeate cooler and the refrigeration system, but considered heat
integration between the column and the refrigeration system, as illustrated in Figure 6.13. This case study aims to illustrate the effectiveness and capabilities of the developed refrigeration model for predicting the shaft work requirement without performing a detailed refrigeration system design. A second aim is to illustrate the potential benefits of heat-integrated hybrid schemes.

Unfortunately, there is data missing from the work of Motelica et al. (2012). No information is provided on the feed molar flow rate, annual operating hours, the permeate product purity and the permeate cooler inlet and outlet temperatures, compressor efficiency, the evaporator and cooler duties (HC1, HC2, HEX1 and HEX2), the compression duty of the refrigeration cycle (Comp1 and Comp2), minimum approach temperature or cooling water supply temperature. To recalculate the author’s results, the following assumptions are made:

i) Annual operating hours is 8000 h. For the given distillate flow rate of 460 kt/y, feed and product purities, the calculated column feed flow rate is 2386 kmol/h.

ii) A minimum approach temperature is assumed to be 5°C and a cooling water supply temperature is set at 30°C.

iii) The retentate temperature is assumed to be equal to the membrane feed temperature (-18°C).

iv) The permeate temperature is determined from energy balance around the membrane.

v) Centrifugal compressor polytropic efficiency is 71%.

The heat integration algorithm introduced in Section 6.3 will be used to minimise total operating costs of the separation processes. The cross-flow membrane model presented in Section 3.3.2 will be used to predict the membrane performance. For the column design, HYSYS is used.

### 6.6.1 Distillation (Base Case)

First, the stand-alone distillation column is considered. The distillation column presented by Motelica et al. (2012) has 98 theoretical sieve trays and operates at a constant pressure of 20 bar. Figure 6.12 shows an indirect heat pump which is used to shift heat from the condenser to the reboiler for the base case, as introduced by
Motelica et al. Integrating the condenser and the reboiler of the column through a vapour compression refrigeration cycle may be advantageous: such integration can result in lower shaft power consumption, compared to the power required by providing utility (refrigeration cycle) for the condenser.

In this case, the column duties and feed stage location are calculated using HYSYS, and compared with Motelica et al. (2012) as shown in Table 6.8. It is clear from the results in Table 6.8 that the proposed assumptions are valid. In this work, optimising the feed stage location reduces the condenser duty by 17% compared with the Motelica et al. base case. To calculate the total operating costs and the minimum shaft work requirement, stream data presented in Table 6.9 are used.

Table 6.8: Operating conditions of the base case

<table>
<thead>
<tr>
<th></th>
<th>Motelica et al. (2012)</th>
<th>This work</th>
<th>Re-simulated</th>
<th>Optimised</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflux ratio</td>
<td>4.23</td>
<td>4.23</td>
<td>3.36</td>
<td></td>
</tr>
<tr>
<td>Condenser duty, MW</td>
<td>27.3</td>
<td>27.3</td>
<td>22.6</td>
<td></td>
</tr>
<tr>
<td>Reboiler duty, MW</td>
<td>20.9</td>
<td>20.9</td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td>Feed stage location</td>
<td>81</td>
<td>78</td>
<td>68</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.9: Process hot and cold stream data for base case

<table>
<thead>
<tr>
<th>Streams</th>
<th>Target temperature, °C</th>
<th>Load, MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condenser</td>
<td>-29.2</td>
<td>27.3</td>
</tr>
<tr>
<td>Reboiler</td>
<td>-7.8</td>
<td>20.9</td>
</tr>
<tr>
<td>Distillate product</td>
<td>-40.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The results in Table 6.10 show that the total power demand predicted by the proposed refrigeration model is in good agreement with that predicted by Motelica et al. (2012). These results indicate that the new models can predict $COP_{act}$ adequately. It may be concluded that the simplified models are valid; therefore, there is no need to conduct a detailed simulation of the refrigeration cycle or deal with a complicated mathematical refrigeration model.
### 6.6.2 Hybrid membrane-distillation

The case in the literature considers sequential hybrid separation as an alternative to distillation. The hybrid membrane-distillation configuration shown in Figure 6.13 is proposed as an alternative design by Motelica et al. (2012) to increase energy efficiency and reduce operational costs of the base case (distillation alone).

Similar to the base case, the sequential hybrid case is validated, and the simulation results are presented in Table 6.11. The table also shows the retentate and permeate stage locations and total operating cost results, compared with Motelica et al. (2012). The results of the hybrid membrane-distillation case shown in the second column of Table 6.11 are close with those presented by Motelica et al.

#### Table 6.10: Model results vs. Motelica et al. (2012) for base case design

<table>
<thead>
<tr>
<th>Power demand, MW</th>
<th>Aspen Plus simulation (Motelica et al., 2012)</th>
<th>This work (Re-simulated)</th>
<th>%Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refrigeration for distillation condenser</td>
<td>11.7</td>
<td>11.9</td>
<td>2</td>
</tr>
<tr>
<td>Refrigeration for distillate storage</td>
<td>0.3</td>
<td>0.32</td>
<td>7</td>
</tr>
<tr>
<td><strong>Total power demand, MW</strong></td>
<td>12.0</td>
<td>12.2</td>
<td>2</td>
</tr>
<tr>
<td><strong>Operating costs, €/t ethylene</strong></td>
<td>16.0</td>
<td>16.5</td>
<td>3</td>
</tr>
</tbody>
</table>

#### Table 6.11: Comparison of operating conditions of fully heat-integrated design (this work) with heat-pumped column design (Motelica et al., 2012) for the hybrid separation process

<table>
<thead>
<tr>
<th></th>
<th>Motelica et al. (2012)</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re-simulated</td>
<td>Optimised</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>3.41</td>
<td>3.41</td>
</tr>
<tr>
<td>Condenser duty, MW</td>
<td>22.3</td>
<td>22.9</td>
</tr>
<tr>
<td>Reboiler duty, MW</td>
<td>16.8</td>
<td>16.7</td>
</tr>
<tr>
<td>Permeate feed stage location</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>Retentate feed stage location</td>
<td>84</td>
<td>81</td>
</tr>
<tr>
<td>Compressor power demand, MW</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Total shaft work, MW</td>
<td>12.1</td>
<td>12.6</td>
</tr>
<tr>
<td>Total operating costs, €/t ethylene</td>
<td>16.2</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Table 6.12: Process hot and cold stream data for sequential hybrid case (this work)

<table>
<thead>
<tr>
<th>Streams</th>
<th>Supply temperature, °C</th>
<th>Target temperature, °C</th>
<th>Load, MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condenser (H₁)</td>
<td>-29.22</td>
<td>-29.23</td>
<td>15.16</td>
</tr>
<tr>
<td>Reboiler (C₁)</td>
<td>-7.76</td>
<td>-7.75</td>
<td>8.95</td>
</tr>
<tr>
<td>Permeate cooler (H₂)</td>
<td>64.59</td>
<td>-29.20</td>
<td>1.61</td>
</tr>
<tr>
<td>Distillate product (H₃)</td>
<td>-39.24</td>
<td>-40.00</td>
<td>0.57</td>
</tr>
</tbody>
</table>

The result of using the hybrid system is a significant decrease in reflux ratio (20%) and column condenser duty over the base case (the conventional separation process), with an 18% reduction in cooling duty in the condenser. In turn, the compression duty of the refrigeration system is also reduced. In contrast to Motelica et al. (2012), the hybrid scheme can provide savings when the retentate and permeate locations are optimised. Process stream data for the optimised case are shown in Table 6.12. Figure 6.14 shows the match matrix, the optimised heat load matrix and the heat exchanger network design for the data from Table 6.12. Figure 6.14(d) shows the fully heat-integrated design.

Figure 6.14: Results of the fully heat-integrated hybrid process. (a) Matching matrix, (b) optimised heat load matrices, (c) heat exchanger network design and (d) fully heat-integrated hybrid design
In the fully heat-integrated hybrid membrane-distillation configuration, the permeate stream rejects a part of its load to the reboiler (process-to-process heat recovery) and the rest to external utility. In this case, process heat recovery is 1.158 MW. There is also indirect process-to-process heat exchange between the distillate cooler and the reboiler. The refrigerate condenser rejects a part of its load to the reboiler, but the reboiler of the column is not large enough to accept the whole condenser cooling duty; therefore, the rest of the refrigerate condenser cooling duty is satisfied by an external utility, i.e., cooling water. The shaft power requirement of the fully heat-integrated case design is 8.9 MW.

In conclusion, the modified heat recovery approach shows the potential benefits that can be achieved by integrating heat within the process and the associated refrigeration system. Compared with Motelica et al. (2012), a significant energy saving is obtained by optimising the feed stage location. Results show that the sequential hybrid scheme can reduce the condenser duty by about 33%. The total operating cost of the heat-integrated hybrid scheme is reduced by 19%, compared to the heat-integrated column (base case).

This example illustrate that net power demand is the indicator that must be used for the evaluation the separation process, rather than distillation condenser duty. This is due to the trade-off between permeate recompression shaft work and refrigeration power requirements. This trade-off will be explained in the sensitivity analysis in Chapter 7.

Furthermore, the case study considered in this section shows that the new methodology may be applied in a retrofit context for energy reduction. The total operating costs can be reduced if the process streams are fully heat-integrated. Significant energy savings can also be achieved if operating conditions are optimised, something which will be shown in Chapter 7.

6.7 Conclusions

This chapter introduces a modified heat integration approach that can be used for evaluating the net power demand of heat-integrated hybrid separation system. A new refrigeration model is used within the approach to predict the coefficient of performance of the refrigeration cycle and to cost the indirect heat exchange. The
assumption of using a constant coefficient of performance ratio of 0.6 or performing a refrigeration system design is no longer needed.

The main features of the proposed approach are:

- Heat exchange between process streams represented using a match matrix which allows direct and indirect heat exchange as well as series heat exchange and splitting streams to be accounted for. Therefore, utility costs can be minimised. In this work, a coefficient of performance matrix is generated and used to optimise the utility cost of the sub-ambient separation system. It is shown in this chapter that the heat integration approach is applicable for hybrid separation processes. The example presented shows that, for a sequential hybrid scheme, substantial energy savings can be achieved by optimising the feed stage locations, compared to the published results of Motelica et al. (2012). Potential energy saving can also be achieved because the heat recovery model considers heat integration opportunities between the reboiler and the permeate cooler, and between the column condenser and the reboiler. In the heat integration approach, the focus is only on minimising either operating costs or total power demand. Operating costs dominate sub-ambient separation process economics. Although in the preliminary screening and evaluation design stage of separation system it may be acceptable to consider the influence of energy (King, 1980), in future work, it is suggested to carry out an optimisation to determine the total annual cost so the trade-off between capital and energy costs is captured. Another drawback of the heat recovery approach is that intermediate temperatures of the heat exchangers in series are restricted to the temperature intervals; therefore, a minimum number of heat exchangers cannot be guaranteed.

- The refrigeration system is heat-integrated with the separation process. To evaluate indirect heat exchange between process streams (via a refrigeration cycle), simple models are developed. The refrigeration models predict the coefficient of performance of the refrigeration system. The refrigeration models are linear and only a function of condensing and evaporation
temperatures; therefore, they are easy to implement for process synthesis and optimisation. In addition, these models are sufficiently flexible and reliable for evaluation of refrigeration requirements during separation process design. In Section 6.6, the refrigeration models proved to be effective in their use in the heat recovery model for predicting the shaft power demand. The results in Table 6.10 reveal a small error (7%) between the new model predictions and the published results of Motelica et al. (2012), which is acceptable for screening and evaluation of separation processes.

- The modified heat recovery approach is faster (refrigeration system design and optimisation are not needed) and easier to use for evaluating and determining the energy performance of the separation system than the unmodified methodology by Farrokhpanah (2009).

- The limitations of the refrigeration models are that only pure refrigerants are considered for simple and cascaded cycles. Also, temperature difference between the process source stream temperature and the evaporating temperature is assumed to be fixed. The minimum approach temperature is a design parameter that can be optimised to reduce the power demand of the cycle and improve the regression parameters of the model. In addition, the refrigeration model cannot be applied for process streams require cooling below -104 °C. However, the heat recovery approach is still applicable if a shortcut refrigeration model or a detailed refrigeration design model is provided to calculate the refrigeration power demand of the refrigeration cycle.

- The LP model is used to minimise operating costs and estimate the power demand for a fixed configuration and given specifications of separation process, reducing the complexity of the modelling approach. This approach facilitates fast screening and evaluation of hybrid configurations, as will be shown in Chapter 7.
Chapter 7 Optimization

7.1 Introduction

In previous chapters, methodologies for modelling and design of different hybrid configurations were discussed. In addition, a heat recovery model was introduced. The method for simulation of various hybrid schemes is presented in Chapter 5 and the adapted model for considering heat integration opportunities is proposed in Chapter 6. At this stage, an optimisation framework is needed in order to employ these simulation approaches for optimising the separation flowsheet. Furthermore, an optimization solution method is required that is capable of finding, reliably and accurately, a global minimum for a given separation task without getting trapped in local optima.

Several methods have been developed for synthesis and design of optimal hybrid separation processes (Kookos, 2003; Barakat et al., 2008; Caballero et al., 2009; Naidu and Malik, 2011). These methods are based on superstructure representation, from which the optimum solution is selected. Different types of approaches for solving the optimisation problem (i.e. to determine the optimal solution) may be used. Among these are the relaxation method for solving MINLP, and the heuristic search method such as Genetic Algorithm (GA) while another solution approach, the pattern search method, has been reported to show promising results for solving derivative-free optimisation problems.

Although various mathematical optimisation techniques have been proposed, the idea of an approach incorporating process heat integration concepts into the optimisation framework of a hybrid system has not yet been addressed. In this chapter, an optimisation strategy to simultaneously optimise various configurations
and design degrees of freedom (e.g. permeate pressure and stage cut) is presented. Process heat recovery significantly affects process performance; therefore, the question of process heat integration is addressed here and a number of case studies are presented to demonstrate the performance of the proposed approach.

### 7.2 Sensitivity study

The first step in the optimisation is to define the optimisation variables, the objective of optimisation and the constraints which limit or bound the values of the optimisation variables. Then, based on the nature of the variables, the type and the difficulty or stiffness of the objective function, an optimisation solution method is decided.

The important optimisation variables which this investigation analyses are permeate pressure, stage cut, membrane feed purity and the molar flow rate of the side stream. The impact of design variables on the performance of the process is assessed through sensitivity analysis. The most important decision variables and the upper bound values are identified based on the sensitivity results. If the variable has a significant influence on the objective function, it should be considered during optimisation. In this work, the focus will be on minimisation of the net power demand required by the process for refrigeration and permeate recompression.

The parallel hybrid scheme, as shown in Figure 5.16 (c), will be selected to conduct parametric optimization for the $C_2$ splitter as it gives the best performance compared to other hybrid configurations. The parallel hybrid system consists of two units: the membrane and its auxiliary units, and the distillation column. The auxiliary units include the compressor, one heater and two coolers. The heater is used to keep the membrane temperature at a certain point (i.e., above or at vapour saturation temperature) while the coolers are used to cool the recompressed permeate stream to the desired temperature.

#### Illustrative Example

The column is fed with a saturated vapour, containing 54 mol% $C_2H_4$ and 46 mol% $C_2H_6$, at the rate of 100 kmol/h. The product purity specifications for the ethylene and ethane are 99.9 and 99.5 mol% respectively. A fixed $R/R_{min}$ ratio of
1.05 is used for the column design, as recommended by Ray et al. (1998) and Douglas (1988) for sub-ambient distillation.

In this example, the influence of various design parameters on the separation performance is presented as follows: Section 7.2.1 discusses the influence of column pressure on the conventional column performance when heat integration is considered. The operating pressure range examined is 1.01-20 bar.

Section 7.2.2 illustrates the influence of stage cut and permeate pressure on the parallel hybrid performance. Representation values are taken as 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 for stage cut and 1.01, 4, 6 and 8 bar for permeate pressure. The membrane feed pressure is set at 20 bar and temperature at 23ºC (experimental condition). The ethylene permeance is $6 \times 10^{-6} \frac{m^3(STP)}{m^2 s bar}$ (extrapolated data of Pinnau and Toy, 2001). Cross-flow model, which is discussed in Section 3.2, is used to predict the purity of ethylene in the permeate, the required membrane area and the fractional ethylene recovery for a membrane module.

The membrane feed flow rate (the side draw rate) and its purity are very important parameters that also influence the column condenser duty and, consequently, the power consumption. The influence of the side draw rate on the separation performance is discussed in Section 7.2.3. Finally, Section 7.2.4 discusses the influence of the thermal state of the recycled permeate stream on the energy performance of the separation system.

### 7.2.1 Effect of column pressure

In the hybrid process, the pressure ratio across the membrane is indirectly related to column pressure. Figure 7.1 illustrates the influence of column pressure on distillation performance. It can be seen in Figures 7.1(a) and 7.1(b) that a lower condenser duty and fewer stages are required when the column operating pressure is reduced. This is due to the influence of pressure on the relative volatility of ethylene and ethane. Moreover, the pressure influences the condenser and reboiler temperature, as shown in Figure 7.1(c).

Heat integration between the separation process and refrigeration system can introduce benefits to the sub-ambient process. Process shaft power demand is
reduced when heat is rejected to a heat sink within the process rather than to an external cooling utility; consequently operating costs are lower.

Figure 7.1: Influence of column pressure on (a) column duty, (b) number of stages and reflux ratio, (c) thermal properties of the column and (d) shaft power demand.

Figure 7.1(d) shows the influence of column pressure on the shaft power consumption of the conventional column before and after including heat integration in the analysis of the C\textsubscript{2} splitter. The shaft power is evaluated as described in Chapter 6 (Section 6.3). It can be seen that the net power demand is reduced as the column pressure increases. This reduction is produced as a result of reducing the condenser temperature. Since the minimum shaft power consumption occurs at 20 bar (the upper bound), this column pressure will be fixed in the sensitivity analysis of the hybrid cases. Note that, the top limit to the pressure explored here is set to 20 bar because this an industrial operating conditions (Zimmermann and Walzl, 2012). Increasing the column pressure beyond 20 bar might lead to high capital costs.

### 7.2.2 Effect of membrane feed ratio (stage cut), permeate pressure and membrane feed purity

Figures 7.2 and 7.3 show the influence of stage cuts, permeate pressures and feed mole fractions of ethylene on membrane unit performance of the parallel hybrid system, for a fixed membrane feed molar flow rate of 50 kmol/h.
As expected, the membrane can produce either a highly pure permeate or a high permeate flow rate (high stage cut) but not both. Note that the permeate purity hardly changes at low stage cut values, as shown in Figure 7.2 (a); therefore, a high membrane selectivity will probably not have a substantial impact on the membrane performance if the stage cut is less than 0.2.

However, the permeate pressure affects the permeate purity and ethylene recovery significantly. For a permeate pressure of 8 bar, a stage cut of 0.7 and a feed purity of 54 mol% of ethylene, the membrane area is about 48,000 $m^2$ for permeate containing over 70 mol% ethylene, as shown in Figure 7.2 (b). Figure 7.3(a) shows that the permeate purity increases as the ethylene feed purity is increased and the ethylene recovery changes slightly at a stage cut above 0.6, for a feed 50 kmol/h and permeate pressure 1.01 bar.
Figure 7.4: Influence of stage cut, permeate pressure (PP) and permeate purity on (a) condenser duty, (b) recompression duty, (c) net shaft power consumption of non-heat-integrated and (d) heat-integrated parallel hybrid scheme at membrane feed flow rate of 50 kmol/h

Figure 7.4 show the influence of stage cuts, permeate pressures and permeate purities on the column performance of the parallel hybrid system. It can be seen that there is a trade-off between the condenser duty and permeate recompression duty, as shown in Figures 7.4(a) and 7.4(b). As the stage cut increases, the permeate flow and the compression power demand increase but the purity of the fast permeating component and the condenser duty decrease. In addition, as the permeate pressure increases, the condenser duty increases but the compression power demand is reduced. Total shaft power captures the trade-off between refrigeration compression and recompression requirement. As Figures 7.4(c) and 7.4(d) demonstrate, increasing the permeate pressure above 8 bar does not significantly reduce the net power demand of the parallel hybrid separation process. Therefore, the upper bound permeate pressure will be set at 8 bar.
Significant energy savings in the separation process can be achieved from altering process conditions and also from performing heat integration. Figure 7.4(d) shows that the total shaft power requirements are reduced by 35% compared with the non-heat-integrated hybrid at permeate pressure of 4 bar and stage cut of 0.6. This result illustrates the importance of considering heat integration between the separation process and refrigeration system in the sensitivity analysis.

### 7.2.3 Effect of membrane feed flow rate and feed composition

The maximum flow rate of the side draw is subject to the column’s thermodynamic constraints (Ayotte-Sauve et al., 2010). The amount of side draw that is fed to the column is varied between 20% and 80% of the vapour flow rate in the column in the published work of Ayotte-Sauve et al., 2010 and Caballero et al., 2009 respectively. In the present work, the maximum molar flow rate fed to the membrane unit is assumed to be 35% of the vapour flow rate inside the rectifying section of the base case. Therefore, the upper bound of the molar flow rate is set at 110 kmol/h. Note that this assumption will be justified in Section 7.2.3.

Figure 7.5(a) shows that the feed purity, which provides the minimum condenser duty at 1.01 bar permeate pressure, is equal to the column feed purity. On the other hand, the minimum power demand is observed at 50 mol% of ethylene, as shown in Figures 7.5(c) and 7.5(d). Therefore, the membrane feed mole fraction of the ethylene is expected to be close to the column feed purity as reported by Pettersen et al. (1996).
Chapter 7  Optimization

Figure 7.5: Influence of membrane feed purity and stage cut on (a) condenser duty, (b) recompression duty, (c) net power of non-heat-integrated and (d) net power of heat-integrated parallel hybrid scheme for permeate pressure of 1.01 bar and membrane feed flow rate of 50 kmol/h

The effect of the side draw flow rate on the column performance for a fixed permeate stream pressure of 1.01 bar is illustrated in Figure 7.6. The condenser duty decreases with both an increase in the membrane feed flow rate and the decrease in the membrane feed purity of ethylene. Also, the permeate flow rate increases as the membrane feed flow rate increases, resulting in increased associated compression and cooling duties. Figures 7.6(a) and 7.6(b) illustrate the simulation results for a permeate pressure of 1.01 bar and a side draw composition of 0.54 mole fraction of ethylene for a different side draw rates. The minimum shaft power demand is observed at a membrane feed flow rate of 50 kmol/h for non-heat-integrated parallel hybrid cases (see Fig. 7.6(c)).
Figure 7.6: Influence of membrane feed flow rate (FM, in kmol/h) and stage cut on (a) condenser duty, (b) recompression duty (c) net power of non-heat-integrated and (d) net power of heat-integrated parallel hybrid scheme for permeate pressure of 1.01 bar and membrane feed purity 54 mol% of ethylene.

Figure 7.7: Influence of stage cut, membrane flow rate and permeate purity total operating cost of heat-integrated parallel hybrid scheme for permeate pressure of 4 bar and membrane feed purity of 0.54

Figures 7.7 and 7.8 demonstrate the influence of membrane feed flow rate, permeate pressure and stage cut on the total operating costs (TOC) of the heat-integrated separation process. In Figure 7.7, when the permeate pressure is set at 4
bar, the minimum TOC is observed at a stage cut between 0.4 and 0.6 for all side draw flow rates. In Figure 7.8, it can be seen clearly that TOC reduces as the permeate pressure increases from 1 to 4 bar. It can be seen in Figure 7.8 that the lowest TOC is obtained at 0.8 permeate purity of ethylene and permeate pressure of 8 bar.

![Figure 7.8: Influence of stage cut, permeate pressure (PP) and permeate purity total operating cost of heat-integrated parallel hybrid scheme for membrane flow rate of 50 kmol/h and membrane feed purity of 0.54](image)

It can be concluded from the above analysis that withdrawing a side draw stream below the feed stage results in a low permeate flow rate, which possibly reduces the compression duties for recompression and refrigeration. However, there are trade-offs between purity and recovery, membrane area and membrane feed purity, and the permeate pressure and the permeate mole fraction of the fast permutating component. A lower membrane area and a high driving force for permeation is observed at low permeate pressure but the recompression duty is high. So, there is an optimum stage location and specifications (flow rate and purity) for the side draw that needs to be identified precisely.

The simulation results reveal that there can be little expectation of reducing power consumption by increasing the membrane feed flow rate above 80 kmol/h, as shown in Figure 7.9. Therefore, it reasonable to assume the upper bound flow rate to be 110 kmol/h is adequate for carrying out the optimisation for the given column and membrane specifications.
Figure 7.9: Influence of side draw flow rate and permeate pressure ($P_p$) on total shaft power demand of non-heat-integrated parallel hybrid scheme for 0.6 stage cut and membrane feed purity 54 mol% of ethylene.

Figure 7.10 shows that the parallel hybrid configuration systems will provide savings when the membrane pressure ratio ($P_P/P_F$) is above 0.05 (i.e., the permeate stream pressure is higher than 1.01 bar). The saving in maximum operating costs is achieved when the membrane pressure ratio is 0.25 for non-heat-integrated cases. Savings decrease for pressure ratios above 0.25 because of the high compression costs.

Figure 7.10: Influence of pressure ratio (permeate pressure/feed pressure) on parallel hybrid performance. Membrane feed purity 54 mol% of ethylene, membrane feed pressure 20 bar.
7.2.4 Effect of thermal state of the recycled permeate stream

The thermal state of the column feed stream is an important design variable and its influence on economic performance should not be ignored at the conceptual design stage. The operating and capital cost would be affected by the addition of a heat exchanger unit to cool the superheated permeate stream. From an energy perspective, it is best to avoid introducing a superheated feed to the column because it will not participate in the separation process until it becomes saturated (King, 1980). Saturating the feed in the column increases the condenser load and, consequently, the associated refrigeration power requirement.

In previous research (e.g., Caballero et al., 2006; Ploegmakers et al., 2013), optimising the feed quality was not considered. In this work, however, the impact of the thermal state of the recycled permeate stream on the hybrid separation process performance is considered where $q$, the feed thermal condition is taken as a continuous variable with the upper bound being the saturated liquid and lower bound is superheated vapour (the stream from the compressor is usually superheated).

Figure 7.11 shows the influence of permeate state on the process cost where the TOC is reduced when the thermal state of permeate stream is saturated vapour.

![Figure 7.11: The influence of recycled permeate thermal condition, $q$, on shaft power and total operating costs of the parallel hybrid separation flowsheet for permeate pressure of 8 bar, membrane feed purity 54 mol% of ethylene and stage cut of 0.61.](image-url)
7.2.5 Summary of sensitivity analyses

In Section 7.2, several design variables are explored by means of sensitivity analysis. The sensitivity analysis identified that stage cut, permeate pressure, side draw flow rate and its purity variables all impact significantly on process performance. The analysis is used to identify upper and lower bounds for each variable where the objective was to minimise net power demand. The influence of the design variables is analysed for a parallel hybrid separation flowsheet of a C₂ splitter. The results reveal that there is a trade-off between permeate recompression and refrigeration compression as an increase in permeate pressure increases the condenser duty but reduces the recompression power demand of the permeate stream. Refrigeration shaft work dominates shaft work requirements unless the stage cut is very high. However, the selected objective function has been able to capture the trade-off between refrigeration power demand and recompression duty requirement, as shown in Figures 7.5 and 7.6.

Also, the examination of the parallel hybrid flowsheet shows that the composition of the feed to the membrane that gives the lowest condenser duty is approximately the same as the process feed composition. This result is similar to the findings of Pettersen et al. (1996). On the other hand, the minimum net power is achieved for membrane feeds that contain less ethylene than the feed. This result implies that the membrane should be placed across or on the feed stage, where the column is most pinched.

The influence of design variables on the performance of the parallel hybrid separation processes is explored. Note that interactions between variables have not been considered fully. An appropriate optimisation technique needs to be proposed in order to determine the optimal values of these variables and the optimal membrane position that minimises the total compression work or total operating cost.

7.3 Optimization framework

Figure 7.12 presents the optimisation approach for the design of heat-integrated hybrid membrane-distillation processes. It can be seen that the optimisation
algorithm and the aspect to be optimised are completely decoupled. The optimisation variables subject to specified bounds are inputs to the simulation. The process simulation, which is the main component of the optimisation framework, includes models for all separation units, heat recovery and refrigeration. These models are described in Sections 3.2, 4.3, 6.3 and 6.5, respectively.

The separation models in Chapters 3 and 4 are used to design and simulate the membrane and column and then calculate the heating and cooling demands of the process streams. The temperature and loads of process streams requiring heating and cooling are sent to the heat recovery model. The purpose of the heat recovery model is to identify opportunities to use hot streams to heat cold streams and to allow heat that needs to be rejected from the refrigeration cycle to be used for process heating. The heat recovery reduces utility requirements, and consequently energy costs. In this work, the optimisation aims to minimise the utility costs (i.e., total operating costs) of the separation system.

The objective value is input to the optimisation algorithm. The results of optimisation will be the optimum operating conditions and the optimal configuration (i.e. feed and side draw stage for a fixed structure).

![Flowchart of optimisation process](image)

**Figure 7.12: Summary of optimisation approach**

### 7.3.1 Implementation of optimisation framework

The first step in the optimisation is to set the initial operating conditions (starting point) and the problem specifications, which include feed and product inputs.
(compositions, pressures, temperatures, and flow rates), column conditions (column pressure drop), membrane conditions (pressures, temperatures, and permeability data) and utility cost data (unit costs of utilities). For the distillation column, the column pressure and the ratio of $R/R_{\text{min}}$ or the number of stages are also given as the input. For a side draw column, the side draw flow rate and its composition are continuous variables for the optimisation. For the membrane module, it is necessary to know the membrane type and its properties (permeability), the flow pattern, and the critical operating conditions (i.e., temperature and pressure). Then, the membrane feed temperature, permeate pressure and permeate-to-feed ratio are design variables.

The optimisation conditions (upper and lower bounds) should also be set prior to starting the optimisation. The bounds of the optimisation variables are selected according to the results of the sensitivity study. The optimisation parameters are selected on the basis of the analysis of optimisation parameters discussed in Section 7.4. Optimisation constraints are also specified, as will be described in Section 7.3.3.

The entire process simulation and optimisation is performed by MATLAB. In this work, MATLAB has been connected with HYSYS through an active client-server application for the calculation of thermodynamic and physical properties, as discussed in Section 5.3.2.

Several previous studies applied the SRK equation of state for the ethylene-ethane separation (e.g., Ploegmakers et al., 2013; Caballero et al., 2009; Al Rabiah, 2001) because of its accurate prediction for a relatively ideal mixture. Therefore, it is also used in this work to calculate physical and thermodynamic properties as well as phase equilibrium behaviour.

Once the design variables are selected and the fixed parameters are specified, the process design can be commenced. As discussed in Chapter 5, for all hybrid schemes, the design starts with the membrane unit. The membrane is simulated first for the given membrane specifications in order to estimate membrane area and predict product purities and flow rates. A compressor and cooler might be required to recompress and cool the permeate stream to the desired pressure and temperature before it enters the column; therefore, if necessary, these units are the next to be designed.
Once the properties (i.e., temperatures, flow rates, mole fractions) of the retentate and permeate streams are fully determined, the column can be designed (taking the membrane feed and products as column products and feeds, as applicable) and heat recovery opportunities can be identified, as described in Chapter 6 (Section 6.3). At this point, the algorithm calculates the heating and cooling demands of the process streams as well as the compressor power demand for refrigeration.

To explore heat integration opportunities between the separation process and refrigeration system, the stream ‘supply’ and ‘target’ temperatures and their heat loads are sent to the heat recovery model, where an LP optimiser is employed to optimise the loads in each match as explained in Section 6.3. The heat recovery model identifies opportunities to reuse heat rejected by hot streams to heat cold streams, including using heat rejected from a refrigeration cycle for process heating, in turn reducing the compression power demand of the refrigeration system.

Thereafter, an economic evaluation of the design in terms of energy is determined for a given objective as discussed in Section 7.3.2. When the objective function value is calculated, its result returned to the optimiser which selects a new set of inputs to the process models. Iteration continues until a termination criterion is met; the optimum operating conditions and location of feeds and side draws in the column are thus determined.

### 7.3.2 Objective function

In this work, the optimisation aims to minimise the total operating cost (TOC) or the total shaft power cost (TSPC) of the separation system. The optimisation problem is formulated as a NLP.

The total operating cost or total shaft power cost (the objective function) depends on the problem boundaries. In particular, the operating cost depends on whether heat recovery is taken into account. Equations 7.1 and 7.2 present the case in which heat integration is not taken into account, where the compression power demand is given by equation 7.3, and equations 7.4 and 7.5 address the case in which heat recovery is considered:
Chapter 7  Optimization

\[ TOC = W C_{\text{elec}} + \sum_{i=1}^{n_{\text{source}-m}} \frac{Q_{\text{evap}_i}}{COP_i} (C_{\text{elec}} + C_{\text{cw}}) \]

\[ + \sum_{j=1}^{n_{\text{sink}}} Q_{H_j} C_{\text{steam}_k} + C_{\text{cw}} \left( \sum_{i=1}^{n_{\text{source}-m}} Q_{\text{evap}_i} + \sum_{i=1}^{m} Q_{C_i} \right) \]  \hspace{1cm} (7.1)

\[ TSPC = \left( W + \sum_{i=1}^{n_{\text{source}-m}} \frac{Q_{\text{evap}_i}}{COP_i} \right) C_{\text{elec}} \]  \hspace{1cm} (7.2)

\[ W = W_p + W_R + W_F \]  \hspace{1cm} (7.3)

\[ TOC = W C_{\text{elec}} + \sum_{i=1}^{n_{\text{source}}} \sum_{j=1}^{n_{\text{sink}}} Q_{ij} C_{ij} \]  \hspace{1cm} (7.4)

\[ TSPC = \left( W + \sum_{i=1}^{n_{\text{source}}} \sum_{j=1}^{n_{\text{sink}}} W_{H_{ij}} \right) C_{\text{elec}} \]  \hspace{1cm} (7.5)

Where

\( W \): Compressor shaft power (P: permeate; R: retentate; F: feed; HP: heat pump)

\( Q \): Duty (evap: evaporator; H: heater; C: cooler; ij: heat duty exchanged between source \( i \) and sink \( j \))

\( COP \): Coefficient of performance of refrigeration system

\( C \): Units of cost per unit of energy (elec: electricity; cw: cooling water; \( C_{\text{steam}_k} \): steam cost in the range of temperature \( k \))

\( C_{ij} \): Is the utility cost of the match between source \( i \) and sink \( j \) per unit of heat load (see Section 6.3)

\( m \): Number of streams cooled using ambient cooling utility (cooling water or air)

\( n_{\text{source}} \): Is the number of source streams (i.e. streams requiring cooling)

\( n_{\text{sink}} \): Is the number of sink streams (i.e. streams requiring heating)

\( i \): Counter for cold streams

\( j \): Counter for hot streams
7.3.3 Constraints

To have a feasible membrane design, the retentate and permeate pressures must be constrained (see equations 7.6 to 7.9). The retentate stream pressure, $P_R$, is set equal to the feed stream pressure, $P_M$, because of a very slight drop in pressure on the feed-side of the membrane. Moreover, this assumption is assumed to avoid recompressing the retentate stream to the column pressure, in turn reducing the operating cost

$$P_R = P_M \quad (7.6)$$

In this work, for the purposes of simplification, the column pressure drop is assumed to be negligible. Although, in reality, a pressure profile is developed along the column as a result of liquid loading in the stages and the pressure drop due to friction. The pressure profile in a column may affect the separation efficiency and the reboiler and condenser duties due to the dependence of the relative volatilities and the enthalpy of vaporisation on the pressure. However, negligible pressure drop assumption is acceptable and does not affect the design results significantly. The simulation results from HYSYS considering a pressure drop of 1 bar over the column show that the condenser and reboiler duty vary by less than 1%.

The membrane feed pressure is set equal to the column pressure, $P_{COL}$. As the membrane feed pressure decreases, the permeate purity of the fast permeating component increases, consequently, the membrane area decreases (low capital). However, retentate recompression may be an issue if the retentate stream needs to be recompressed to the column feed (higher capital and operating costs). Note that less energy is required for recompressing a low-temperature permeate stream compared to a high-temperature (high pressure) stream. Future work could consider optimising the feed-side operating pressure.

$$P_M = P_{COL} \quad (7.7)$$

The permeate stream pressure is set to be less than the membrane feed pressure to achieve the pressure gradient and obtain a separation. For optimisation of operational variables, the upper and lower bounds for the variables $P_P$ and $\theta$ (stage cut) can be specified as follows: A lower bound for stage cut can be set to a small value such as
0.01 and the upper bound to one. A lower bound of permeate pressure can be set to the atmospheric pressure and the upper bound value can be set to 0.4 of the membrane feed pressure; according to the sensitivity results in Section 7.2.3.

\[ P_P < P_M \]  \hspace{1cm} (7.8)

\[ P_P^L \leq P_P \leq P_P^U \]  \hspace{1cm} (7.9)

\[ \theta^L \leq \theta \leq \theta^U \]  \hspace{1cm} (7.10)

Another constraint on the membrane feed flow rate and its feed purity is specified in the case of optimization for parallel hybrid configurations shown in Figure 5.2.

\[ F_M^L \leq F_M \leq F_M^U \]  \hspace{1cm} (7.11)

\[ y_{FM,i}^L \leq y_{FM,i} \leq y_{FM}^U \]  \hspace{1cm} (7.12)

### 7.3.4 Summary of optimization framework

In this section a new systematic design and optimisation framework is introduced. The optimisation problem has been formulated as nonlinear. The optimum operating conditions of hybrid membrane-distillation system can be evaluated in terms of minimum utility demand. Variables that are considered for optimisation are: stage cut; permeate pressure; molar flow rate and mole fraction of the membrane feed stream (in the case of parallel hybrid processes).

The key challenge in the developed framework is the selection of the optimisation method. The optimisation method has to be computationally efficient and effective in finding the optimal solution for a given separation problem. Therefore, two optimisation methods—namely, pattern search and Simulated Annealing—are explored in Section 7.4.

### 7.4 Optimization algorithm

MATLAB’s Global Optimization Toolbox provides a diverse set of algorithms that can be used to solve a variety of optimization problems. For example, it includes pattern search, genetic algorithm and a Simulated Annealing algorithm.
In the optimization toolbox, all the methods include options to define bound, equation constraints, termination criterion, etc. These options, as well as an initial starting point, need to be specified before the optimiser can be run for a given objective function. The tool displays the results of the optimization in the Run solver and view results pane. In the present work, the methods from the global optimisation toolbox are used to minimise the objective function (total operating cost).

This section is organised as follows: Section 7.4.1 introduces the pattern search method. In Section 7.4.2, Simulated Annealing (SA) is described. An illustrative example is introduced in Section 7.4.3 to evaluate and compare the performance of Simulated Annealing with Pattern Search (PS). Finally Section 7.4.4 summarises the performance of the optimisation methods.

### 7.4.1 Pattern search method

The pattern search method belongs to a class of optimization methods known as direct search methods. Section 2.4.2.3 presents the advantages of direct search methods. Due to these advantages, direct search methods generally (pattern search specifically) may be applied for optimisation of design of hybrid separation flowsheets.

#### 7.4.1.1 Algorithm description

The pattern search method starts with an initial guess point and performs a sequence of iterations in an effort to improve upon this initial guess (The Math Works Inc., 2013). At each iteration, two steps are performed; a ‘search’ step and a ‘poll’ step. In the search step, the algorithm determines pattern vectors that produce a set of mesh points. Figure 7.13 shows the mesh points and pattern vectors.

![Pattern search mesh points](image)

Figure 7.13: Pattern search mesh points in the first iteration for a mesh size of 0.5, where \( v_i \) is the pattern vector and \( x_0 \) is the initial guess point.
The set of vector, \( v_i \), is defined by the number of variables and the positive basis set. Two positive basis sets are usually used in pattern search; the maximal basis (2N), with double the number of variable vectors, and the minimal basis (NP1), with the number of vector equal to the number of variables plus one (The Math Works Inc., 2013). For example, if there are two variables in the optimisation problem, the maximal basis consists of the following pattern vectors:

\[
\begin{align*}
v_1 &= [1 \ 0] \\
v_2 &= [0 \ 1] \\
v_3 &= [-1 \ 0] \\
v_4 &= [0 \ -1] \\
\end{align*}
\]  
(7.13)

The minimal basis consists of the following pattern vectors:

\[
\begin{align*}
v_1 &= [1 \ 0] \\
v_2 &= [0 \ 1] \\
v_3 &= [-1 \ -1] \\
\end{align*}
\]  
(7.14)

Then, the algorithm forms the mesh through multiplying the pattern vectors (equation 7.13) by a scalar value of ‘mesh size’ and then adding the resulting vectors to the present point. For instance, suppose that the present point is \( x_0 \) and the positive basis is set to maximum for the generalized pattern search (GPS) algorithm, the following mesh will be obtained for a given mesh size of 0.5.

\[
\begin{align*}
x_0 + 0.5v_1 \\
x_0 + 0.5v_2 \\
x_0 + 0.5v_3 \\
x_0 + 0.5v_4 \\
\end{align*}
\]  
(7.15)

Subsequently the algorithm polls the mesh point by computing the objective function at the mesh points. The algorithm compares the value of the objective for all five points. The point with the smallest objective function becomes the new point in the next iteration. The ‘poll’ is called successful if the algorithm finds an objective function value that is smaller than the objective function value of \( x_0 \).

After a successful ‘poll’, the algorithm steps to the second iteration and multiplies the current mesh size by an expansion factor of 2 (i.e., the next iteration searches a larger space, starting from the (new) present point). Figure 7.14 illustrates the formation of the mesh point in the second iteration. If the algorithm fails to find a point that improves the objective function, i.e., none of the mesh points have a smaller objective function value than the value at the present point (\( x_1 \)), the ‘poll’ is called ‘unsuccessful’ and the current point remains the same at the next iteration.
Then the algorithm will poll with a smaller mesh size, multiplying the current mesh size by contraction factor equal to 0.5, as shown in Figure 7.15.

![Figure 7.14: Pattern search mesh points in the second iteration for a mesh size of 0.5 and expansion factor equals 2, where \( v_i \) is the pattern vector and \( x_1 \) is the present point.](image)

![Figure 7.15: Pattern search mesh points in the third iteration for a mesh size of 0.5 and contraction factor equals 0.5; where \( v_i \) is the pattern vector and \( x_1 \) is the present point.](image)

The evaluation of the objective function and the search for optimal (minimum) solution is continued. The algorithm stops when termination conditions are met. The criteria employed for stopping the algorithm are as follows:

- **Mesh tolerance:** The optimization will be terminated if the mesh size becomes smaller than the acceptable tolerance value for the mesh size, which is \( 1 \times 10^{-6} \).

- **Number of iteration:** The algorithm stops when the maximum number of iterations is reached.

- **Number of function evaluation:** The algorithm stops when the total number of function evaluation exceeds \( 2000 \times \) number of variables.
7.4.1.2 Pattern search options

Pattern search has many options which can make a considerable difference to the optimisation’s performance. These options can be summarized as follows:

1. Poll methods
2. Search methods
3. Mesh contraction and expansion

In MATLAB, there are different ‘polling’ methods that can used to explore the search space such as Generalized Pattern Search (GPS), Generalized Set Search (GSS) and Mesh Adaptive Direct Search (MADS).

The pattern of GPS consists of a number of vectors that depends on the number of variables and the positive basis sets. The GSS pattern is similar to GPS, but adjusts the ‘basis vectors’ to account for linear constraints. The pattern of MADS consists of a number of vector that is randomly generated. For instance, MADS positive basis 2N, where \( N \) is the number of variable, pattern is generated using a random permutation of an \( N \)-by-\( N \) linearly lower triangular matrix that is regenerated at each iteration. The detailed description of these methods is given in the User’s Guide (The Math Works Inc., 2013).

To avoid being trapped in local minima, it is useful to explore all the mesh points around the current point. The condition that controls these options is the ‘complete poll’ setting and the ‘pattern positive basis’ sets (2N and NP1), which is used to generate a pattern of points. If the ‘complete poll’ is set to ‘on’, the algorithm will evaluate the objective function for all mesh points. Then, the algorithm compares the mesh points with the smallest objective function value to the current point. The minimum point found becomes the current point. When the ‘complete poll’ is set to ‘off’, the algorithm will stop calculating the other mesh points if a better solution than the current solution is found (The Math Works Inc., 2013). The pattern search can also specify the order in which the algorithm searches the points in the current mesh. The ‘polling order’ can be set to ‘random’ or ‘consecutive’ according to the order of the pattern vector (The Math Works Inc., 2013).
In addition to ‘polling’ the mesh points, the pattern search algorithm can perform an optional search step. The search step, similar to the poll step, searches for a better solution (i.e. a small value for the objective function) around the current point. The distance between mesh points and the current point is expanded or decreased when a solution is not found, as discussed in Section 7.4.1.1. The default values for the mesh expansion and contraction are 2 and 0.5, respectively. For more details on pattern search algorithms, the reader can refer to Kolda et al. (2003) or The MathWorks Global Optimization Toolbox User's Guide (2013).

7.4.1.3 Summary of Pattern search

The review of the pattern search method showed that the pattern search algorithm handles optimisation problem without the need for gradient information (function derivative). The pattern search method can find a close global optimum solution if the function is convex. The principle of the pattern search algorithm is simple. It generates a set of mesh points around the current point in an attempt to find one that yields a lower objective function than the current point.

An important issue that might influence the performance (the accuracy and the speed) of the optimizer is the magnitude difference between variables. For example, if the optimisation variables are molar flow rate and mole fraction, the flow rate will be in the range of 0 to 110 kmol/h and mole fraction will be in the range of 0 to 1. It can be seen that the magnitude of the difference in upper and lower bounds varies by a large amount. To give each variable the same importance and treat them in the same way, the optimised variables are normalised by scaling between 0 and 1. To normalise the variable in MATLAB, subtract the value of the variable from its lower bound value and then divide it by the difference between its upper and lower bound value.

7.4.2 Simulated Annealing

Simulated Annealing is a global search method as discussed in Section 2.4.2.3. The first Simulated Annealing algorithms were introduced by Kirkpatrick et al. in 1983. The method was developed to solve highly nonlinear, unconstrained or bound-constrained optimisation problems (The Math Works Inc., 2013).
Simulated Annealing is based on heating a material and then cooling it slowly to ensure thermal equilibrium and consequently a global energy minimum of a perfect crystal (Kirkpatrick et al., 1983). By analogy with this physical process, each step in the Simulated Annealing algorithm replaces a current point by a new point that is chosen depending on the difference between the objective function value of the new point and the objective function value of the current point and the annealing temperature, which is decreased over time according to an updating function (i.e. cooling schedule).

The solution strategy of Simulated Annealing is different from the standard optimisation methods, which only accept new points (i.e., points that are different from the starting point) that improve the objective function value. Simulated Annealing accepts updates that do not improve solution with a probability. By accepting such updates, the algorithm avoids being trapped in local minima in early iterations and is able to explore globally for better solutions.

### 7.4.2.1 Algorithm description

The Simulated Annealing process starts with an initial value of the annealing temperature and an initial feasible starting point (The Math Works Inc., 2013). If the initial annealing temperature is low, the optimizer could become trapped in a local optimum (The Math Works Inc., 2013). However, a very high initial annealing temperature would increase the run time (Kirkpatrick et al., 1983). Thus, an optimum temperature must be somewhere between these two values. Misevi (2003) proposes setting the initial annealing temperature at the maximum difference of the objective function values between two solutions.

Then, the algorithm generates a random new point. To generate a random new point, a step length (the distance of the new point from the present point) is chosen by a probability distribution with a scale based on the current annealing temperature. In MATLAB, the step length is set as a function with the annealing function option described in The MathWorks, 2013 as follows:

*Annealingfast:* Step length equals the current annealing temperature.

*Annealingboltz:* Step length equals the square root of annealing temperature.
The objective function of the new point is calculated and compared with that of the initial point. The new point is accepted as the next solution with probability 1 if it has a lower objective value than the initial point and as having some probability if it has a higher objective value, in the case that the objective is to minimise the value. In MATLAB, the probability of acceptance is set by the Simulated Annealing acceptance function (7.16). The probability of acceptance is used to avoid getting trapped in a search space (The Math Works Inc., 2013). It can be seen that the temperature strongly affects the probability of accepting a worse solution (i.e., a solution with a higher objective function value). Lower temperature leads to smaller acceptance probability. Also, larger $\Delta$ leads to smaller acceptance probability.

\[
\frac{1}{1 + e^{(\Delta/T)}}
\]  

(7.16)

Where $\Delta = \text{new objective} - \text{old objective}$, and $T$ is the current temperature.

Following this, the algorithm checks for a reannealing option. Reannealing raises the temperature after it accepts a certain number of solutions, and starts the search again at the higher temperature. This is done to avoid getting caught at local minima (The Math Works Inc., 2013). If there is no reannealing, the annealing temperature is reduced. To gradually lower the annealing temperature, the following cooling (annealing) schedule options can be used (MathWorks, 2013):

- Temperatureexp

  \[
  T = T_0 \times 0.95^K
  \]  

(7.17)

- Temperaturefast

  \[
  T = \frac{T_0}{K}
  \]  

(7.18)

- temperatureboltz

  \[
  T = \frac{T_0}{log(K)}
  \]  

(7.19)

Where $T_0$ is an initial annealing temperature and $K$ is the annealing parameter. The annealing parameter remains the same as the iteration number until reannealing. Note that the slower the decrease in temperature, the better the
chances are of finding an optimal solution, but the longer the computation time. This process is repeated until the termination criterion is satisfied. The algorithm stops when one of the following stopping criteria is reached.

- The change in the objective function is small relative to the tolerance function (default of 0.001 in this work).
- The number of iterations exceeds the maximum.
- The number of function evaluations exceeds the value of maximum function evaluation.
- The maximum algorithm running time exceeds the time limit.

7.4.2.2 Summary of Simulated Annealing

Similar to pattern search, no gradient information of the objective function to guide the direction of search is required. A key feature of Simulated Annealing is its ability to escape local optima. This is because it uses a probabilistic acceptance scheme, which accepts solutions that increase the objective function value in the case of minimization. Thus, Simulated Annealing algorithm is appropriate for minimising a function that has multiple local minima. However, a drawback of the method is the long computation time requirement.

The performance of the algorithm depends on the cooling schedule, which is specified by an initial annealing temperature and the updating function for changing the temperature, and the termination criterion.

7.4.3 Illustrative Example: Comparison between Simulated Annealing and Pattern search

This example applies two mathematical optimisation methods for simultaneous design and optimisation of non-heat-integrated parallel hybrid separation system. The results of the two methods are compared. In ‘both cases’ the algorithm is implemented using the global optimisation toolbox in MATLAB.

To solve the parallel hybrid optimisation problem, the same column feed purity, flow rate and product purities given in Section 7.2 are used. Shortcut model described in Chapter 4 is used to design the column. The reflux ratio and the column pressure are set to 1.05 $R/R_{\text{min}}$ and 20 bar, respectively. The column pressure drop is
assumed to be negligible. A Facilitated transport membrane reported in the literature (Pinnau and Toy, 2001) is employed with a feed pressure and temperature of 20 bar and 23°C, respectively. The membrane selectivity to ethylene is 54 (see Figure 5.11). The flow rate of the side draw stream is set to 100 kmol/h and its mole fraction set to 0.54 for \( \text{C}_2\text{H}_4 \). Cross-flow discussed in Section 3.3.1.2 is used for the membrane.

In this example the objective is to minimise the total operating costs. The decision variables manipulated for the optimisation are listed in Table 7.1. The starting point, upper and lower bounds are also given in Table 7.1.

### Table 7.1: Optimisation variables and their constraints for illustrative example

<table>
<thead>
<tr>
<th>Decision variable</th>
<th>Description</th>
<th>Starting point</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_1 )</td>
<td>Stage cut</td>
<td>0.3</td>
<td>0.01</td>
<td>0.75</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>Permeate pressure, bar</td>
<td>4</td>
<td>1.01</td>
<td>8</td>
</tr>
</tbody>
</table>

#### 7.4.3.1 Results and discussion

In this section, the results of the two optimisation methods are presented. For each method, different options were tested to find suitable conditions for running the optimisation. Different poll and search methods and key parameters of pattern search such as the initial mesh size, the mesh expansion and contraction factors are examined, as shown in Table 7.2. In Simulated Annealing, the performance of the algorithm is dictated by its initial temperature and cooling schedule. Therefore, the influence of Simulated Annealing algorithm with its parameters is examined for different initial annealing temperature and annealing schedules as shown in Table 7.3.

The optimisation problem solved using the algorithms in the global optimisation Toolbox. The algorithm can be the pattern search described in Section 7.4.1.1 or Simulated Annealing described in Section 7.4.2.1. To fine tune the optimisation parameters, several runs are performed for the given objective function (total operating cost). In each run, different options which can be specified using optimisation function option.
Table 7.2: Influence of pattern search parameters on optimisation performance of the parallel hybrid system

<table>
<thead>
<tr>
<th>Poll method/complete poll</th>
<th>Search method</th>
<th>Mesh size/contraction/expansion</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>FC</td>
</tr>
<tr>
<td>GSSNP1/off</td>
<td>off</td>
<td>1/0.5/2</td>
<td>68</td>
</tr>
<tr>
<td>GSS2N/off</td>
<td>off</td>
<td>1/0.5/2</td>
<td>79</td>
</tr>
<tr>
<td>GPSNP1/off</td>
<td>off</td>
<td>1/0.5/2</td>
<td>128</td>
</tr>
<tr>
<td>GPSNP1/off</td>
<td>off</td>
<td>1/0.5/2</td>
<td>127</td>
</tr>
<tr>
<td>GPS2N/off</td>
<td>off</td>
<td>1/0.5/2</td>
<td>232</td>
</tr>
<tr>
<td>GPSNP1/on</td>
<td>off</td>
<td>1/0.5/2</td>
<td>135</td>
</tr>
<tr>
<td>GSSNP1/on</td>
<td>off</td>
<td>1/0.5/2</td>
<td>77</td>
</tr>
<tr>
<td>GPSNP1/on</td>
<td>MADSNP1</td>
<td>1/0.5/2</td>
<td>241</td>
</tr>
<tr>
<td>GSSNP1/on</td>
<td>MADSNP1</td>
<td>1/0.5/2</td>
<td>275</td>
</tr>
<tr>
<td>GSSNP1/off</td>
<td>MADSNP1</td>
<td>0.5/0.5/1</td>
<td>71</td>
</tr>
<tr>
<td>GSSNP1/on</td>
<td>MADSNP1</td>
<td>0.5/0.5/2</td>
<td>552</td>
</tr>
<tr>
<td>GPSNP1/off</td>
<td>off</td>
<td>1/0.75/3</td>
<td>247</td>
</tr>
<tr>
<td>GPSNP1/off</td>
<td>off</td>
<td>0.5/0.5/1</td>
<td>112</td>
</tr>
<tr>
<td>GPSNP1/off</td>
<td>off</td>
<td>0.5/0.5/2</td>
<td>523</td>
</tr>
<tr>
<td>GSSNP1/off</td>
<td>off</td>
<td>0.5/0.5/1</td>
<td>833</td>
</tr>
</tbody>
</table>

*Different starting point [0.2, 3.5]; FC: function count; K: number of iteration; $x_1$: stage cut; $x_2$: permeate pressure; TOC: total operating cost, £/y

Table 7.2 shows that setting the ‘complete poll’ to ‘ON’ lowers the number of iterations ($K$) for the GSS and the GPS, but increases the number of function evaluations ($FC$) in the search. The number of function evaluations is also substantially increased when the search method is set to Mesh Adaptive Direct Search. Note that using the GSS algorithm positive basis NP1 with complete poll set to ON for a mesh size of 1, mesh contraction of 0.5 and mesh expansion of 2, the lowest objective function value is obtained after 52 iterations compared to 43 iterations for GPS. In this case, the most efficient poll is GPS positive basis NP1 with complete poll and search method set to OFF, 1 mesh size, 0.5 mesh contraction and 2 of mesh expansion.

In Table 7.2, it can be seen that the minimum total operating cost is 146,208 £/y at the optimal variables value, which comprises a permeate pressure of 6.7 bar and a stage cut value of 0.606. However, the comparison of the results of the pattern search with several inputs shows insignificant difference between the optimal results. The
optimal solution deviates from the average optimal solution (a permeate pressure of 7.468 bar and a stage cut value of 0.609) by around 10% for a permeate pressure and by around 0.5% for a stage cut.

Table 7.3 shows that setting the reannealing interval at 100 with the combination of Boltzmann annealing and temperature exponential results in the lowest value (146,176 £/y). Note that the number of iterations is high in all cases.

Table 7.3: Influence of Simulated Annealing parameters on optimisation performance of the parallel hybrid system (Function tolerance = 0.001)

<table>
<thead>
<tr>
<th>Annealing function</th>
<th>Reannealing interval</th>
<th>Temperature update function</th>
<th>$T_0$</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$K$ $x_1$ $x_2$ TOC</td>
</tr>
<tr>
<td>Fast annealing</td>
<td>100</td>
<td>Exponential</td>
<td>100</td>
<td>1400 0.59 3.81 150855</td>
</tr>
<tr>
<td>Boltzmann annealing</td>
<td>100</td>
<td>Exponential</td>
<td>100</td>
<td>1908 0.608 6.95 146207</td>
</tr>
<tr>
<td>Boltzmann annealing</td>
<td>300</td>
<td>Exponential</td>
<td>100</td>
<td>5267 0.605 6.33 146304</td>
</tr>
<tr>
<td>Boltzmann annealing</td>
<td>100</td>
<td>Logarithmic</td>
<td>100</td>
<td>1800 0.611 7.95 146586</td>
</tr>
<tr>
<td>Boltzmann annealing</td>
<td>100</td>
<td>Exponential</td>
<td>100</td>
<td>3051 0.605 6.30 146321*</td>
</tr>
<tr>
<td>Boltzmann annealing</td>
<td>100</td>
<td>Exponential</td>
<td>70</td>
<td>5996 0.606 6.65 146215</td>
</tr>
<tr>
<td>Boltzmann annealing</td>
<td>100</td>
<td>Exponential</td>
<td>200</td>
<td>1000 0.608 7.04 146176</td>
</tr>
</tbody>
</table>

*Different starting point [0.2, 3.5]; $T_0$: initial temperature; $K$: number of iteration; $x_1$: stage cut; $x_2$: permeate pressure; TOC: total operating cost, £/y

The lowest elapsed time is 216 sec for pattern search and about 1800 sec for SA. Comparing SA with pattern search it can be concluded that pattern search is faster than SA but that SA is more accurate. The important observation here is that, in this case, both methods found the minimum value of the objective function, but with a different starting point for pattern search. Compared to the sensitivity results reported in Figure 7.16, the optimal results of the optimisation are very close (permeate pressure = 7 bar and stage cut = 0.6). Figure 7.16 shows a three-dimension plot with the minimum point as indicated; and the two-dimensional contour plot.

The performance of pattern search depends on the initial point. Pattern search is fast, easily to implement and it can find a good solution since the total operating cost is within 0.021% of the optimal solution. In order to guarantee an optimal solution, different starting points should be tested.
7.4.4 Summary of optimization algorithm

In this section, a pattern search algorithm and a Simulated Annealing algorithm are described. Also, an illustrative example is provided to illustrate the accuracy and computational efficiency of the two optimisation methods for the optimal operation of the parallel hybrid system. When pattern search is compared with Simulated Annealing, it is observed that pattern search needs less computation time for reaching the optimal solution. In addition, pattern search is not very sensitive to the initial guess. The maximum difference between the optimal solution found by Simulated Annealing and pattern search is 0.25% for the total operating costs, 0.2% for the stage cut and 13% for the permeate pressure. It seems that the optimiser converges to a local optimum, because the change of TOC is not significant when the permeate pressure is increased (see Figure 7.8). However, the deviation between the optimal results—particularly the optimal permeate pressure—of Simulated Annealing and pattern search (with a mesh size of 1, mesh contraction of 0.5 and mesh expansion of 2) is less than 0.4, which is acceptable.
From Figure 7.16, it can be seen that there is only a local minimum. These findings suggest that it is possible to use the pattern search algorithm for optimisation. However, to locate an optimal solution and increase confidence in the result, a variety of initial points could be tested. The next step will be to apply the systematic design and optimisation procedure described in this chapter to four case studies.

7.5 Case studies

7.5.1 Case 1: Optimisation of a parallel hybrid scheme design

To illustrate the implementation of the optimisation framework for simultaneous structural and operational optimisation in order to separate a close boiling mixture, the case study considers a mixture with the feed composition and column specifications shown in Table 7.4. To illustrate the accuracy of the model prediction, the optimisation results will also be compared with the value from a rigorous model at the same ratio of reflux ratios and the same number of stages.

Table 7.4: Column specifications for Case 1 and Case 2

<table>
<thead>
<tr>
<th>Stream</th>
<th>Feed</th>
<th>Distillate</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Flow rate (kmol h(^{-1}))</td>
<td>100</td>
<td>53.82</td>
<td>46.18</td>
</tr>
<tr>
<td>C(_2)H(_4) (mole fraction)</td>
<td>0.54</td>
<td>0.999</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Table 7.5: Membrane properties for Case 1 and Case 2

<table>
<thead>
<tr>
<th>Membrane property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane feed pressure (bar)</td>
<td>20</td>
</tr>
<tr>
<td>Membrane retentate pressure (bar)</td>
<td>20</td>
</tr>
<tr>
<td>Membrane feed temperature (°C)</td>
<td>23</td>
</tr>
<tr>
<td>Permeability of C(_2)H(_4) (mol m s(^{-1}) m(^{-2}) Pa(^{-1}))</td>
<td>0.3×10(^{-14})</td>
</tr>
<tr>
<td>Membrane thickness (m)</td>
<td>5×10(^{-6})</td>
</tr>
<tr>
<td>Membrane selectivity</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 7.5 lists the facilitated transport membrane properties of Pinnau and Toy (2001) for ethylene-ethane separation. Cross flow is assumed for the membrane. The feed is introduced to the membrane at a temperature of 23°C (experimental...
condition). To predict the membrane performance (i.e. product purities), the modelling approach described in Chapter 3 is used. When designing the column using the modified shortcut method described in Section 4.3.2, the ratio of the reflux ratio (R/Rmin) is set to 1.05.

A superstructure representation for the ‘parallel hybrid separation flowsheet’ is shown in Figure 7.17. The superstructure involves four parallel hybrid schemes, as illustrated in Figures 5.2(a) and 5.2(b), where the membrane is placed across the feed stage and above the feed stage, respectively. The optimisation determines the optimal operating conditions and the optimal locations for the feed and side draw streams.

![Superstructure representation for parallel hybrid schemes](image)

**Figure 7.17: Superstructure representation for parallel hybrid schemes**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane permeate pressure (bar)</td>
<td>1.01</td>
<td>8</td>
</tr>
<tr>
<td>Stage cut (fraction of feed permeated)</td>
<td>0.01</td>
<td>0.75</td>
</tr>
<tr>
<td>Side stream (mole fraction of ( \text{C}_2\text{H}_4 ))</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Molar flow rate of membrane feed (kmol h(^{-1}))</td>
<td>10</td>
<td>110</td>
</tr>
</tbody>
</table>

A generalized pattern search method is used to solve the optimisation problem with the upper and lower bound values given in Table 7.5. The optimisation variables and their limits are selected on the basis of the sensitivity analysis reported in Section 7.2. The objective is to minimise the total operating cost, TOC, of the separation flowsheet. The optimisation is carried out for two scenarios: (1) in the absence of heat recovery, and (2) with heat integration between the separation
system and the associated refrigeration system. The heat recovery approach used in this case follows that explained in Chapter 6. Utility cost data are given in Table 7.6.

Table 7.6: Utility specifications for Case studies (Farrokhpanah, 2009)

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature (°C)</th>
<th>Cost (£/kW/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot water</td>
<td>90 – 25</td>
<td>25</td>
</tr>
<tr>
<td>Low-pressure steam</td>
<td>150</td>
<td>27.8</td>
</tr>
<tr>
<td>Cooling water</td>
<td>20 – 30</td>
<td>33</td>
</tr>
<tr>
<td>Electrical power</td>
<td></td>
<td>330</td>
</tr>
</tbody>
</table>

Table 7.7: Optimisation parameters for Case 1 and Case 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value/method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poll method</td>
<td>GPS minimum positive basis</td>
</tr>
<tr>
<td>Polling order</td>
<td>Consecutive</td>
</tr>
<tr>
<td>Initial mesh size</td>
<td>1</td>
</tr>
<tr>
<td>Mesh contraction</td>
<td>0.5</td>
</tr>
<tr>
<td>Mesh expansion</td>
<td>2</td>
</tr>
<tr>
<td>Mesh tolerance</td>
<td>$1 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

To obtain information for phase equilibrium and enthalpy calculations, MATLAB has been interfaced with Aspen HYSYS. The Soave-Redlich-Kwong (SRK) equation of state is used to calculate fluid and thermodynamic properties because of its accurate prediction for describing small nonpolar hydrocarbons (Ploegmakers et al., 2013).

Tables 7.8 and 7.9 show that the modified shortcut method gives more accurate predictions of the reflux ratio, compared with rigorous HYSYS simulation for a fixed ratio of reflux ratios (RR) of 1.05. For a given number of stages of a column, a rigorous simulation can provide the actual reflux required to meet the product specifications. The minimum reflux ratio is obtained when the actual reflux ratio does not change as the number of stages increases. To calculate the minimum reflux ratio, rigorous simulation of the column with a large number of stages (more than 200) is performed. The optimum feed locations are defined by iteration (i.e., carrying
out the simulations for a fixed number of stages with different feed stages). The feed stage resulting in the smallest actual reflux ratio is chosen.

Table 7.8: Optimisation results of the conventional column design (base case)

<table>
<thead>
<tr>
<th></th>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R/R_{\text{min}}$</td>
<td>1.05*</td>
<td>1.05*</td>
<td>1.028</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>4.704</td>
<td>4.982</td>
<td>4.981</td>
</tr>
<tr>
<td>$R_{\text{act}}$</td>
<td>4.939</td>
<td>5.231</td>
<td>5.121</td>
</tr>
<tr>
<td>$Q_{\text{C}}$, kW</td>
<td>642</td>
<td>714</td>
<td>699</td>
</tr>
<tr>
<td>$Q_{\text{R}}$, kW</td>
<td>515</td>
<td>587</td>
<td>573</td>
</tr>
<tr>
<td>$N$</td>
<td>86</td>
<td>86</td>
<td>86*</td>
</tr>
</tbody>
</table>

Feed location

| Stage | 49 | 49 | 52 | 48 |

* Specified values; FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; $N$: Number of stages; $RR$: Ratio of reflux ratios ($R_{\text{act}}/R_{\text{min}}$)

Table 7.9: Optimisation results of the heat-integrated parallel hybrid separation–column (Case 1)

<table>
<thead>
<tr>
<th></th>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R/R_{\text{min}}$</td>
<td>1.05*</td>
<td>1.05*</td>
<td>1.23</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>3.138</td>
<td>3.323</td>
<td>3.323</td>
</tr>
<tr>
<td>$R_{\text{act}}$</td>
<td>3.3</td>
<td>3.49</td>
<td>4.1</td>
</tr>
<tr>
<td>$Q_{\text{C}}$, kW</td>
<td>449</td>
<td>476</td>
<td>557</td>
</tr>
<tr>
<td>$Q_{\text{R}}$, kW</td>
<td>312</td>
<td>339</td>
<td>420</td>
</tr>
<tr>
<td>$N$</td>
<td>92</td>
<td>92</td>
<td>92*</td>
</tr>
</tbody>
</table>

Feed and draw location

<table>
<thead>
<tr>
<th>Location</th>
<th>53</th>
<th>53</th>
<th>57</th>
<th>96</th>
</tr>
</thead>
</table>

* Specified values; FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; $N$: Number of stages; $RR$: Ratio of reflux ratio ($R_{\text{act}}/R_{\text{min}}$)

However, the shortcut method underestimates the number of stages compared with that obtained from the rigorous model. Also, the prediction of condenser and
reboiler duties from the modified Fenske-Underwood-Gilliland (MFUG) calculations method is not good when compared with the value from the rigorous model at a fixed number of stages (see Table 7.8). Thus, the number of stages specified in HYSYS needs to be adjusted to meet the fixed specification of $R/R_{\text{min}}$.

Comparing the results of conventional separation with the optimal hybrid results, the stand-alone distillation column has a reflux requirement that is 33% higher and hence a condenser duty that is 33% higher than in the parallel hybrid scheme. Table 7.10 shows the corresponding optimal variables for the parallel hybrid system for fixed $RR$.

It may be seen that the optimal membrane feed purity is equal to the column feed purity. This implies that the optimal position for the membrane is located across the column feed near the pinch composition. The optimal energy saving can be accomplished with a membrane area of 98958 $m^2$, a stage cut (i.e., fraction of feed permeated) of 0.6 and a permeate pressure of 8 bar. These results are consistent with the results obtained by sensitivity analysis; where power requirements are shown to decrease with the increase of both permeate pressure and stage cut.

Table 7.10: Optimisation results of the heat-integrated parallel hybrid separation–membrane unit (Case 1)

<table>
<thead>
<tr>
<th>Optimised variables</th>
<th>Heat-integrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane feed molar flow rate, kmol/h</td>
<td>57</td>
</tr>
<tr>
<td>Stage cut</td>
<td>0.6</td>
</tr>
<tr>
<td>Membrane feed mole fraction, $C_2H_4$</td>
<td>0.54</td>
</tr>
<tr>
<td>Permeate mole fraction, $C_2H_4$</td>
<td>0.78</td>
</tr>
<tr>
<td>Retentate mole fraction, $C_2H_4$</td>
<td>0.18</td>
</tr>
<tr>
<td>Recovery mole fraction, $C_2H_4$</td>
<td>0.87</td>
</tr>
<tr>
<td>Permeate pressure, bar</td>
<td>8</td>
</tr>
<tr>
<td>Dimensionless membrane area</td>
<td>12.5</td>
</tr>
<tr>
<td>Area, $m^2$</td>
<td>989.58</td>
</tr>
<tr>
<td>$T_R$, (°C)</td>
<td>15.606</td>
</tr>
</tbody>
</table>

For the optimal hybrid, the stream data for the heat recovery problem are presented in Table 7.11. A minimum temperature approach of 5°C is used to
calculate the minimum hot and cold utility requirements. First, the conventional column and the parallel hybrid scheme are compared for the case in which the heat integration is not considered. This is followed by a discussion of the effect of introducing heat recovery to the conventional column and the parallel hybrid scheme.

Table 7.11: Optimised process streams data for heat-integrated Case 1

<table>
<thead>
<tr>
<th>Stream</th>
<th>Type</th>
<th>$T_{in}$ (°C)</th>
<th>$T_{out}$ (°C)</th>
<th>$Q$ (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate cooler 1</td>
<td>Source</td>
<td>85.10</td>
<td>30.00</td>
<td>28.17</td>
</tr>
<tr>
<td>Permeate cooler 2</td>
<td>Source</td>
<td>30.00</td>
<td>-24.39</td>
<td>28.25</td>
</tr>
<tr>
<td>Column condenser</td>
<td>Source</td>
<td>-29.20</td>
<td>-29.21</td>
<td>476.00</td>
</tr>
<tr>
<td>Membrane heater</td>
<td>Sink</td>
<td>-19.06</td>
<td>23.00</td>
<td>38.42</td>
</tr>
<tr>
<td>Column reboiler</td>
<td>Sink</td>
<td>-7.94</td>
<td>-7.89</td>
<td>339.00</td>
</tr>
</tbody>
</table>

Table 7.12: Optimised heat loads and recompression duty for Case 1

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>Type of exchange</th>
<th>Duty (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td>0</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>714.00</td>
</tr>
<tr>
<td>Process-to-hot utility</td>
<td>Direct heat exchange</td>
<td>587.00</td>
</tr>
</tbody>
</table>

Parallel hybrid case

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>Type of exchange</th>
<th>Duty (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td>286.70</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>504.25</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Direct heat exchange</td>
<td>28.17</td>
</tr>
<tr>
<td>Process-to-hot utility</td>
<td></td>
<td>377.42</td>
</tr>
<tr>
<td>Heat recovery</td>
<td></td>
<td>34.00</td>
</tr>
<tr>
<td>Recompression duty</td>
<td></td>
<td>28.70</td>
</tr>
</tbody>
</table>

In the non-heat-integrated scenario, heating and cooling duties are specified by external utilities. For the hybrid scheme, a propylene refrigeration cycle is used to provide cooling to the condenser and the sub-ambient cooler. The refrigeration and recompression power demand is evaluated as described in Chapter 6. It may be seen that membrane can reduce the total power demand by about 26%; the compression
required for refrigeration decreases by 33% but recompression of the permeate is required (see Tables 7.12 and 7.13).

In the heat-integrated scenario, there is direct heat exchange between the membrane heater and the permeate cooler and between the permeate cooler and the reboiler. Therefore, the need for hot and cold utilities to cool and heat up these streams to the target temperature is reduced and the total shaft power demand is further reduced to 0.19 MW compared to conventional distillation, as shown in Table 7.13.

Part of condenser cooling duty is rejected to the reboiler. The rest of the cooling duty of the condenser and the second permeate cooler are pumped to the ambient heat sink, cooling water. Thus the optimised hybrid system reduces total operating costs (TOC) by around 11% compared to the heat-integrated base case.

Table 7.13: Optimal economic results for Case1

<table>
<thead>
<tr>
<th>Cases</th>
<th>Without heat integration</th>
<th>With heat integration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power, MW</td>
<td>TOC, £/y</td>
</tr>
<tr>
<td>Conventional column</td>
<td>0.38</td>
<td>178,000</td>
</tr>
<tr>
<td>Parallel Hybrid scheme</td>
<td>0.28</td>
<td>127,000</td>
</tr>
<tr>
<td>Saving % relative to distillation</td>
<td>26</td>
<td>28</td>
</tr>
</tbody>
</table>

7.5.1.1 Summary of Case 1

In this case, the structure and operation of the parallel hybrid membrane-distillation systems are optimised. Figure 7.18 shows the optimal hybrid scheme and the optimum operating conditions for ethylene-ethane separation. It can be seen that the optimal location for the membrane is across the column feed.
Although the optimisation of the design and operation of hybrid membrane-distillation processes for ethylene-ethane separation has been explored before (e.g., Ploegmakers et al., 2013; Benali and Aydin, 2010; Al-Rabiah, 2001), this is the first time heat recovery is considered. Table 7.10 lists the optimization results for the optimal parallel hybrid flowsheet. The total operating costs of the heat-integrated parallel hybrid process is 83,000 £/y, a relative reduction of 11% compared with the operating cost of the heat-integrated conventional column (74,000 £/y).

In case 2, the sequential hybrid scheme will be optimised and compared with the parallel hybrid scheme and the conventional column.

### 7.5.2 Case 2: Optimisation of sequential hybrid scheme design

The main goal of Case 2 is to evaluate and compare the optimal economic performance of the sequential hybrid scheme with the conventional column and with the parallel hybrid system. The objective is to minimise the total operating cost of the separation system.

In this case, the configuration is fixed, as shown in Figure 7.19, but the operating conditions (stage cut and permeate pressure) are optimised. The two key continuous variables are optimised; with the lower bound being the atmospheric pressure for permeate pressure and 0.01 for the stage cut. The upper bound is selected to be 8 bar and 0.7 for the permeate pressure and the stage cut, respectively.

![Figure 7.19: Fixed sequential hybrid scheme (Case 2)](image)

In this case, the product purities, column feed specifications and membrane properties given in Case1 are used. Heat recovery between the hybrid separation flowsheet and the refrigeration system is considered during the optimisation process. In the optimisation framework, the whole hybrid flowsheet is simulated as described
in Section 5.3.3. A generalized pattern search method is used to solve the optimisation problem. To illustrate the accuracy of the model prediction, the optimisation results have been compared against rigorous simulation results.

Table 7.14: Optimisation results of the heat-integrated sequential hybrid separation - double feed column

<table>
<thead>
<tr>
<th></th>
<th>Shortcut model (FUG)</th>
<th>Shortcut model (MFUG)</th>
<th>HYSYS Fixed stages</th>
<th>HYSYS Fixed RR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R/R_{\text{min}}$</td>
<td>1.05*</td>
<td>1.05*</td>
<td>1.162</td>
<td>1.05*</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>3.176</td>
<td>3.281</td>
<td>3.281</td>
<td>3.281</td>
</tr>
<tr>
<td>$R_{\text{act}}$</td>
<td>3.335</td>
<td>3.445</td>
<td>3.812</td>
<td>3.445</td>
</tr>
<tr>
<td>$Q_{C}$, kW</td>
<td>455</td>
<td>470</td>
<td>520</td>
<td>470</td>
</tr>
<tr>
<td>$Q_{R}$, kW</td>
<td>310</td>
<td>325</td>
<td>375</td>
<td>325</td>
</tr>
<tr>
<td>$N_t$</td>
<td>93</td>
<td>93</td>
<td>93*</td>
<td>130</td>
</tr>
</tbody>
</table>

Feed location ($N_t$)

<table>
<thead>
<tr>
<th></th>
<th>Permeate feed</th>
<th>Retentate feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_t$</td>
<td>45</td>
<td>66</td>
</tr>
</tbody>
</table>

* Specified values; FUG: Fenske-Underwood-Gilliland; MFUG: Modified Fenske-Underwood-Gilliland; $N$: Number of stages; $RR$: Ratio of reflux ratio ($R_{\text{act}}/R_{\text{min}}$)

Table 7.14 illustrates the optimal results for a double-feed column simulated using the Fenske-Underwood-Gilliland method and the modified shortcut method explained in Chapter 4. Table 7.14 shows that the modified shortcut method gives good predictions as to the reflux ratio and energy requirement compared with rigorous HYSYS simulation for a fixed reflux ratio ($RR$) of 1.05. However, the number of stages is increased. This could be attributed to the fact that the Gilliland correlation underestimates the number of stages when the controlling thermal state of the feed is above the saturated liquid condition. The difference between the rigorous simulation and the shortcut method increases as $R/R_{\text{min}}$ gets closer to the minimum reflux area. The ratio of the optimal inlet stream for the feed to the optimal total number of stages calculated by shortcut is close to that determined through stage by stage calculations. Therefore, knowing $N_t/N_f$ could reduce the time required to find the optimal feed location in HYSYS, where trial and error is required.
It is evident from the results in Table 7.14 that the refrigeration power could be lower because the condenser duty is reduced by 34% compared to the base case (see Table 7.8). However, the influence of other important units, e.g., the compressor and the cooler, needs to be considered before making the final judgment on the economic advantages of using the hybrid membrane-distillation process. As can be seen from the separation flowsheet shown in Figure 7.19, the hybrid flowsheet introduces five additional units—three heat exchanger units, a membrane unit and a compressor—compared to the base case. These units improve the separation performance but could increase the capital costs.

The optimal results in terms of total operating costs for the membrane unit are presented in Table 7.15. The optimal permeate pressure is extremely close to the upper bound. A lower permeate pressure results in an increased driving force and thus higher permeate purity and lower membrane area. At the same time, the condenser duty is reduced by lowering permeate pressure. However, a high compression power will be needed to recompress the permeate stream to 20 bar before entering the column again.

Table 7.15: Optimisation results of the heat-integrated sequential hybrid separation–membrane unit

<table>
<thead>
<tr>
<th>Optimised variables</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage cut</td>
<td>0.61</td>
</tr>
<tr>
<td>Permeate mole fraction, (\text{C}_2\text{H}_4)</td>
<td>0.77</td>
</tr>
<tr>
<td>Retentate mole fraction, (\text{C}_2\text{H}_4)</td>
<td>0.18</td>
</tr>
<tr>
<td>Recovery mole fraction, (\text{C}_2\text{H}_4)</td>
<td>0.87</td>
</tr>
<tr>
<td>Permeate pressure, bar</td>
<td>7.99</td>
</tr>
<tr>
<td>Dimensionless membrane area</td>
<td>13.32</td>
</tr>
<tr>
<td>(T_R), (°C)</td>
<td>15.48</td>
</tr>
</tbody>
</table>

A summary of the process stream data of the optimal hybrid membrane-distillation process is given in Table 7.16. Applying the heat recovery model proposed in Chapter 6 to the hybrid process, the total power requirement is reduced from 0.33 MW to 0.21 MW and the hot utility demand is eliminated. This reduction comes from both direct process-to-process heat recovery and indirect process-to-
process heat recovery where a part of the process heat (0.290 MW) is pumped to a lower temperature level above the pinch point (see Table 7.17). The remaining process heat (0.188 MW) is rejected from the refrigeration cycle to cooling water. In the heat-integrated process, the process heat of 0.0493 MW is also rejected to cooling water.

Table 7.16: Optimised process stream data for Case 2

<table>
<thead>
<tr>
<th>Stream</th>
<th>Type</th>
<th>T&lt;sub&gt;in&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;out&lt;/sub&gt; (°C)</th>
<th>Q (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate cooler 1</td>
<td>Source</td>
<td>83.89</td>
<td>30.00</td>
<td>49.28</td>
</tr>
<tr>
<td>Permeate cooler 2</td>
<td>Source</td>
<td>30.00</td>
<td>-24.20</td>
<td>50.42</td>
</tr>
<tr>
<td>Column condenser</td>
<td>Source</td>
<td>-29.20</td>
<td>-29.21</td>
<td>470.00</td>
</tr>
<tr>
<td>Membrane heater</td>
<td>Sink</td>
<td>-19.06</td>
<td>23.00</td>
<td>67.48</td>
</tr>
<tr>
<td>Column reboiler</td>
<td>Sink</td>
<td>-7.94</td>
<td>-7.89</td>
<td>325.00</td>
</tr>
</tbody>
</table>

Table 7.17: Optimised heat loads and recompression duty for Case 2

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>Type of exchange</th>
<th>Duty (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td>0</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>714.00</td>
</tr>
<tr>
<td>Hot utility</td>
<td></td>
<td>587.00</td>
</tr>
</tbody>
</table>

**Base case (conventional column)**

**Sequential hybrid case**

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>Type of exchange</th>
<th>Duty (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td></td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>520.42</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Direct heat exchange</td>
<td>49.28</td>
</tr>
<tr>
<td>Process-to-hot utility</td>
<td>Direct heat exchange</td>
<td>392.48</td>
</tr>
<tr>
<td>Heat recovery</td>
<td></td>
<td>40.98</td>
</tr>
<tr>
<td>Recompression duty (power demand, kW)</td>
<td></td>
<td>50.48</td>
</tr>
</tbody>
</table>

The total operating costs for Case 2 are presented in Table 7.18. It can be seen that the total operating cost for this case is 0.152 M£/y compared to 0.178 M£/y in the base case. Thus the optimal results show a saving of about 14% in both the total power demand and the operating cost compared to the base case. More energy saving is achieved by applying heat integration, but the TOC saving is only 4% less than
that in the heat-integrated conventional column. Compared to the parallel hybrid case reported in Table 7.13, the sequential hybrid case is less cost effective.

Table 7.18: Optimal economic results for Case 2

<table>
<thead>
<tr>
<th>Cases</th>
<th>Without heat integration</th>
<th>With heat integration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power, MW</td>
<td>TOC, £/y</td>
</tr>
<tr>
<td>Conventional column</td>
<td>0.38</td>
<td>178,000</td>
</tr>
<tr>
<td>Series hybrid scheme</td>
<td>0.33</td>
<td>152,000</td>
</tr>
<tr>
<td>Saving % relative to distillation</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

### 7.5.2.1 Summary of Case 2

Case 2 presents the application of the developed approach to find the optimum operation conditions of the sequential hybrid membrane-distillation process.

The results from Case 2 are compared with Case 1 to identify the most cost effective separation flowsheets for the ethylene-ethane separation. It is found that the heat-integrated parallel hybrid scheme gives the best performance in terms of power saving, as compared to the conventional column and the sequential hybrid configurations. It is interesting to note that neither of the non-heat-integrated hybrid separation processes (sequential and parallel) is cost effective compared to the heat-integrated conventional column.

To investigate the possibility that the hybrid system could offer more energy savings for the separation system, the sequential hybrid configuration is assessed for high selective membranes, as shown in Case 3.

### 7.5.3 Case 3: Optimisation of hybrid separation system design for different membrane types

Facilitated transport membranes, FTMs, which have been demonstrated in laboratories and pilot plants to have high olefin-paraffin selectivity and high olefin permeability, are explored here. The first type of FTM is an immobilized liquid membrane, ILM, which consists of an aqueous solution of silver nitrate held by capillary force in the pores of a microporous membrane (Al Rabiah, 2001). The
second type is a solid polymer electrolyte membrane, SPEM. Solid polymer electrolyte membrane made from polyethylene oxide loaded with AgBF₄ (Pinnau et al., 2001).

Merkel et al. (2007) have continued to investigate the solid polymer electrolyte facilitated transport membranes first described by Pinnau and Toy (2001). A polyether-polyamide block copolymer (Pebax® 2533) membrane that contains 80 wt% of AgBF₄ is found to give suitable permeance and selectivity for mixed feed compositions (Merkel et al., 2007).

The transport mechanism in facilitated ILM comprises carrier-mediated transportation plus solution-diffusion (Benali et al., 2010), while the transport mechanism in SPEM includes only a solution-diffusion transfer phenomena. Section 2.2.1 discussed in detail the transport mechanisms through facilitated transport membranes. The feasibility of using facilitated transport membranes such as ILM for improving the separation performance of the C₂ splitter has been investigated by Al Rabiah (2001) and Benali et al. (2010).

SPEM is reported to overcome most of the problems encountered by ILM. Furthermore, experimental data for operating at high feed pressures and a range of feed compositions is available for SPEM. The economic performance of the hybrid systems with the conventional distillation column for the two types of FTMs are evaluated and compared. The objective function is to minimise the TOC of the separation flowsheet.

This case study is examined for a sequential hybrid separation system, as shown in Figure 7.19. The feed stream is heated to 23°C (experimental condition) before being fed to the membrane unit. Then, the permeate stream is recompressed and cooled to saturated vapour temperature prior to entering the distillation column, where the overhead stream is partially condensed, i.e., the distillate is in the vapour phase. The membrane properties, which are based on the experimental data of Teramoto et al. (1986) and Hughes et al. (1986) for immobilized liquid membrane and that are reported by Pinnau and Toy (2001) and Merkel et al. (2007) for solid polymer electrolyte membranes, separation process specifications and optimisation variables, with their upper and lower bounds, are summarized in Table 7.19. The external utilities and their costs are listed in Table 7.6.
Table 7.19: Fixed parameters and optimisation variables with their boundaries for Case 3

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuous optimisation variables</strong></td>
<td></td>
</tr>
<tr>
<td>Membrane permeate pressure (bar)</td>
<td>1.01 – 8</td>
</tr>
<tr>
<td>Fraction of feed permeated</td>
<td>0.01 – 0.7</td>
</tr>
<tr>
<td><strong>Fixed parameters</strong></td>
<td></td>
</tr>
<tr>
<td>R/R\text{\textsubscript{min}}</td>
<td>1.05</td>
</tr>
<tr>
<td>Column pressure (bar)</td>
<td>20</td>
</tr>
<tr>
<td>Molar flow rate of membrane feed (kmol h\textsuperscript{-1})</td>
<td>100</td>
</tr>
<tr>
<td>Membrane feed pressure (bar)</td>
<td>20</td>
</tr>
<tr>
<td>Membrane retentate pressure (bar)</td>
<td>20</td>
</tr>
<tr>
<td>Membrane feed temperature (\textdegree C)</td>
<td>23</td>
</tr>
<tr>
<td>Membrane feed purity of C\textsubscript{2}H\textsubscript{4} (mol%)</td>
<td>54</td>
</tr>
<tr>
<td>Condition of recycled permeate stream, q</td>
<td>1</td>
</tr>
<tr>
<td>Minimum approach temperature (\textdegree C)</td>
<td>5</td>
</tr>
<tr>
<td><strong>Column specifications</strong></td>
<td></td>
</tr>
<tr>
<td>Feed molar flow rate of the base case (kmol h\textsuperscript{-1})</td>
<td>100</td>
</tr>
<tr>
<td>Condition of column feed stream, q, of the base case</td>
<td>1</td>
</tr>
<tr>
<td>Column feed purity of C\textsubscript{2}H\textsubscript{4} (mol%) of the base case</td>
<td>54</td>
</tr>
<tr>
<td>Bottom molar purity % of C\textsubscript{2}H\textsubscript{6}</td>
<td>99.5</td>
</tr>
<tr>
<td>Distillate molar purity % of C\textsubscript{2}H\textsubscript{4}</td>
<td>99.9</td>
</tr>
</tbody>
</table>

**Cross-flow module**

<table>
<thead>
<tr>
<th>Membrane properties</th>
<th>Type: ILM\textsuperscript{a}</th>
<th>Type: SPEM\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pebp\textsuperscript{b}</td>
<td>Pebax\textsuperscript{2553}\textsuperscript{c}</td>
</tr>
<tr>
<td>Permeability of C\textsubscript{2}H\textsubscript{4} \text{(mol m s\textsuperscript{-1} m\textsuperscript{-2} Pa\textsuperscript{-1})}</td>
<td>8.820×10\textsuperscript{-14}</td>
<td>1.339×10\textsuperscript{-14}</td>
</tr>
<tr>
<td>Permeability of C\textsubscript{2}H\textsubscript{6} \text{(mol m s\textsuperscript{-1} m\textsuperscript{-2} Pa\textsuperscript{-1})}</td>
<td>3.251×10\textsuperscript{-14}</td>
<td>5.581×10\textsuperscript{-17}</td>
</tr>
<tr>
<td>Diffusivity of C\textsubscript{2}H\textsubscript{4}-Ag complex \text{(m\textsuperscript{2} s\textsuperscript{-1})}</td>
<td>1.66×10\textsuperscript{-9}</td>
<td></td>
</tr>
<tr>
<td>Equilibrium constant \text{(m\textsuperscript{3} mol\textsuperscript{-1})}</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Concentration of AgNO\textsubscript{3} \text{(mol l\textsuperscript{-1})}</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Ratio of porosity to tortuosity</td>
<td>0.258</td>
<td></td>
</tr>
<tr>
<td>Membrane thickness (m)</td>
<td>1.7×10\textsuperscript{-6}</td>
<td>5×10\textsuperscript{-6}</td>
</tr>
<tr>
<td>Membrane selectivity</td>
<td>139.5\textsuperscript{*}</td>
<td>240</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Membrane selectivity is calculated from equation (3.38) for 1 bar of permeate pressure; \textsuperscript{b}: Al-Rabiah (2001); \textsuperscript{c}: Pinnau and Toy (2001); \textsuperscript{c}: Merkel et al. (2007).
The pattern search algorithm is used to optimise the operating cost of the design problem presented in Table 7.19. The results presented in Table 7.20 reveal that the optimal permeate and retentate purities of the three membranes are comparable, but the immobilized liquid membrane (ILM) requires a smaller area than solid polymer electrolyte membranes (Pebp and pebax®2553).

### Table 7.20: Optimisation results of the heat-integrated hybrid separation systems

<table>
<thead>
<tr>
<th></th>
<th>ILM</th>
<th>Pebp</th>
<th>Pebax®2553</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condenser duty (kW)</td>
<td>474</td>
<td>468</td>
<td>482</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>331</td>
<td>324</td>
<td>338</td>
</tr>
<tr>
<td>Membrane heater duty (kW)</td>
<td>67</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>Permeate Cooler 1 duty (kW)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Permeate Cooler 2 duty (kW)</td>
<td>52</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>Stage cut</td>
<td>0.628</td>
<td>0.627</td>
<td>0.629</td>
</tr>
<tr>
<td>Permeate mole fraction, C$_2$H$_4$</td>
<td>0.7660</td>
<td>0.7751</td>
<td>0.7558</td>
</tr>
<tr>
<td>Retentate mole fraction, C$_2$H$_4$</td>
<td>0.1578</td>
<td>0.1441</td>
<td>0.1739</td>
</tr>
<tr>
<td>Permeate pressure, bar</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Area (m$^2$)</td>
<td>117</td>
<td>186,201</td>
<td>901,7</td>
</tr>
<tr>
<td>Total operating cost (£/y)</td>
<td>81,834</td>
<td>81,250</td>
<td>82,510</td>
</tr>
</tbody>
</table>

### Table 7.21: Optimised heat loads and recompression duty for Case 3

**Base case**

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>Type of exchange</th>
<th>Duty, kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td>490.30</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>223.70</td>
</tr>
</tbody>
</table>

**Hybrid case**

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>ILM</th>
<th>Pebp</th>
<th>Pebax®2553</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td>232.7</td>
<td>231.7</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>251.1</td>
<td>245.8</td>
</tr>
<tr>
<td>Heat recovery</td>
<td>92.5</td>
<td>92.5</td>
<td>92.8</td>
</tr>
<tr>
<td>Recompression duty (power demand, kW)</td>
<td>51.9</td>
<td>51.8</td>
<td>51.9</td>
</tr>
</tbody>
</table>

The recompression duty and the heat sources are presented in Table 7.21 for the optimised designs. Compared with the base case, the heat integration enhances the system performance in two ways: (1) the condenser duty is reduced, and (2) the hot utility is eliminated. Compared to the heat-integrated base case, the economic
analysis shows that total power demand is not significantly reduced because of the recompression and cooling which is required by the permeate stream.

The comparison of costs for Case 3 is presented in Figures 7.20 and 7.21. It can be seen that the refrigeration power cost is the dominant cost, representing 66% of total operating cost. The cost of refrigeration (the cost of electricity plus the cost of cooling water) represents 76% of the total operating cost. Figure 7.21 shows that the utility costs are slightly reduced with the increase in selectivity.

Figure 7.20: Comparisons of the utility costs of various configurations: heat-integrated conventional column (base) and heat-integrated sequential hybrid system with different membrane types (ILM, Pebp and Pebax® 2553)

Figure 7.21: Influence of membrane selectivity on optimal total operating cost of the sequential hybrid system.
7.5.3.1 Summary of Case 3

The influences of membrane selectivity on the sequential hybrid separation performances are examined. As the selectivity increases, the optimum permeate purity of the fast permeating component is slightly increased. The optimal stage cuts are similar (approximately 0.63) and the permeate pressures are equal to the upper bound (8 bar) for all types of membranes.

It can be concluded from Case 3 that the membrane with the highest selectivity may not be the best option for improving the energy performance of the hybrid separation system. Nevertheless, high permeance membranes can be useful for reducing the membrane area requirement, as reported in Table 7.20.

Membrane feed temperature is an important parameter affecting the energy consumption of the whole separation system. This factor has not been optimised in the previous cases. To illustrate the advantages and capability of the proposed design and optimisation approach for the optimisation of feed temperature, Case 4 is introduced.

7.5.4 Case 4: Optimisation of membrane feed temperature and operating variables of sequential hybrid flowsheet

The same product purities, column feed specifications and cost data that have been used in Case 1 is used here; these are summarised in Tables 7.4 and 7.6. In Case 4, the membrane temperature is a design variable; the design objective is to minimise the total operating cost. It is assumed that all the membrane streams are vapour. The lower bound of the membrane feed temperature is selected to be –19.05°C, which is the dew point temperature of the feed stream. The results of Case 4 are compared with these of Case 2 in which the membrane feed temperature is set fixed to 23°C.

Comparing the results of Case 4 with these of Case 2, a lower recompression power and condenser duty is achieved when the membrane temperature is reduced to –2.45°C. The reduction of condenser duty is caused by the reducing the permeate molar flow rate and the retentate stream temperature. In Table 7.22, it can be seen that the optimal retentate temperature is –11.44°C, which is the dew point
temperature of the retentate stream. In the column, the separation will not start until
the feed streams become saturated. Saturating the feed in the column increases the
condenser duty and the operating cost of separation.

Table 7.22: Optimisation results of the heat-integrated sequential hybrid separation—
membrane unit

<table>
<thead>
<tr>
<th>Optimised variables</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage cut</td>
<td>0.6</td>
</tr>
<tr>
<td>Permeate mole fraction, C₂H₄</td>
<td>0.7781</td>
</tr>
<tr>
<td>Retentate mole fraction, C₂H₄</td>
<td>0.1829</td>
</tr>
<tr>
<td>Permeate pressure, bar</td>
<td>8</td>
</tr>
<tr>
<td>Membrane feed temperature (°C)</td>
<td>-2.45</td>
</tr>
<tr>
<td>Membrane retentate &amp; permeate temperature (°C)</td>
<td>-11.44</td>
</tr>
</tbody>
</table>

Note that reducing the membrane temperature to −19.05°C reduces the condenser
duty to 456 kW and the total operating costs of the process to 76,000 £/y. An
implication of this decrease of temperature is that the retentate will be partially
vaporised. The generation of a two-phase mixture contradicts the assumptions
proposed for the membrane vapour separation.

Table 7.23: Optimised process stream data for Case 4

<table>
<thead>
<tr>
<th>Stream</th>
<th>Type</th>
<th>Tᵢn (°C)</th>
<th>Tᵢout (°C)</th>
<th>Q (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate cooler 1</td>
<td>Source</td>
<td>54.75</td>
<td>30</td>
<td>21.98</td>
</tr>
<tr>
<td>Permeate cooler 2</td>
<td>Source</td>
<td>30</td>
<td>-24.34</td>
<td>49.60</td>
</tr>
<tr>
<td>Column condenser</td>
<td>Source</td>
<td>-29.205</td>
<td>-29.212</td>
<td>465.78</td>
</tr>
<tr>
<td>Membrane heater</td>
<td>Sink</td>
<td>-19.06</td>
<td>-2.450</td>
<td>27.51</td>
</tr>
<tr>
<td>Column reboiler</td>
<td>Sink</td>
<td>-7.945</td>
<td>-7.891</td>
<td>339.37</td>
</tr>
</tbody>
</table>

A summary of the stream data for the process is given in Table 7.23. Figure 7.23
and Table 7.24 summarise the results for the determination of the optimum heat
source loads of the sequential hybrid scheme. The column of the hybrid system has
92 stages, with the permeate feed on stage 45 and the retentate feed on stage 65
(from the top of the column). Comparing the conventional column (Figure 7.22) with
the hybrid scheme for the heat integration option, the hybrid scheme reduces the
condenser duty (34% relative reduction compared to the conventional base case).
However, the hybrid scheme has energy requirements for recompressing the permeate and cooling. Clearly, less power is required for recompressing and cooling the permeate stream in Case 4 compared to Case 2. This is because the permeate stream is colder and the fraction of feed permeated is lower (see Table 7.15), which results in more savings in power consumption compared to the conventional column and to the hybrid scheme of Case 2.
Table 7.24: Optimised heat loads and recompression duty for Case 4

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>Type of exchange</th>
<th>Duty (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td>490</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>224</td>
</tr>
</tbody>
</table>

**Sequential hybrid case**

<table>
<thead>
<tr>
<th>Heat exchange</th>
<th>Type of exchange</th>
<th>Duty (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process-to-process</td>
<td>Indirect heat exchange</td>
<td>250</td>
</tr>
<tr>
<td>Process-to-cooling water</td>
<td>Indirect heat exchange</td>
<td>225</td>
</tr>
<tr>
<td>Heat recovery</td>
<td></td>
<td>62</td>
</tr>
<tr>
<td>Recompression duty</td>
<td></td>
<td>44</td>
</tr>
</tbody>
</table>

It may be seen in Table 7.25 that opportunities to reject heat from the refrigeration cycle to the process (at low temperatures) can reduce the compression shaft work by 6%.

Table 7.25: Economic performance of Case 4 (With heat integration)

<table>
<thead>
<tr>
<th>Cases</th>
<th>Power, MW</th>
<th>TOC, £/y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional column</td>
<td>0.220</td>
<td>83,000</td>
</tr>
<tr>
<td>Sequential hybrid scheme</td>
<td>0.207</td>
<td>78,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Saving % relative to distillation</th>
<th>6</th>
</tr>
</thead>
</table>

7.5.4.1 **Summary of Case 4**

The results obtained in Case 4 show the advantages of optimising the membrane feed temperature. It can be seen that the optimisation of membrane feed temperature, and the corresponding retentate temperature, reduces the total operating cost of the separation process by 6%. Figure 7.24 summarises the percentage of utility costs for Case 4.

Figure 7.24: Total operating costs of heat-integrated sequential hybrid system
7.5.5 Case studies conclusions

In this section, case studies are presented to illustrate the implementation of the proposed approach to the design and optimisation of the ethylene-ethane separation. Various design options such as sequential and parallel hybrid schemes are optimised and compared. Case studies show that the heat-integrated hybrid membrane-distillation systems could result in less power savings than expected, as compared to the heat-integrated conventional case.

The comparison of the systems’ performances indicates that placing the membrane in parallel to the column gives the best performance in terms of net power demand and total operating cost savings. The case studies show that the heat-integrated parallel hybrid system could reduce operating costs by up to 11%, compared to the heat-integrated conventional case. Membrane feed composition, flow rates, stage cut and permeate pressure are key degrees of freedom that can be manipulated for greater cost savings.

The optimised sequential heat-integrated hybrid system shows a reduction in total operating costs of around 4% compared to the heat-integrated conventional case. These savings can be increased to up to 6% by optimising the membrane feed temperature.

It is seen that the net power saving is minor when the membrane selectivity is increased. This is because the permeate purity is slightly changed at the optimum permeate pressures and stage cut values which were similar for all types of membrane. It seems that the permeate purity reaches a plateau above 40 membrane selectivity. Therefore, for the given membrane feed mole fraction, which is 0.54 for ethylene, a highly selective membrane will not improve the energy performance of the separation system. However, a membrane with some selectivity is still necessary to get benefit from hybrid separation system.

7.6 Conclusions

In this chapter, an optimisation framework is developed and employed to design and optimise hybrid membrane-distillation separation processes. Since heat integration between separation process and refrigeration system could bring benefits
to the process, it has been considered in the approach. To solve the optimisation problem, a pattern search method is used. Regarding its performance, a pattern search algorithm with a GPS positive basis NP1 poll method is shown to be competitive when compared to Simulated Annealing. This conclusion is drawn from the comparison of the results of the two optimisation algorithms for the ‘parallel’ hybrid membrane-distillation optimisation process (see Section 7.4.3).

In Section 7.2, key design variables are identified by sensitivity analysis and their impacts on the performance of the separation system are examined. It is found that, as the column pressure increases, the condensing temperature, the number of stages, reflux ratio and column duties increase, but the refrigeration power demand decreases. Therefore, all optimisations are carried out at a fixed pressure of 20 bar. By considering heat integration, the net power demand is reduced, compared with non-heat-integrated cases. In the hybrid cases, it can be seen that the condenser duty reduces with lower permeate pressure. A lower permeate pressure results in a higher permeate purity and reduces the membrane area but increases total power demand. Also, permeate compression shaft work increases as the permeate flow increases, whereas refrigeration power demand has a minimum point at stage cut of approximately 0.6. The optimal pressure ratio (ratio of permeate pressure to feed pressure) is between 0.34 and 0.4. Increasing the pressure ratio above this range is not found to improve system performance because the refrigeration power is high (note that the condenser duty increases as the permeate pressure increases, as shown in Figure 7.4 (a)). In addition, the membrane area increases as the permeate pressure increases (see Figure 7.2(b)). Moreover, it is found that the condenser duty is minimised when membrane feed purity and column feed purity are the same.

To demonstrate the performance of the proposed approach, the developed optimisation framework has been applied to four case studies for ethylene-ethane separation. Scrutiny of the results (in Sections 7.5.1 and 7.5.2) confirms that the distillation models used give good predictions compared to rigorous simulation results obtained from HYSYS.

The performance of two hybrid membrane-distillation processes is compared. The parallel hybrid configuration shows better performance than conventional distillation columns in terms of energy savings. The highest operating cost saving is obtained at a stage cut value of 0.6 and permeate pressure of 8 bar. The recompression duty for
the parallel hybrid system is less than that of the sequential hybrid system by 43% (see Tables 7.11 and 7.14).

The facilitated transport membrane can reduce the condenser duty by about 33%. The total operating cost of the parallel hybrid scheme can be reduced by 11% compared to the heat-integrated base case. The main features of the parallel hybrid system are that high purity separation in membrane is not required, and the membrane performs the separation in a purity range where the efficiency of the distillation column is lowest.

The optimisation results of the sequential hybrid system (in Section 7.5.3) show that increasing the membrane selectivity has only a limited effect on reducing the utility cost. A less selective and more permeable membrane requires a smaller membrane area than a highly selective and less permeable membrane. These findings suggest that a super-selective membrane is not required to reduce the energy consumption of the separation system for the given feed purity. However, a different trend could be observed in the higher feed purity of the fast permeating component, as reported by Ploegmakers et al. (2013). This is because the effect of membrane selectivity on the product purity could be significant in this case.

This chapter has conclusively shown that the developed approach is applicable to design and optimisation of hybrid separation systems. The results show that the approach gives good predictions for new designs. A major advantage of the approach is that it provides a systematic, quick method for investigating potential process technologies and design alternatives while taking into account opportunities for heat recovery. The optimisation could be solved in 250 seconds.

Although the approach was mainly applied to ethylene-ethane separation, the design and optimisation framework is still valid and can be applied to other systems such as propane-propylene separation. Also, the approach can be applied to a retrofit design of an existing distillation column to achieve energy reduction.

The shortcoming of the approach is that the capital costs are not included in the objective function. There is a trade-off between the operating costs and the capital costs. In order to have a cost-effective design, total annualised cost should be calculated, something that is proposed as part of future work in Chapter 8.
Chapter 8 Conclusions and Future Work

In this thesis, a novel approach to heat-integrated hybrid separation process design and optimisation has been presented. Distillation and membrane separation in various configurations are explored and key decision variables that influence the separation system performance are identified. In the developed approach, the Modified Fenske-Underwood-Gilliland shortcut method, as proposed by Suphanit (1999), is used to determine the operating parameters of a simple column. For complex columns, the model proposed by Nikolaides and Malone (1987) is used and modified by including energy balances in the calculation of minimum reflux ratio. To design and simulate solid polymer electrolyte membrane, the modelling approach presented by Shindo et al. (1985) is employed. However, this solution method is modified to overcome the sensitivity to initializations, convergence to unfeasible solutions and long computation times. Also, models for the refrigeration system and for heat recovery have been developed and included in the design and optimisation approach. These models are run in MATLAB software connected with HYSYS through an active client-server application for the calculation of thermodynamic and physical properties. This thesis presents the application of the proposed approach for the separation of a binary mixture, particularly an ethylene-ethane mixture. A brief conclusion on the main contributions of this thesis is presented in this chapter together with recommendations for future work.

8.1 Conclusions

Mathematical models for a single-stage membrane separating a multicomponent mixture are modified to attain computational efficiency and to overcome convergence problems that lead to infeasible solutions (i.e., negative mole fraction). A robust computation strategy for solving the membrane model in Chapter 3 (Section 3.3) permits simulation to high stage cuts and low pressure ratios, as well as providing a stable solution within a reasonable time. The maximum absolute error
for permeate mole fraction is 0.4% compared to the numerical reference solution (Shindo et al., 1985). Facilitated transport membranes, particularly immobilized liquid membrane (Teramoto et al., 1986) and solid polymer electrolyte membranes (Pinna and Toy, 2001; Merkel et al., 2007), facilitated with various transport mechanisms are explored. The membrane code developed in this work is flexible, making it possible to choose between different flux models, and is capable of predicting the membrane performance for diverse flow patterns (perfect mixing, co-current, counter-current and cross-flow). This flexibility enables its use in both feasibility studies and comparison of stand-alone membrane unit or hybrid process.

In addition, an approximate analytical method is introduced for cross-flow membrane module that includes two types of transport: solution-diffusion and diffusion of a carrier-solute complex. The analytical solution can be applied for a binary mixture to determine the membrane selectivity and to perform a quick calculation of product purity and recovery. Results reported in Section 3.6.2 show that the prediction of the approximate membrane model regarding the permeate purity is quite good, since the maximum absolute error between the approximate and exact models is 0.3%. In terms of computational efficiency, the algorithm takes less than a second to converge.

The analysis of the membrane results for the ethylene-ethane separation in Chapter 5 confirms, as expected, that a single membrane unit is unable to produce both high product purity and recovery. Therefore, a set of membrane units (membrane systems) needs to be connected in parallel or in series to achieve the desired product specifications.

To design a simple- and multi-feed and multi-product column, a modified shortcut distillation design method is developed in Chapter 4 to provide more accurate predictions of the minimum vapour flow rate than the Underwood method. The vapour flow is only assumed to be constant in the pinch zone, and the minimum vapour flow in the top section of the column is calculated by performing an enthalpy balance. The agreement between rigorous simulations carried out using HYSYS and the modified shortcut method is shown to be satisfactory.
The hybrid system under investigation is a combination of two separation technologies. A large number of configurations can be produced from this combination. In Chapter 5, a systematic process design approach is presented. In the approach, different process options are screened first for feasibility. In this thesis, to eliminate unfeasible hybrid configurations, three heuristics for the hybrid design are proposed based on numerous simulations and sensitivity studies.

- Do not consider a ‘bottom parallel’ hybrid scheme (Figure 5.2 (C)) as a design option if the following limits are not present: the permeate purity is below the column feed purity and the retentate purity is above the bottom product purity of the fast permeating component.
- Do not consider a ‘bottom series’ hybrid scheme (Figure D.3) as a design option if the permeate stream has a mole fraction that is less than the column feed mole fraction for the fast-permeating component. This is because the condenser duty will hardly change.
- If the ‘sequential’ hybrid scheme (single-feed column, Figure 5.4(a)) is considered as a design option, the maximum energy saving is achieved when $\theta \rightarrow \theta_{\text{min}}$. A new relationship derived from mass balance equations around the membrane, column and mixer can be used to find $\theta_{\text{min}}$.

To design and evaluate feasible options (e.g. top, sequential (double-feed column) and parallel hybrid systems), shortcut methods are used. Shortcut methods allow fast evaluation of the separation without the need for detailed information. They are also suitable for optimisation and can be combined with a heat recovery model to reduce the energy consumption of the separation system. In this work, feasible schemes are evaluated with respect to energy efficiency, in particular power consumption of the process and refrigeration compressors (or total operating costs). This evaluation is based on the fact that the cost of energy supply is the dominant cost. Parallel and sequential hybrid flowsheets are shown to be the most competitive configurations, as shown in the results presented in the case study in Chapter 5, with the fraction of feed permeated (stage cut) close to the mole fraction of the faster permeating component. These findings are comparable to the results presented by Pettersen et al. (1996) for propylene-propane separation.
One of the benefits of the proposed design approach is that it provides an accurate prediction for the process performance with less effort than a rigorous simulation. Also, the approach allows either total or partial condensers to be considered as design options. Another advantage is that it is not only taking the design aspect into account, but also opportunities for heat recovery. In the design approach, a heat integration model can be used as an option to identify opportunities to reuse heat rejected by hot streams to heat cold streams, including the use of heat rejected from a refrigeration cycle for process heating and thus reducing the compression power demand of the refrigeration system.

To account for heat integration, the heat recovery model used is a modified version of that proposed by Farrokhpanah (2009). Farrokhpanah applied a matrix-based approach to assessing opportunities for heat integration. However, while the focus of her work was the synthesis and optimisation of refrigeration systems in this work, a simple model for the refrigeration system is used to predict the coefficient of performance of the refrigeration system and the cost of indirect heat exchange (i.e., heat exchange between the separation process and the refrigeration system). A major advantage of the heat recovery model is its ability to predict accurately minimum utility and power requirements within very short time (Elapsed time is 2.4 s) without the need for refrigeration design.

Chapter 6 discusses a simple refrigeration model developed to reduce the modelling complexity. The refrigeration model is developed by simulating the refrigeration performance predicted using HYSYS and then regressing the data (the actual coefficient performance and the ideal coefficient performance) via EXCEL. Simplified linear models are found to be adequate for representing the refrigeration cycle performance for a range of operating conditions. The refrigeration model makes it possible to determine the actual refrigeration power demand as a function of the ideal (Carnot) performance of the refrigeration cycle. The benefits of the new approach is that, not only it is easy to implement the model in the design and optimisation framework for evaluating the refrigeration power demand, but also the model can be applied over a wide range of temperatures and can therefore accommodate the needs of diverse separation processes efficiently. However, detailed design of the refrigeration cycle cannot be achieved.
In chapter 7 sensitivity analysis is performed to identify the key parameters which affect the parallel hybrid flowsheet performance. Results from sensitivity analysis in Section 7.2 demonstrates that an increase in permeate pressure increases the condenser duty but reduces the recompression power demand of the permeate stream. It has been seen that the condenser duty when the permeate pressure is set to 1 bar can be reduced to 44%, while in the case of a permeate pressure of 8 bar, this reduction in the condenser duty is about 33%. However, the permeate recompression duty at 8 bar (0.025MW) is higher than that at 1 bar (0.111 MW) by 77%. This accomplished by a stage cut of 0.6 and membrane feed flow rate of 50 kmol/h. It should be noted that the total operating cost is not significantly reduced by increasing the permeate pressure above 6 bar and by increasing the side draw flow rate above 70 kmol/h. Moreover, the condenser duty is minimised when membrane feed composition and column feed composition are the same (\(y_{\text{C2H4}} = 0.54\)).

An optimisation framework is introduced in Chapter 7 to evaluate and optimise various hybrid flowsheets. The optimisation problem is formulated as a nonlinear constrained problem, where the objective is to minimise the total operating cost of the separation flowsheets. The design variables, such as the permeate pressure, stage cut, side draw molar flow rate and membrane feed purity are treated as a continuous variables. The optimisation problem is solved by a direct search method (the pattern search method) to speed up the computation time. The pattern search method is found to be efficient and relatively accurate compared to a stochastic optimisation algorithm (Simulated Annealing). The maximum difference between the optimal solution (total operating costs) found by Simulated Annealing and pattern search is 0.25%, which is acceptable.

Case studies are presented in order to demonstrate the performance of the synthesis and optimisation approach in this work. Schemes that apply a membrane in parallel to or in sequential to a distillation column are examined. The economic energy evaluation shows that the parallel configuration hybrid system is the best scheme compared to the base case. An 11% decrease in total operating cost is obtained compared with the conventional column, which indicates that the hybrid system is a possible alternative technology for reducing energy consumption. However, long life and stable membrane material with good performance are needed.
to make the application practical. Polymer membranes do not have high selectivity while facilitated transport membranes are selective but not stable, as explained in Chapter 2 of this thesis. Facilitated transport membranes use a carrier (e.g., silver ions) to facilitate the transport of olefin across the membrane. If the membrane feed stream contains trace elements of H$_2$S or C$_2$H$_2$, the membrane can be damaged, and regeneration of silver-containing membranes is difficult (Merkel et al., 2013). In addition, silver ions are prone to reduction, thereby reducing the membrane selectivity as no enough silver ions will be available to facilitate olefin transport.

The results presented in Case Study 4 show that the membrane feed temperature is an important design variable and its influence on energy performance should not be ignored in the conceptual design stage. Optimising the membrane feed temperature of the heat-integrated sequential hybrid scheme increases the total operating cost saving by 6%, compared with the heat-integrated conventional case. Case studies demonstrated that the refrigeration power cost is the dominant cost. Refrigeration power cost (the cost of electricity) represents 66 to 70 % of total operating cost while the recompression cost represents 19 to 20% of the total operating.

### 8.2 Future Work

The following recommendations are made for future work:

In this thesis, a membrane separation system, either as standalone or coupled with distillation, was examined for ethylene-ethane separation. It would be interesting to explore the economic viability of multistage or recycled membrane systems, which can provide high product purity and recovery simultaneously. Also, as a future direction, it is suggested to assess other membranes, e.g., Chitoson based Imex membrane (Hamza et al., 2013) and Carbon Molecular Sieve membranes (Xu et al., 2012 and Rungta et al., 2013), which are still under development. These membranes have been reported to be stable at high feed pressure up to 1000 psi and have a reasonable selectivity for C$_2$H$_6$/C$_2$H$_4$ separation (Rungta et al., 2012). The influence of pressure drop along the membrane, Joule Thomson effect (the temperature change in membrane module), service life, and sensitivity to contamination on the membrane separation performance should also be examined.
The present methodology optimises different degrees of freedom for various hybrid configurations in order to minimise total operating cost. Future work could be carried further, taking into account the capital cost investment, and capturing trade-offs between total operating cost and total capital cost.

The design and optimisation framework developed in this thesis can be used to analyse other separation systems that could have possible hybrid applications, such as propane-propylene, and hydrogen separation in the ethylene separation processes. Another desirable area of extension to the present work would be to apply the approach to retrofit design options and to extend the approach to consider multicomponent mixtures. An additional future research direction could be to consider other separation options such as adsorption, absorption and reflux exchangers (i.e. dephlegmators), or base cases with an industrial configuration.
References


Baldus and Tillman, 1986. Conditions which need to be fulfilled by membrane systems in order to compete with existing methods of gas separation. The Proceeding of the Fourth BOC Priestley Conference, Royal Society of Chemistry, 26-29.


Liu, J., 2012. Predicting the Products of Crude Oil Distillation Columns. MPhil Thesis, the University of Manchester, UK.


References


APPENDIX A

Calculation of Facilitated Transport Membrane Selectivity

This appendix illustrates the derivation of a correlation to predict the selectivity of Immobilized Liquid membrane presented in Chapter 3 (Section 3.6.1) for the separation of a binary gas mixture (ethylene-ethane).

In case of fast, instantaneous ethylene-silver reaction and thermodynamic equilibrium between the product and reactant species at the boundaries along the entire membrane and for a negligible mass-transfer resistance, the transport fluxes can be described by (Teramoto et al., 1986):

\[
N_A = P\gamma_{A,P} = A_M \frac{\varepsilon}{\tau} \overline{P_M} M A P_{A,F} - y_{A,P} P_P + \frac{\varepsilon A_M D_c H_A C K_{eq}}{\tau \delta} \left[ \frac{x_{A,R} P_F}{1 + K_{eq} H_A x_{A,R} P_F} - \frac{y_{A,P} P_P}{1 + K_{eq} H_A y_{A,P} P_P} \right] \tag{A.1}
\]

\[
N_B = P\gamma_{B,P} = A_M \frac{\varepsilon}{\tau} \overline{P_M} B P_{B,F} - y_{B,P} P_P \tag{A.2}
\]

Where \( N \) is the flux of component \( A \) (ethylene) or \( B \) (ethane), \( P_F \) is the membrane feed pressure; \( P_P \) is the membrane permeate pressure; \( x \) is the mole fraction of component \( A \) or \( B \) at the feed side; \( y \) is the mole fraction of component \( A \) or \( B \) at the permeate side; \( A_M \) is the membrane area; \( \overline{P_M} \) is the permeance of component \( A \) or \( B \); \( \varepsilon \) is the membrane porosity; \( \tau \) is the membrane tortuosity; \( \delta \) is the membrane thickness; \( H_A \) is Henry’s coefficient of component \( A \); \( D_c \) is the diffusivity coefficient of the complex; \( K_{eq} \) is the equilibrium constant; \( C \) is the molar concentration of the silver-ethylene complex in the membrane.

An overall mole balance is

\[ 1 = y_{A,P} + y_{B,P} \tag{A.3} \]

\[ x_B = 1 - x_A \tag{A.4} \]

The separation factor (\( \alpha_{AB} \)) can be defined as (Seader and Henley, 1998):

\[ \alpha_{AB} = \left( \frac{y_{A,P}}{x_A} \right) \left( \frac{y_{B,P}}{x_B} \right) = \left( \frac{y_{A,P}}{x_A} \right) \left( \frac{1 - y_{A,P}}{1 - x_A} \right) \tag{A.5} \]
Rearranging equation A.5 yields

\[ x_A \alpha_{AB} = \frac{y_{A,P} \cdot y_B}{y_{B,P}} \]  
(A.6)

\[ y_{P,A} = \frac{x_A \alpha_{AB}}{1 + x_A (\alpha_{AB} - 1)} \]  
(A.7)

The ratio of \( N_A \) to \( N_B \) gives

\[ \frac{y_{AP}}{y_{BP}} = \frac{P_{MA}(x_{AP} - y_{AP} \cdot p_p) + \frac{D_{CH_A} C^C K_{eq}}{\delta} \left[ \frac{x_{AP}}{1 + K_{eq} H_A x_A P_F} - \frac{y_{AP} \cdot p_p}{1 + K_{eq} H_A y_{AP} P_P} \right]}{P_{MB}(x_{BP} - y_{BP} \cdot p_p)} \]  
(A.8)

Equation A.8 can be rearranged to obtain an expression for \( \alpha_{AB} \) in terms of the pressure ratio, \( \gamma = \frac{P_F}{P_p} \), and the mole fraction of A on the feed or retentate side of the membrane. Combining A.5 and the definition of \( \gamma \) with A.8:

\[ \alpha_{AB} = \frac{P_{MA}}{P_{MB}} \left( \frac{x_B}{y_{B,P} - \gamma} \right) \]  
(A.9)

Combine A.4, A.6, A.7 and A.9 to obtain

\[ \alpha_{AB} = \frac{x_A (\alpha_{AB} - 1) + 1 - \alpha_{AB} \gamma + \frac{D_{CH_A} C^C K_{eq}}{\delta P_{MA}} \left[ \frac{x_A (\alpha_{AB} - 1)}{1 + K_{eq} H_A x_A P_F} - \frac{\alpha_{AB} \gamma}{1 + K_{eq} H_A y_{AP} P_P} \right]}{1 - \gamma + x_A (\alpha_{AB} - 1)} \]  
(A.10)
APPENDIX B

The Calculation of the modified Minimum Reflux Ratio of a Simple Column

This appendix provides the logic diagram for minimum reflux calculations for a binary mixture.

Input
- Number of components = 2
- Feed specifications (pressure, temperature, purities)
- Product purities
- Light and heavy key component

Calculate \( R_{\text{min}} \) (\( L_u/D \)) using the Underwood equations (2.28) & (2.29)

Iterate to estimate a new root for the Underwood equation (2.28)
\[ 0 < \vartheta < 1 \]

Calculate vapour & liquid mole fractions and their enthalpies at the rectifying pinch using equations (4.6), (4.7) & (4.14)

Total condenser
- \( x_{v,D} = x_{v,L} = y_{v,V} \)

Partial condenser
- \( x_{v,D} \neq x_{v,L} \neq y_{v,V} \)

Calculate top vapour & liquid purities (envelope 1 in Figure 4.1) and their enthalpies (equation 4.14)

Calculate the modified minimum reflux ratio using equation (4.13)

Output
- Minimum reflux ratio
APPENDIX C

Interface Code for The Calculation of Thermo-Physical Properties

Example: Calculation of Enthalpy, temperature and relative volatility of a binary mixture

The example illustrates the calculation of the enthalpy of a saturated vapour mixture having 46 mol% ethane and 54 mol% ethylene. The pressure of the stream is 20 bar.

The method involves the following steps:

1. Start HYSYS with only one active file and flowsheet. Specify the components in HYSYS and select fluid property package (Soave-Redlich-Kwong in this example)
2. Create a material stream (named ‘FEED’). The pressure, vapour fraction and purities of this stream are provided by MATLAB.
3. Create a spreadsheet (named ‘SPRDSHT’). This spreadsheet is used for receiving mole fractions of the stream from MATLAB and sending them to the material stream created in the previous step.
   a) The mole fractions of the stream sent from MATLAB will be stored in cells A1 (for ethane) and A2 (for ethylene).
   b) Define the values in cells B1 and B2 to be equal to those in cells A1 and A2, respectively.
   c) Make connections between cells B1 and B2 and mole fractions of the material stream created in step 2 using ‘Exported Variables’ in ‘Connections’ top of the spreadsheet

MATLAB Code

```matlab
% Specify number of component (n), stream pressure (P), vapour fraction (q) and the molar composition of mixture ([xf]).
%function [alphF, H_FEED, TempF] = fun(n, P, q, xf)
```
Appendix

```
hy = actxserver('HYSYS.Application'); %Start the MATLAB-HYSYS communication
hyActive = hy.ActiveDocument; % Active the HYSYS document and flowsheet
hyActive.Visible = 1;
hyFlowsheet = hyActive.Flowsheet;
hySolver = hyActive.Solver; % Connect to HYSYS solver
hSprd = hyFlowsheet.Operations.Item('SPRDSHT'); % Link to the spreadsheet 'SPRDSHT'

hCellB1 = hSprd.Cell('A1'); %Link to cells A1 and A2 in 'SPRDSHT'

hCellB2 = hSprd.Cell('A2');

hFEED = hyFlowsheet.Streams.Item('FEED'); % Link to the material stream 'FEED'

hSolver.CanSolve = 0; % Turn HYSYS Solver off

% Delete the current values in cells B1 and B2
hCellB1.Erase;

hCellB2.Erase;

% Delete the current values of the vapour fraction and pressure of the material stream 'FEED'

hFEED.VapourFraction.Erase;

hFEED.Pressure.Erase;

% Set the mole fraction of components as given by xf
hCellB1.CellValue = xf(1);

hCellB2.CellValue = xf(2);

hFEED.Pressure.SetValue(P,'bar'); % Set the pressure of 'STREAM' to P

hFEED.VapourFraction.SetValue(q); % Set the vapour fraction of 'STREAM' to q

hSolver.CanSolve = 1; % Turn HYSYS Solver on

hFluid = hFEED.DuplicateFluid; % Define 'hFluid' to use for retrieving phase equilibrium data

H_FEED = hFluid.MolarEnthalpyValue; %Get the molar enthalpy of given phase % (kJ/kmol)

TempF = hFluid.TemperatureValue; %Get the stream temperature (C)

% Get the liquid & vapour equilibrium compositions
```
XFE = hFluid.LightLiquidPhase.MolarFractionsValue;
YFE = hFluid.VapourPhase.MolarFractionsValue;

% calculate K value for the stream
HK = 1; % set the arrangement of heavy key from the total number of component
to be 1 (ethane)
LK = 2; % set the arrangement of light key from the total number of component to
to be 2 (ethylene)
for i = 1:n
  K_VALUE(1,i) = YFE(i)/XFE(i);
end
HK_VALUE = K_VALUE(1,HK); % K value for the heavy key component
% LK_VALUE = K_VALUE(1,LK); % K value for the light key component
% calculate relative volatility value for the stream
for i = 1:n
  ALPHA(1,i) = K_VALUE(1,i)/HK_VALUE;
end
alphF = ALPHA(1,:);

Results

<table>
<thead>
<tr>
<th>Component</th>
<th>K-value</th>
<th>Relative volatility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.825</td>
<td>1</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.221</td>
<td>1.479</td>
</tr>
<tr>
<td>Molar enthalpy, kJ/k mol</td>
<td>$-1.437 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>-19.06</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX D

Analysis of Bottom Hybrid Membrane-Distillation System

This appendix provides the feasibility analysis of the bottom hybrid separation process option discussed in Chapter 5 (Section 5.2.2).

Bottom parallel hybrid configuration

A bottom parallel hybrid configuration is shown in Figure 5.2 (c). The product purity in this configuration should meet the following constraints: the permeate purity is below the column feed purity and the retentate purity is above the bottom product purity of the fast permeating component.

To illustrate the feasibility of this separation, consider the separation of a close-boiling binary mixture (ethylene-ethane). The column feed is containing a 0.54 mole fraction of ethylene. The overhead product purity is 99.9 mol% of ethylene and the bottoms product purity of ethane is 99.5 mol%. Table D.1 lists the facilitated transport membrane properties of the solid polymer electrolyte membrane. Representation values for membrane feed mole fraction of ethylene are taken as 0.5, 0.4, 0.3 and 0.2. Cross-flow is assumed for the membrane.

Table D.1: Membrane properties

<table>
<thead>
<tr>
<th>Membrane feed pressure (bar)</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane permeate pressure (bar)</td>
<td>1.01</td>
</tr>
<tr>
<td>Membrane retentate pressure (bar)</td>
<td>20</td>
</tr>
<tr>
<td>Permeability of C\textsubscript{2}H\textsubscript{4} (mol m s\textsuperscript{-1} m\textsuperscript{-2} Pa\textsuperscript{-1})</td>
<td>\texttimes\textsuperscript{0.3}\times10\textsuperscript{-14}</td>
</tr>
<tr>
<td>Membrane thickness (m)</td>
<td>5\times10\textsuperscript{-6}</td>
</tr>
<tr>
<td>Membrane selectivity</td>
<td>54</td>
</tr>
</tbody>
</table>

*Extrapolated data of Pinnau and Toy (2001)*

Membrane simulation results in Figure D.1 shows that the above constraints (\textit{y\textsubscript{P,C2H4} < 0.54 \& \textit{x\textsubscript{R,C2H4} > 0.005}) cannot both be met for the given separation problem for a range of stage cuts and membrane feed purities of ethylene.
Therefore, the ‘bottom parallel’ hybrid membrane-distillation scheme is disregarded for analysis, in this work.

Figure D.2 shows that the membrane area is much lower when the column is lean in the more volatile component and the membrane feed is rich in the fast-permeating component. Note that it is possible to place the membrane above the column feed stage because retentate purity above the column feed purity and permeate purity below the top product purity of the fast permeating component can be achieved.

Figure D.1: Effect of membrane feed composition and stage cut on (a) the permeate purity, (b) the retentate purity and (c) the required membrane area for ethylene-ethane separation. In this case the membrane feed mole fraction of ethylene is less than the column feed purity.
Figure D.2: Effect of membrane feed composition and stage cut on (a) the permeate purity, (b) the retentate purity and (c) the required membrane area for ethylene-ethane separation. In this case the membrane feed mole fraction of ethylene is higher than the column feed purity.

**Bottom series hybrid configuration**

A bottom series hybrid scheme for the ethylene-ethane separation system is shown in Figure D.3.
In this configuration, the retentate stream has the same molar flow rate and purity of the bottom product in the conventional distillation column. A compressor and three heat exchangers are needed. The first heat exchanger is used to heat up the membrane feed stream to avoid condensing the membrane vapour product streams, the compressor and the other two heat exchangers are used to recompress and cool the permeate stream to its dew point temperature. The performance of the bottom series hybrid system for a fixed number of stages, as in the conventional column, is shown in Figure D.4.

Figure D.4: Performance of the bottom series hybrid scheme for the ethylene-ethane separation at \( N = 86 \) for permeate pressure of 1.01 bar.
In this case, two options are exist; the permeate stream may be recycled to the column below or above the column feed stream. When the permeate stream has a mole fraction that is less than the column feed mole fraction for the fast-permeating component, the condenser duty is hardly changed. Note that the condenser duty for the base case (conventional column) is 699 kW. A significant change on the condenser duty is observed when the permeate stream has a mole fraction that is higher than the column feed mole fraction for the ethylene. This is accompanied by a large membrane flow rate and utility requirements to recompress and cool the permeate stream before being sent back to the column. In this case, any reduction in the condenser duty will be offset by the increase of compression duty and the refrigerant cooling duty. This analysis leads to the conclusion that both of the options will not bring energy saving; therefore, the ‘bottom series’ configuration is omitted.
APPENDIX E

Derivation of Retentate Mole Balance Equation for Sequential Hybrid Membrane-Distillation (Single-Feed Column)

This appendix derives equation 5.3 in Chapter 5.

A material balance and component material balance around the mixer gives:

$$B = B_c + R \quad \text{(E.1)}$$

$$x_{i,B}B = x_{i,Bc}B_c + x_{i,R}R \quad \text{(E.2)}$$

Where $B_c$ is the column bottom product molar flow rate, $B$ is the mixer output molar flow rate, $R$ is the retentate molar flow rate, $x_{Bc}$ is the column bottom product mole fraction, $x_{i,B}$ is the mixer output mole fraction of component $i$ and $x_{i,R}$ is the retentate mole fraction of component $i$.

Dividing equation E.2 by $M$ yields

$$\frac{B}{M}x_{i,B} = \frac{B_c}{M}x_{i,Bc} + \frac{R}{M}x_{i,R} \quad \text{(E.3)}$$

Where $M$ is the membrane feed molar flow rate

A material balance around the column gives:

$$B_c = P - D \quad \text{(E.4)}$$

Where $P$ is the permeate molar flow rate (column feed) and $D$ is the distillate molar flow rate.

Substituting equation E.4 into equation E.3 yields

$$\frac{P}{M}x_{i,Bc} - \frac{D}{M}x_{i,Bc} = \frac{B}{M}x_{i,B} - \frac{R}{M}x_{i,R} \quad \text{(E.5)}$$

A material balance around the membrane gives:
Appendix

\[ M = P + R \quad \text{(E.6)} \]

Incorporating the definition of stage cut (equation E.7) into equation E.8 results:

\[ \theta = \frac{P}{M} \quad \text{(E.7)} \]

\[ \frac{R}{M} = 1 - \theta \quad \text{(E.8)} \]

Substituting equations E.7 and E.8 into equation E.5 and rearranging yields

\[ x_{i,R} = \frac{\theta x_{i,BC} - \frac{D}{M} x_{i,BC} - x_{i,B} \frac{B}{M}}{(\theta - 1)} \quad \text{(E.9)} \]

Writing equation E.9 for ethane gives:

\[ x_{C2H6,R} = \frac{\theta x_{C2H6,BC} - \frac{D}{M} x_{C2H6,BC} - \frac{b_{C2H6}}{M}}{(\theta - 1)} \quad \text{(E.10)} \]

Where \( b_{C2H6} \) is the mixer output molar flow rate of ethane