Integrated and Multi-Period design of Diesel Hydrotreating Process

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INTEGRATED AND MULTI-PERIOD DESIGN OF
DIESEL HYDROTREATING PROCESS

A thesis submitted to The University of Manchester for the degree of
Doctor of Philosophy
in the Faculty of Engineering and Physical Sciences

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ABSTRACT

Hydrotreating processes play a vital role in petroleum refineries to meet the increasing demand of transportation fuels. The recent trends in processing of heavier crudes with higher sulphur contents and more stringent product specifications for cleaner transportation fuels, such as ultra-low sulphur diesel, are resulting in more severe operating conditions and higher hydrogen consumption of hydrotreating processes. In order to carry out any revamp or design projects for improving the performance and efficiency of hydrotreating units molecular kinetic models of hydrotreating reactions may be required to provide detailed and accurate information of the composition and properties of hydrotreating products. The overall hydrotreating process consisting of the hydrotreater, the separation system and the associated heat recovery system need to be modelled on a consistent basis of detailed characterisation of petroleum fractions and the interactions of these individual subsystems with each other and with the refinery hydrogen network handled simultaneously for overall process optimisation.

A molecular pathways level model of diesel hydrotreating reactions using the molecular type and homologous series matrix is employed for prediction of detailed molecular level information of composition and properties of diesel hydrotreating products. The molecular type and homologous series matrix representation of petroleum fractions is a detailed characterisation approach that represents the composition of a stream in a matrix in terms of the carbon number range and compound classes existing in the petroleum fraction. A new strategy is developed for estimation of physical properties of middle distillate and heavy petroleum fractions with molecular type and homologous series matrix representation using group contribution methods.
A delumping methodology is developed for prediction of detailed product composition for distillation processes using Fenske-Underwood-Gilliland method for short-cut calculations of distillation. This methodology helps retain detailed molecular information of composition of diesel hydrotreating process streams and extends the premise of molecular modelling to separation processes such as single stage flash units and distillation.

An Integrated approach for design of diesel hydrotreating process is developed employing the simulated annealing optimisation algorithm. The proposed integrated approach handles the design of reaction, separation, and associated heat recovery system simultaneously to account for all the trade-offs and interactions between these individual sub-systems. A comparison with conventional approach to process design, i.e. sequential evolution of design, illustrates the ability of proposed integrated design approach to obtain overall hydrotreating process designs with minimum total annualised costs.

The multi-period operation of diesel hydrotreating process in response to catalyst deactivation is explored to develop novel optimisation-based methodologies to obtain designs, for heat exchanger networks and refinery hydrogen networks that can remain operable under different operating conditions with minimum total annualised cost. The multi-period heat exchanger network design approach developed in this work is the first implementation of simulated annealing optimisation algorithm for multi-period heat exchanger network design. A novel approach is developed for design of hydrogen networks that can remain operable under multiple modes of operation with minimum total annualised cost. Case studies show that the integrated and multi-period design methods developed in this work not only provide practicable and cost effective overall process designs but may also be used to investigate the effects of changes in operating conditions of individual units on the overall process performance.
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.

Muhammad Imran Ahmad
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NOMENCLATURE

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<tr>
<td>$a$</td>
<td>capital cost coefficient</td>
</tr>
<tr>
<td>$A$</td>
<td>heat transfer area, m$^2$</td>
</tr>
<tr>
<td>AF</td>
<td>annualisation factor</td>
</tr>
<tr>
<td>$A_{max}$</td>
<td>maximum heat transfer area of a heat exchanger, m$^2$</td>
</tr>
<tr>
<td>$A_{MEM}$</td>
<td>membrane area, m$^2$</td>
</tr>
<tr>
<td>$b$</td>
<td>capital cost coefficient</td>
</tr>
<tr>
<td>$B$</td>
<td>exponent for area cost, also used to represent flow rate of bottom product of distillation column</td>
</tr>
<tr>
<td>$c$</td>
<td>coefficient to calculate compression power</td>
</tr>
<tr>
<td>$C$</td>
<td>number of carbon atoms in physical property estimation, also used to represent area cost coefficient for heat exchangers (€/unit)</td>
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<td>$C_{ar}$</td>
<td>fraction of aromatic carbon content in a mixture</td>
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<td>number of alkyl substituent carbon atoms</td>
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<td>$C_f$</td>
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</tr>
<tr>
<td>$DB_O$</td>
<td>number of olefinic double bonds</td>
</tr>
<tr>
<td>$d_{ij}$</td>
<td>molar flow of a component in top product of distillation column</td>
</tr>
<tr>
<td>$d_o$</td>
<td>limiting value of density at an infinite number of carbon atoms</td>
</tr>
<tr>
<td>$DOP$</td>
<td>duration of period</td>
</tr>
<tr>
<td>$E_{a,g}$</td>
<td>activation energy of hydrodesulphurisation reactions in equation 4.19</td>
</tr>
<tr>
<td>$F$</td>
<td>feed flow rate for distillation column, also used to represent flow rate of hydrogen stream (MMscfd or t/h)</td>
</tr>
<tr>
<td>$F^*$</td>
<td>constant flow rate</td>
</tr>
<tr>
<td>$f_{ij}$</td>
<td>molar flow of a component in feed stream</td>
</tr>
<tr>
<td>$F_T$</td>
<td>logarithmic mean temperature difference correction factor</td>
</tr>
<tr>
<td>$F_y$</td>
<td>variable representing a bilinear term i.e. product of flow rate and purity</td>
</tr>
<tr>
<td>$HU_{up}$</td>
<td>upper bound on total hot utility available, kW</td>
</tr>
</tbody>
</table>
$HV$ lower heating value of combustion

$hvk$ group contribution factor for molar enthalpy of vaporisation

$I$ capital cost

$If$ integer variable to identify the existence of equipment or piping

$K$ vaporisation equilibrium ratio in equation 3.17

$K_{ads}$ adsorption constant of coke precursor

$k_{c,o}$ initial activity for catalytic coke formation in equation 4.35

$K_m$ adsorption constant of molecule $m$ in equation 4.9, L/mol

$K_{ni}$ adsorption constant of nitrogen species in equation 4.28

$k_{ni}$ rate constant of hydrodenitrogenation reaction in equation 4.28

$k_{op}$ combined rate parameter in equation 4.9, L/kg$_{cat,s}$

$K_{op}$ equilibrium ratio in equation 4.9

$K_p$ equilibrium constant

$k_t$ rate constant for thermal coke formation

$L$ length of the pipeline between a source and a sink

$L_{g,n}$ permeability of component $n$ through membrane

$Lm_{MEM}$ maximum pressure ratio across membrane

$LWB$ lower bound for composition of a homologous series in equation 2.29

$M.Wt$ molecular weight

$N_{CS}$ number of cold streams

$N_{EQ}$ number of equations in the heat exchanger network model
$N_{HS}$ number of hot streams

$N_{min}$ minimum number of stages at total reflux condition, equation 3.9

$N_{ND}$ number of nodes in the heat exchanger network

$N_{PHX}$ number of process heat exchangers

$N_{R}$ number of theoretical stages in rectifying section in equation 3.14

$N_{S}$ number of theoretical stages in stripping section of distillation column

$N_{SP}$ number of stream splitter-mixer units

$N_{ST}$ number of process streams

$N_{TP}$ number of operating periods

$N_{UHX}$ number of utility heat exchangers

$N_{UT}$ number of utilities

$n$ number of years

$oy$ annual operating hours

$P$ pressure, also used to represent a physical property of a mixture

$P_c$ critical pressure in equation 2.15, bar

$P_{calculated}$ calculated bulk property of a mixture, used in equation 2.26

$pck$ contribution of a molecular group for critical pressure in equation 2.15

$P_{H_2}$ hydrogen partial pressure

$P_{H_2S}$ partial pressure of hydrogen sulphide

$p_{i,j}$ physical constant of a matrix entry of $i^{th}$ row and $j^{th}$ column
*Power* compressor power, kW

*Q* heat exchanger duty, kW

*q* liquid fraction of feed stream at feed stage condition

*R* reflux ratio of distillation column. Also used to represent the radius of diesel hydrotreater in equation 4.44, and universal gas constant

*r*<sub>g</sub> rate of reaction of sulphur compound

*R*<sub>HK</sub> recovery of heavy key component in bottom product

*R*<sub>RI</sub> reactivity index for quantitative structure reactivity correlations in equation 4.41

*R*<sub>ij</sub> recovery ratio of a matrix component of *i*<sup>th</sup> column and *j*<sup>th</sup> row in equation 3.2

*R*<sub>LK</sub> recovery of light key component in top product

*R*<sub>min</sub> minimum reflux ratio

*r*<sub>ni</sub> rate of hydrodenitrogenation reaction in equation 4.28

*r*<sub>op</sub> rate of aromatic hydrogenation reaction in equation 4.9, mol/kg<sub>cat</sub>-s

*R*<sub>PSA</sub> hydrogen recovery in PSA

*SF* flow rate splitting fraction in a stream splitter

*SG* specific gravity at 60 °F relative to water

*T* temperature, °C

*T*<sub>10</sub> true boiling temperature at which 10 % liquid is vaporised, °C

*T*<sub>50</sub> true boiling temperature at which 50 % liquid is vaporised, °C

*T*<sub>95</sub> true boiling temperature at which 95 % liquid is vaporised, °C

*T*<sub>b</sub> normal boiling temperature in equation 2.13, K
tbk contribution of a molecular group for normal boiling temperature in equation 2.13

$T_c$ critical temperature in equation 2.14, K

$TC$ temperature of the cold stream in a heat exchanger, °C

$tck$ contribution of a molecular group for critical temperature in equation 2.14

$TH$ temperature of the hot stream in a heat exchanger, °C

$TMX$ temperature of a stream of a mixer, °C

$TS$ supply temperature of a stream, °C

$TSP$ temperature of a stream of a splitter, °C

$U$ upper bound, also used to represent overall heat transfer coefficient, kW/m².K

$u$ a lower bound. Can be a small positive number

$V_c$ critical volume in equation 2.16, cm³/mol

$vck$ contribution of a molecular group for critical volume in equation 2.16

$V_{min}'$ minimum vapour flow in bottom section of distillation column, equation 3.8

$V_{min}$ minimum vapour flow in top section of distillation column

$V_s$ saturated liquid volume in equation 2.22

$W_c$ amount of coke deposited on catalyst

$W_{c,max}$ maximum amount of coke deposited on catalyst in equation 4.35

$w_{i,j}$ weight fraction of a matrix entry of $i^{th}$ row and $j^{th}$ column in equation 2.28
\( x \)  
mole fraction of a component in liquid phase

\( X \)  
physical constant of a hydrocarbon

\( X_{\infty} \)  
limiting value of a physical property at an infinite number of carbon atoms

\( X_{BC} \)  
bypassed flow rate fraction of the cold stream in a heat exchanger

\( X_{BH} \)  
bypassed flow rate fraction of the hot stream in a heat exchanger

\( X_{\text{cracking}} \)  
yield of light gases in equation 4.29

\( x_{i,j} \)  
mole fraction of a matrix entry of \( i^{th} \) row and \( j^{th} \) column in equation 2.19

\( y \)  
hydrogen purity in volume basis. Also used to represent mole fraction of a component in vapour phase in equation 3.16

\( y^* \)  
constant hydrogen purity

\( Y_A \)  
equilibrium mole fraction of aromatic species

\( Y_{A_{\text{H}}} \)  
equilibrium mole fraction of hydrogenated aromatic species

\( z \)  
existence of process-to-process heat exchanger, also used to represent mole fraction of a component in a feed mixture

\( Z \)  
compressibility factor in equation 3.32, also used to represent length of reactor (m) in equation 4.30 and 4.31, and hydrogen deficiency of a molecule

\( z_{\text{ut}} \)  
existence of utility heat exchanger
## Abbreviations:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH</td>
<td>aromatic hydrogenation</td>
</tr>
<tr>
<td>ASTM</td>
<td>America society of testing and measurements</td>
</tr>
<tr>
<td>CCR</td>
<td>continuous catalytic reformer</td>
</tr>
<tr>
<td>CHPS</td>
<td>cold high pressure separator</td>
</tr>
<tr>
<td>CNHT</td>
<td>cracked naphtha hydrotreater</td>
</tr>
<tr>
<td>CPROC</td>
<td>combined process sink</td>
</tr>
<tr>
<td>CRU</td>
<td>catalytic reformer unit</td>
</tr>
<tr>
<td>DBE</td>
<td>double bond equivalent</td>
</tr>
<tr>
<td>DBT</td>
<td>dibenzothiophene</td>
</tr>
<tr>
<td>DHT</td>
<td>diesel hydrotreater</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>HCU</td>
<td>hydrocracker unit</td>
</tr>
<tr>
<td>HDA</td>
<td>hydrodealkylation unit</td>
</tr>
<tr>
<td>HDM</td>
<td>hydrodemetallation</td>
</tr>
<tr>
<td>HDN</td>
<td>hydrodenitrogenation</td>
</tr>
<tr>
<td>HDS</td>
<td>hydrodesulphurisation</td>
</tr>
<tr>
<td>HEN</td>
<td>heat exchanger network</td>
</tr>
<tr>
<td>HHPS</td>
<td>hot high pressure separator</td>
</tr>
<tr>
<td>HO</td>
<td>olefin hydrogenation</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>ISOM</td>
<td>isomerisation process</td>
</tr>
<tr>
<td>KHT</td>
<td>kerosene hydrotreater</td>
</tr>
<tr>
<td>LHHW</td>
<td>Langmuir-Hinshelwood-Hougen-Watson</td>
</tr>
<tr>
<td>LMTD</td>
<td>logarithmic mean temperature difference</td>
</tr>
<tr>
<td>LP</td>
<td>linear programming</td>
</tr>
<tr>
<td>MILP</td>
<td>mixed integer linear programming</td>
</tr>
<tr>
<td>MINLP</td>
<td>mixed integer nonlinear programming</td>
</tr>
<tr>
<td>MTHS</td>
<td>molecular type and homologous series</td>
</tr>
<tr>
<td>NHT</td>
<td>naphtha hydrotreater</td>
</tr>
<tr>
<td>NLP</td>
<td>nonlinear programming</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>PIONA</td>
<td>paraffins, iso-paraffins, olefins, naphthenes, and aromatics</td>
</tr>
<tr>
<td>PNA</td>
<td>paraffins, naphthenes, and aromatics. Also used to denote poly nuclear aromatics</td>
</tr>
<tr>
<td>PONA</td>
<td>paraffins, olefins, naphthenes, and aromatics</td>
</tr>
<tr>
<td>PSA</td>
<td>pressure swing adsorption</td>
</tr>
<tr>
<td>SA</td>
<td>simulated annealing</td>
</tr>
<tr>
<td>SARA</td>
<td>saturates, aromatics, resins, and asphaltenes</td>
</tr>
<tr>
<td>TAC</td>
<td>total annualised cost</td>
</tr>
<tr>
<td>TBP</td>
<td>true boiling point</td>
</tr>
<tr>
<td>ULSD</td>
<td>ultra low sulphur diesel</td>
</tr>
<tr>
<td>WABT</td>
<td>weighed average bed temperature</td>
</tr>
</tbody>
</table>
Greek letters:

\[ \Delta C_k \] delumping coefficients in equation 3.42

\[ \Delta C_p \] difference of heat capacity of reaction products and reactants as a function of temperature in equation 4.43

\[ \Delta H_r \] heat of reaction in equation 4.31

\[ \Delta H_{\text{ron}} \] standard heat of reaction

\[ \Delta H_{T_0}^0 \] standard enthalpy of formation at \( T_0 \) in equation 4.43

\[ \Delta H_v \] enthalpy of vaporisation, kJ/mol

\[ \Delta H_{a,g} \] heat of adsorption for hydrodesulphurisation reactions in equation 4.20

\[ \Delta U_i \] energy required to isothermally evaporate liquid \( i \) from saturated liquid to ideal gas, equation 2.23

\( \alpha \) relative volatility of a component

\( \gamma \) activity coefficient of a component in liquid mixture

\( \delta \) solubility parameter of a component

\( \theta \) adsorbent selectivity, also used for representing the root of Underwood equation (3.5)

\( \sigma \) catalyst site for hydrogenolysis pathway of hydrodesulphurisation reactions

\( \tau \) catalyst site for hydrogenation pathway of hydrodesulphurisation reactions

\( \Phi \) fugacity coefficient

\( \omega \) acentric factor of a component
Indices:

\(comp\) a compressor between a source and a sink

\(Compv\) a compressor source

\(Compw\) a compressor sink

\(cs\) cold stream of a heat exchanger

\(hs\) hot stream of a heat exchanger

\(i\) process heat exchanger

\(j\) utility heat exchanger

\(k\) heat exchanger

\(l\) stream splitter

\(n\) hot process stream

\(nd\) temperature node

\(ndc\) temperature node on a cold stream

\(ndh\) temperature node on a hot stream

\(o\) cold process stream

\(p\) period of operation

\(pipe\) a pipeline between a source and a sink

\(s\) stage number or temperature interval

\(Sk\) a sink decomposed from a hydrogen consumer

\(SkFixed\) a sink with fixed pressure

\(SkVaried\) a sink with variable pressure
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>a source decomposed from a hydrogen consumer</td>
</tr>
<tr>
<td>SrFixed</td>
<td>a source with fixed pressure</td>
</tr>
<tr>
<td>SrVaried</td>
<td>a source with variable pressure</td>
</tr>
<tr>
<td>st</td>
<td>stream of a splitter</td>
</tr>
<tr>
<td>v</td>
<td>a source in the hydrogen network</td>
</tr>
<tr>
<td>w</td>
<td>a sink in the hydrogen network</td>
</tr>
</tbody>
</table>

**Sets:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMP</td>
<td>set of compressors</td>
</tr>
<tr>
<td>COMPV</td>
<td>set of compressor sources</td>
</tr>
<tr>
<td>COMPW</td>
<td>set of compressor sinks</td>
</tr>
<tr>
<td>CS</td>
<td>set of cold streams</td>
</tr>
<tr>
<td>HS</td>
<td>set of hot streams</td>
</tr>
<tr>
<td>HX</td>
<td>set of heat exchangers</td>
</tr>
<tr>
<td>PHX</td>
<td>set of process heat exchangers</td>
</tr>
<tr>
<td>PIPE</td>
<td>set of pipelines</td>
</tr>
<tr>
<td>SK</td>
<td>set of sinks decomposed from hydrogen consumers</td>
</tr>
<tr>
<td>SKFIXED</td>
<td>set of sinks with fixed pressures</td>
</tr>
<tr>
<td>SKVARIED</td>
<td>set of sinks with variable pressures</td>
</tr>
<tr>
<td>SP</td>
<td>set of stream splitters</td>
</tr>
<tr>
<td>SR</td>
<td>set of sources decomposed from hydrogen consumers</td>
</tr>
<tr>
<td>SRFIXED</td>
<td>set of sources with fixed pressures</td>
</tr>
</tbody>
</table>
SRVARIED set of sources with variables pressures

ST set of streams

TP set of operating periods

UHX set of utility heat exchangers

V set of sources in hydrogen network

Subscripts:

AH hydrogenated aromatic species

ar aromatic compound, also represented by A in equation 4.8 and o in equation 4.9

AS alkyl substituent carbon atoms

c critical property

COMP a compressor which can be decomposed into a sink Compw and a source Compv

E excess value of a variable

feed purifier feed stream

fuel fuel gas system

g sulphur compounds

H₂U hydrogen utility

HK heavy key component in distillation

HV lower heating value of combustion

LK light key component in distillation

M make-up gas
$m$ molecules in molecular type and homologous series matrix, also represented by $s$ in equations 4.30 and 4.31

$MEM_f$ feed stream of a membrane

$MEM_p$ product stream of a membrane

$MEM_r$ residue stream of a membrane

$N$ naphthenic compound, also represented by $p$ in equation 4.9

$n$ n-alkyl carbon atoms

$ni$ nitrogen compounds

$o$ olefin

$P$ purge gas from a hydrogen consumer

$p$ normal paraffin

PIPE pipe

product purifier product stream

$PSA_f$ feed stream of PSA

$PSA_p$ product stream of PSA

$PSA_r$ residue stream of PSA

$R$ recycle gas for a hydrogen consumer

residue residue purifier residue stream
**Superscripts:**

- *: constant flow rate or purity
- $dp$: pressure difference between source and sink is greater than zero
- $I,II$: number of branches in a split stream
- $in$: inlet
- $L$: liquid phase
- $Low$: lower bound
- $Max$: maximum value
- $np$: number of moles of hydrogen required for saturation reaction
- $out$: outlet
- $Up$: upper bound
- $V$: vapour phase
Chapter 1 Introduction

Hydrotreating may be defined as a process to remove environmentally objectionable compounds, such as sulphur and nitrogen containing compounds, from petroleum products by catalytic reactions with hydrogen (Gary and Handwerk, 2001). Hydrotreating processes mainly produce transportation fuels such as gasoline, diesel in refineries. The recent trends in increasing demand for cleaner and more environmentally benign transportation fuels have motivated refineries to revamp existing units and increase hydrotreating capacities. In order to meet the cleaner fuel specifications a framework for design and optimisation of the overall hydrotreating process based on molecular modelling techniques is desired.

1.1 Overview of diesel hydrotreating process

A hydrotreating process consists of three subsystems, i.e. a reactor, a separation system and an associated heat recovery system. A typical diesel hydrotreating process flow sheet is shown in Figure 1.1.
The feed to diesel hydrotreating process is mixed with hydrogen rich gas and heated to the reactor operating temperature. This mixture is fed to the diesel hydrotreater, a fixed bed catalytic reactor. The diesel hydrotreating reactions occurring in the presence of metal-oxide catalyst produce hydrogen sulphide, ammonia, and saturated hydrocarbons as the main products (Gary and Handwerk, 2001). The reactor effluent, consisting of the reaction products and the un-reacted feedstock along with hydrogen, is cooled before being sent to the separation system. The separation system of diesel hydrotreating process consists of high and low pressure flash separation units and a distillation column. There are two high pressure flash separation units namely hot high pressure separator (HHPS) and cold high pressure separator (CHPS). The first high pressure flash separator recovers hydrogen and makes a rough split between light and heavy reaction products. The liquid from this high pressure flash unit is sent to the low pressure separator and then to distillation column for the separation of the final diesel product, taken out as the bottom product of the distillation column (Meyers, 1997).

The vapour from the first high pressure flash separator is cooled and fed to the cold high pressure separator after water injection, in order to absorb hydrogen sulphide, and ammonia. The liquid light hydrocarbon is separated from the vapour and liquid water in the cold high pressure separator and sent to the low pressure separator.
The hydrogen rich gas from this flash unit is sent to the amine unit for further purification i.e. removal of hydrogen sulphide, that was not absorbed in water, through contact with lean amine solution. The hydrogen rich gas after purification is recycled back to the diesel hydrotreater after necessary compression. A fraction of this gas is purged, and fresh hydrogen is mixed with the recycle gas, to avoid build-up of light hydrocarbons and to maintain the desired hydrogen partial pressure in the reactor.

1.1.1 Hydrotreating catalysts

The catalysts employed commercially in hydrotreating processes include cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulphides, and vanadium oxide. Cobalt and molybdenum oxides on alumina are the most widely used catalysts in diesel hydrotreating processes due to the ease of regeneration, resistance to poisoning and selectivity (Gary and Handwerk, 2001).

Nitrogen is usually more difficult to remove from hydrocarbon compounds compared to sulphur and any treatment that reduces nitrogen content to a satisfactory level will usually remove excess sulphur as well (Gary and Handwerk, 2001). For nitrogen removal nickel-molybdenum catalysts supported on alumina are more efficient than cobalt-molybdenum oxides. However, if sulphur removal is the primary objective, then cobalt-molybdenum catalysts can support the hydrotreating reactions at less severe operating conditions with lower hydrogen consumption than nickel-molybdenum catalysts (Gary and Handwerk, 2001).

1.1.2 Operating conditions of diesel hydrotreater

The key operating variables in terms of the performance of a diesel hydrotreater are the operating temperature, hydrogen partial pressure and space velocity, i.e. the number of volumes of reacting mixture reacted per unit time in the reactor (Gary and Handwerk, 2001).
The diesel hydrotreating reactions, such as hydrodesulphurisation and aromatic hydrogenation, are exothermic and cause an increase in the catalyst bed temperature of the reactor. Typically, the weighted average bed temperature (WABT) at the start-of-run, when the reactor is operating with a 100% active catalyst, is 320°C and at the end-of-run, when the catalyst needs replacement due to loss of activity, around 380°C (Sun, 2004). An increase in hydrogen partial pressure results in improved product quality, due to higher conversion of hydrogen saturation reactions, and reduction in coke formation resulting in longer catalyst life (Ancheyta et al., 1999). Space velocity is an indicator of the reaction time and production capacity of the hydrotreater. A decrease in the space velocity favours higher conversion of hydrotreating reactions. However, a decrease in the space velocity decreases the rate of production of a hydrotreating unit. A typical range of operating conditions for a 15000 barrels per day diesel hydrotreater unit with 1.3 wt % sulphur content in a gas oil feedstock is shown in Table 1.1.

<table>
<thead>
<tr>
<th>Average reactor temperature (°C)</th>
<th>&lt; 343</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average reactor pressure, bar</td>
<td>&lt; 42.4</td>
</tr>
<tr>
<td>Average hydrogen consumption, standard cubic feet per barrel</td>
<td>230</td>
</tr>
<tr>
<td>Run length, years</td>
<td>&gt; 2</td>
</tr>
</tbody>
</table>

Table 1.1 Typical operating conditions of diesel hydrotreater (Meyers, 1997)

### 1.1.3 Diesel hydrotreating product specifications

The recent trend in product specifications for diesel and other transportation fuels has been towards cleaner and more environmentally benign fuels with minimal toxic emissions. A major concern regarding the quality of diesel fuel is the sulphur content. Currently ultra-low sulphur diesel regulation, i.e. diesel fuel with a maximum sulphur content of 10 ppm, is enforced in European Union from 2009. Table 1.2 shows the diesel fuel specifications, for European Union under the Auto oil program II, that were planned for 2009 (Bacha et al., 2007) and have been implemented.
### Diesel fuel specifications

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur content (ppm wt)</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Cetane number (minimum)</td>
<td>54-58</td>
</tr>
<tr>
<td>Polynuclear aromatics (wt %)</td>
<td>1-4</td>
</tr>
<tr>
<td>Density, kg/m$^3$ (maximum)</td>
<td>&lt; 830</td>
</tr>
<tr>
<td>Distillation T95 (°C)</td>
<td>&lt; 350</td>
</tr>
</tbody>
</table>

Table 1.2 Diesel fuel specifications under Auto oil program II (Bacha et al., 2007)

#### 1.1.4 Multi-period operation in hydrotreating process

Multi-period operation refers to the periodic change in operating conditions of a process in order to maintain satisfactory performance, and meet the product specifications and market demands. The main reason behind multi-period operation of a diesel hydrotreating process is catalyst de-activation. Catalyst de-activation occurs in a hydrotreater when carbon-containing deposits form on the catalyst surface. In order to compensate for this loss of catalyst activity, the operating conditions of the hydrotreater are changed periodically, i.e. there is a gradual increase in reactor operating temperature from the start-of-run to the end-of-run. Another cause of changing operating conditions in hydrotreating processes is the change in feedstock composition. Such changes are very common as crudes from various sources are processed in refineries. This variation in feedstock may result in a change in the hydrogen consumption of a hydrotreating process.

The multi-period operation of the diesel hydrotreater affects the separation and heat recovery system and therefore the overall performance of diesel hydrotreating process. In order to operate a diesel hydrotreating process efficiently and economically a framework to account for the multi-period operation of a diesel hydrotreater, and the interaction between subsystems of a hydrotreating process is needed. An integrated and multi-period framework for design and optimisation of hydrotreating processes may predict the affects of catalyst de-activation on the conversion of a hydrotreater, and on the performance of the overall hydrotreating
process. Such a design and optimisation framework may help maximise the profit of a hydrotreating process throughout the whole catalyst life.

1.2 Characterisation of petroleum fractions

Characterisation of petroleum fractions is the systematic analysis and representation of composition and properties of petroleum fractions. Characterisation of petroleum fractions is vital for the development of models to understand and improve petroleum refining processes. The level of detail and accuracy of a model to describe and predict the performance of a refinery process depends on the method of characterisation chosen for the petroleum fractions under consideration. The conventional characterisation methods may only broadly classify petroleum fractions and do not provide detailed chemical information required for molecular modelling of refinery processes. In order to cope with increasing environmental concerns and stringent product specifications for cleaner transportation fuels, refinery processes need to be modelled at molecular level to account for detailed reaction chemistry and therefore make accurate predictions of composition and properties of refinery products. In order to allow detailed modelling of refinery processes, only characterisation methods that can provide detailed information of petroleum fractions will suffice.

1.3 Reaction models

Kinetic models for refinery processes may be classified into three types depending on the level of detail employed in characterisation and modelling (Klein et al., 2006). The three different classes of kinetic models are: lumped models, pathways level models and mechanistic models.

Lumped models characterise petroleum fractions in terms of broad physical or chemical lumps such as boiling point cuts or compound classes (paraffins, aromatics and naphthenes etc.). The reaction networks are then constructed using these lumps lacking in fundamental kinetics information. Lumped models cannot be extrapolated to different feedstocks, process configurations and lack the ability to interpret the effects of changes in operating conditions (Klein et al., 2006).
Both pathways level and mechanistic models are more detailed compared to lumped models in terms of characterisation of mixtures. The pathways level models and mechanistic models take into account the detailed reaction chemistry of refinery processes (Klein et al., 2006). Mechanistic models have received considerable attention as a result of advancements in analytical techniques and computational power. Mechanistic models are based on detailed reaction mechanisms including intermediate species and thus consist of fundamental rate parameters. However, due to the large number of species and reactions these models are difficult to solve computationally (Klein et al., 2006).

Molecular pathways level models employ reaction mechanisms in terms of the observed species only, i.e. reactant and products, and not the intermediates. The rate laws are approximate, and require assumptions such as the rate-determining step. However, the resulting models are numerically tractable, compared to mechanistic models, and capture detailed reaction chemistry of refinery processes (Klein et al., 2006). In order to analyse the effect of changes in feedstock and operating conditions on the performance of refinery processes and to make better predictions of properties and molecular level composition of refinery products molecular models are needed.

1.4 Separation modelling and heat recovery system design

Modelling of refinery separation processes, such as distillation and single stage flash separation, is traditionally carried out by lumping petroleum fractions into pseudo-components using bulk properties such as true boiling point and specific gravity. This pseudo-component approach using physical properties, as opposed to the chemical lumps employed in conventional models for reaction systems, makes the two lumping strategies incompatible (Peng, 1999). In order to retain the molecular level information of the reactor effluent obtained using molecular level models for the reaction system, while utilising the existing tools for modelling of separation processes requires a delumping mechanism.
The molecular characterisation methods describe petroleum fractions by taking into account all existing compound classes with a specific range of carbon number i.e. molecular weights of components. However, even these detailed characterisation methods may be classified as fine-grained lumping techniques because of lumping at isomer level as will be discussed in Chapter 2. This lumping at isomer level in molecular reaction models brings back the incompatibility issue of the two different lumping strategies followed for modelling of reaction and separation systems respectively. Therefore, a consistent modelling framework along with requisite lumping and delumping methodologies is needed for integrated design and optimisation of refinery processes.

The heat recovery system of diesel hydrotreating process supports the reaction and separation system by satisfying the heating and cooling requirements of the process streams. In order to develop a framework for overall design and optimisation of hydrotreating processes using molecular modelling techniques we need a mechanism to translate the molecular information obtained using pathways level reaction models to macroscopic thermal properties required for design of heat exchanger networks, i.e. the heat recovery system. The gap between the detailed molecular information, in terms of composition and structure of individual molecules, and bulk physical properties of petroleum fractions such as heat capacities needs to be addressed.

1.5 Refinery hydrogen management

Refinery hydrogen management refers to the optimal allocation of hydrogen between refinery processes that produce hydrogen, namely the catalytic reforming process and hydrogen production plants, and hydrogen consuming processes, such as hydrocracking, hydrotreating, and isomerisation processes. A hydrogen network may be described as a system of these refinery processes interacting with each other through the hydrogen distribution system. The refinery processes operating with hydrogen as a shared commodity constitute the components of a hydrogen network.
The existing tools and methods for design of refinery hydrogen networks assume constant operating conditions of refinery processes. The operating conditions of refinery processes are changing from time to time depending on the feedstock and market demands. Therefore, the hydrogen balance of a given hydrogen network may also vary resulting in changing performance of refinery processes. A framework is needed for design of flexible hydrogen networks, i.e. hydrogen networks that can remain optimally operable under changing operating conditions of refinery processes.

The design and optimisation techniques for hydrogen management minimise the hydrogen utility of a given hydrogen network. A window of opportunity that may require further research is the improvement of performance of hydrogen consuming processes by utilising the hydrogen freed-up using hydrogen management techniques. The hydrogen consumption of refinery processes is bound to keep increasing in this era of cleaner transportation fuels and consequently design approaches are needed that can provide not only flexible hydrogen distribution systems but also optimal utilisation of hydrogen for increasing the overall profit margins of refineries.

1.6 Aims of the research work

In order to meet the increasing demand for cleaner and more environmentally benign transportation fuels, refineries are increasing hydrotreating capacities. Molecular modelling of refinery processes may provide a way forward for design and revamp of hydrotreating processes in this era of cleaner transportation fuels. The aim of this research work is to develop a framework for detailed modelling of the hydrotreating process subsystems, i.e. the reaction, separation system, and associated heat recovery system, to enable the integrated design of diesel hydrotreating process so that the operation of individual subsystems and their interactions may be analysed in the context of performance of the overall process.
Hydrotreating processes are run under multi-period operation where catalyst deactivation in the diesel hydrotreater affects the performance of the separation system, heat recovery system, and the refinery hydrogen network. A multi-period approach is developed for the design of multi-period heat exchanger networks and flexible hydrogen networks that can remain operable under changing operating conditions.

1.7 Structure of thesis

This thesis consists of seven chapters. A brief overview of each chapter is as follows:

Chapter 1

An introduction of diesel hydrotreating processes is presented. Limitations in the research area of modelling of hydrotreating process along with needs for research efforts are identified.

Chapter 2

An overview of various methods of analysis and characterisation of petroleum fractions is presented along with an introduction to the molecular type and homologous series matrix representation of petroleum fractions. The limitations of previous work on molecular type and homologous series matrix characterisation framework are outlined and improvements are proposed for the application of this characterisation approach in modelling of refinery processes.
Chapter 3

Modelling of the separation system of the diesel hydrotreating process is discussed in this chapter. An overview of the existing models and tools is presented and a delumping methodology is developed for prediction of detailed product distribution for separation system of diesel hydrotreating process using short-cut distillation model.

Chapter 4

The molecular model of diesel hydrotreater employed in this work is discussed. A novel integrated approach for design of diesel hydrotreating process is developed. An optimisation framework for the integrated design of diesel hydrotreating process is developed using simulated annealing algorithm.

Chapter 5

This chapter focuses on the design of heat exchanger networks for multiple periods of operation. A review of methodologies for design of heat exchanger networks is presented and a new approach for design of heat exchanger networks for multi-period operation is developed. The new design approach is developed using simulated annealing algorithm for optimisation.

Chapter 6

A novel approach for design of hydrogen networks for multi-period operation is presented to account for the interaction between the diesel hydrotreating process and refinery hydrogen distribution system.
Chapter 7

Finally the conclusions of this research work are presented. Possible improvements and directions for further research work in the area of integrated and multi-period design of hydrotreating processes are identified.
Chapter 2  Characterisation of petroleum fractions

2.1 Introduction

Characterisation of petroleum fractions is the systematic analysis and representation of composition and properties of petroleum fractions. Characterisation methods play an important role in the understanding of physical and chemical behaviour of a petroleum fraction and its individual constituents, and are essential for modelling of refinery processes. In order to comply with the current and future product specifications for cleaner fuels, refineries are employing new processing technologies and more severe operating conditions in existing operating units. Consequently refinery process models should capture the chemistry of conversion processes employing characterisation of petroleum fractions at molecular level.

This chapter presents an overview of the conventional characterisation methods, used for modelling of refinery processes, and introduces the molecular type and homologous series matrix representation, developed by Peng (1999), employed in this work for representation of petroleum fractions. The shortcomings of previous work, on molecular type and homologous series matrix representation, are identified and addressed here. A new strategy is proposed for estimation of physical properties of individual components of the petroleum fractions using group contribution methods.
2.2 Characterisation of petroleum fractions

A petroleum fraction is considered well defined if the composition and structure of all its constituents is known (Riazi, 2005). However, a comprehensive analysis of a petroleum fraction is a very tedious task. For this reason refinery processes have been modelled conventionally using lumped models (Saine Aye, 2003). Some of the most important ways of expressing composition of petroleum fractions, some of which have been used extensively for conventional refinery process models, are (Riazi, 2005):

- PNA (paraffins, naphthenes, and aromatics)
- PONA (paraffins, olefins, naphthenes, and aromatics)
- PIONA (paraffins, iso paraffins, olefins, naphthenes, and aromatics)
- SARA (saturates, aromatics, resins, and asphaltenes)
- Elemental analysis (C, H, S, N, O)

2.2.1 Conventional characterisation methods

Three characterisation methods have been widely used for modelling refinery processes. These are bulk property characterisation, compound class characterisation and average structural property characterisation methods. A brief introduction of these methods for characterisation of petroleum fractions is given here and detailed accounts can be found elsewhere (Zhang, 1999; Saine Aye, 2003).

Bulk property characterisation methods are based on the classification of petroleum fractions in terms of boiling point cuts using bulk properties such as true boiling point curve, density, and API gravity, etc. Commercial simulation packages such as ASPENPLUS, HYSYS (AspenTech), and PROII (Simulation Sciences) make use of these methods to characterise streams in terms of pseudo-components, treating these pseudo-components as real components for simulation purposes.
Compound class characterisation methods are based on chromatographic separation techniques, taking into account the solubility characteristics of the components of a mixture. A typical example of compound class characterisation is the SARA method.

Average structural parameter characterisation methods classify petroleum mixtures on the basis of functional groups or structural parameters such as the number of aromatic rings, carbon/hydrogen ratio in an aromatic structure, weight percentage of carbon atoms in CH₂ groups, etc. Some of the examples of this type of characterisation methods are the Brown-Ladner method (Brown and Ladner, 1960), computer assisted molecular construction (Oka et al., 1977), and functional group analysis by linear programming (Petrakis et al., 1983).

These methods broadly classify mixtures on the basis of existing compound classes or overall characteristics such as bulk properties or average structural parameters and do not provide information about the individual components which has become fundamental to refinery process modelling due to stringent product specifications.

2.2.2 Chemical analysis for characterisation of petroleum fractions

Modern analytical instruments analyse the composition and properties of petroleum fractions at molecular level i.e. providing composition and structural information of individual components of compound classes existing in a mixture. These analytical techniques provide the information expressed systematically in characterisation methods and can be classified into three different categories (Riazi, 2005):

- Chromatographic techniques
- Separation by solvents
- Spectroscopic and spectrometric methods
Gas chromatography is a technique for analysis of petroleum fractions by separating components of a mixture based on volatility of compounds (Riazi, 2005). Gas chromatography is used for detailed analysis of gasoline range, i.e. fractions boiling below 180°C, but has limitations for fractions with high boiling point range due to low volatilities of components (Saine Aye, 2003). Teng et al., (1994) developed a method for detailed analysis of hydrocarbon components of gasoline using gas chromatography with mass spectrometry. Liquid chromatography is typically applied for separation of aromatic compounds according to the number of aromatic rings in heavy petroleum fractions.

The separation by solvents method is based on the solubility of components of a mixture in a particular solvent thereby separating soluble components from insoluble ones. This method is useful for the SARA analysis of heavy petroleum fractions and residues (Riazi, 2005).

The third category of chemical analysis of petroleum fractions is based on identification of individual molecular groups present in a petroleum fraction using spectroscopic or spectrometric methods: In spectroscopic methods, molecules are excited by various sources and returned to their normal state, while in spectrometric methods different molecules present in a mixture are ionised and fragmented for composition analysis (Riazi, 2005). Nuclear magnetic resonance (NMR) spectroscopy is an example of spectroscopic analysis which, combined with elemental analysis, can measure the aromatic and aliphatic carbon, hydrogen distributions and concentrations of various structural groups (Zhang, 1999). Mass spectrometric methods analyse the composition of petroleum fractions based on the molecular weight and chemical structure of the components present in the mixture and provide the most detailed analysis (Riazi, 2005).
These analytical techniques provide information about the composition, structure, and properties of individual components of petroleum fractions and facilitate molecular modelling of refinery processes.

2.3 Molecular type and homologous series (MTHS) matrix representation of petroleum fractions

Peng (1999) proposed a matrix representation to incorporate the composition and structural information of individual components of mixtures available due to modern analytical techniques for chemical analysis of petroleum fractions. The molecular type and homologous series (MTHS) matrix characterisation approach represents the composition of a petroleum fraction in terms of homologous series and carbon number information. The columns of the matrix are the molecular types existing in the petroleum fraction, e.g. paraffins, aromatics, and naphthenes while the rows represent the carbon numbers, i.e. the molecular size of components.

The size of molecular type and homologous series matrix, i.e. the different compound classes forming matrix columns and carbon number range determining the number of rows of the MTHS matrix may vary from one case to another depending on the petroleum fraction represented. Some of the compound classes, used to represent middle distillate diesel fractions in this work, are as follows:

nP, iP: normal and iso-paraffins;

1N, 2N, 3N: naphthenic compounds containing up to three rings, e.g., decalin belongs to the 2N column;

A, 2A, 3A: one-ring to three-ring aromatic compounds: e.g. and are isomers that are both included in the same lump of the 3A column;

AN, AAN, ANA, ANN: compounds containing both naphthenic and aromatic rings, e.g. the AN column contains and ;
A_A, A_AA: biphenyl type compounds, e.g. \( \text{\ding{192}} \text{\ding{192}} \) and \( \text{\ding{192}} \text{\ding{192}} \);

A_N: cyclohexylbenzene, which is important as a hydrodesulphurisation product;

SI, SII, SIII, SIV, SV: sulphur containing compounds:
- SI: mercaptans, e.g. CH\(_3\)SH, C\(_2\)H\(_5\)SH;
- SII: sulphides, disulphides, thiophenes and benzothiophenes, e.g. \( \text{\ding{192}} \text{\ding{192}} \), CS\(_2\), CH\(_3\)-S-C\(_2\)H\(_5\) all belong to this column;
- SIII: dibenzothiophenes not substituted at the 4 or 6 position, e.g. \( \text{\ding{192}} \text{\ding{192}} \);
- SIV: dibenzothiophenes substituted at the 4 or 6 position, e.g. \( \text{\ding{192}} \text{\ding{192}} \);
- SV: dibenzothiophenes substituted at both 4 and 6 positions, e.g. \( \text{\ding{192}} \text{\ding{192}} \);

NI, NII: nitrogen containing compounds:
- NI: basic nitrogen compounds, e.g. pyridine \( \text{\ding{192}} \text{\ding{192}} \) and quinoline \( \text{\ding{192}} \text{\ding{192}} \);
- NII: non-basic nitrogen compounds, e.g. indole \( \text{\ding{192}} \text{\ding{192}} \);

The elements of the matrix may represent the composition of a mixture on molar, weight or volume basis. Each matrix entry represents either a single compound or a lump of structural isomers. Figure 2.1 shows the structure of molecular type and homologous series matrix.
Figure 2.1 Molecular type and homologous series matrix representation of petroleum fractions (Peng, 1999)

<table>
<thead>
<tr>
<th>C_0</th>
<th>C_1</th>
<th>...</th>
<th>...</th>
<th>...</th>
<th>...</th>
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<th>...</th>
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<th>...</th>
<th>...</th>
<th>...</th>
<th>...</th>
</tr>
</thead>
<tbody>
<tr>
<td>nP</td>
<td>iP</td>
<td>1N</td>
<td>2N</td>
<td>3N</td>
<td>1A</td>
<td>AN</td>
<td>ANN</td>
<td>2A</td>
<td>AAN</td>
<td>ANA</td>
<td>3A</td>
<td>4A</td>
<td>SI</td>
<td>SII</td>
<td>SIII</td>
</tr>
</tbody>
</table>

- Columns represent homologous series.
- Rows represent carbon numbers.
- Mass or molar fraction of molecule or isomer lump.
- Sulphur and nitrogen compounds.
For example, the $C_1$, $C_2$, and $C_3$ rows under the nP column in Figure 2.1 represent the composition of methane, ethane, and propane. The first row of the matrix i.e. $C_0$ consists of compounds without any carbon atoms. This row of the matrix captures the information of important inorganic molecules such as Hydrogen ($C_0$, nP), hydrogen sulphide ($C_0$, SI), and ammonia ($C_0$, NI).

The matrix framework lumps all the structural isomers of a particular molecular size into one matrix entry. The reason behind this lumping simplification is that the current analytical techniques provide information of all structural isomers existing in a petroleum fraction for only lower carbon numbers i.e. gasoline range fractions. On the other hand this strategy of lumping structural isomers as one matrix element reduces the complexity of the possible molecular model with around $10^{14}$ molecules to less than $10^3$ matrix components (Peng, 1999).

The analytical techniques introduced in the Section 2.2.2 provide composition analysis for petroleum fractions up to $C_{45}$ (Boduszynski, 1988). Fafet and Magne-Drisch (1995) analysed petroleum fractions in the middle distillate range using a combination of chromatographic and spectrometric techniques. The composition (wt %) obtained from this analysis is shown in Figure 2.2.
Figure 2.2 Composition analysis of middle distillate petroleum fraction (Fafet and Magne-Drisch, 1995)

With this detailed level of analysis, composition can be directly represented in the molecular type and homologous series matrix framework. For example, the composition analysis shown in Figure 2.2 can be represented in the matrix form as shown in Table 2.1 (Peng, 1999). The matrix entries given in Table 2.1 represent the weight percentage of individual components of the middle distillate fraction analysed.
Table 2.1 Molecular type and homologous series matrix representation of composition analysis of Figure 2.2 (Peng, 1999)

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>1N</th>
<th>2N</th>
<th>3N</th>
<th>1A</th>
<th>1A1N6</th>
<th>1A2N6</th>
<th>2A</th>
<th>2A1N6</th>
<th>3A</th>
<th>4A+</th>
<th>SII</th>
<th>SIII</th>
</tr>
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<tr>
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<td></td>
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<td></td>
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<tr>
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<td>0.05</td>
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<tr>
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<td>0.06</td>
<td></td>
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<td>0.05</td>
<td></td>
<td></td>
<td>1.9</td>
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<td>2</td>
<td>0.47</td>
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<tr>
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<td>1.4</td>
<td>0.54</td>
<td>0.34</td>
<td>4.5</td>
<td>1.07</td>
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<td>0.1</td>
<td>1</td>
<td>0.39</td>
<td>0.24</td>
<td>7</td>
<td>1.66</td>
<td>0.5</td>
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<td>0.2</td>
<td>0.5</td>
<td>0.19</td>
<td>0.12</td>
<td>6</td>
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<td>0.19</td>
<td>0.23</td>
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<td>0.5</td>
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<td>0.19</td>
<td>0.12</td>
<td>5</td>
<td>1.19</td>
<td>1.3</td>
<td>0.29</td>
<td>0.28</td>
<td>0.34</td>
</tr>
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<td>0.22</td>
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<td>0.15</td>
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<td>4.2</td>
<td>1</td>
<td>2</td>
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</tbody>
</table>
2.3.1 Molecular type and homologous series matrix generation

The analytical techniques introduced in Section 2.2.2 for the molecular analysis of petroleum fractions can be very expensive and time consuming and are therefore not employed in refining operations (Saine Aye, 2003). In order to avoid experimental measurements for obtaining molecular composition of petroleum fractions, previous researchers have developed methods for generation of molecular composition matrices. The concept of molecular type and homologous series matrix generation, i.e. methods to determine the composition of individual matrix entries without comprehensive chemical analysis, relies on the assumption that properties of a mixture are resultant of the properties of individual components and thus depend on the mixture composition. This assumption implies that if the bulk properties of a mixture and the individual component properties are available then the composition of the mixture can be predicted using representative compound classes of the petroleum fraction under consideration.

Zhang (1999) proposed a method of generation of molecular type and homologous series matrix for composition of petroleum fractions using interpolation of available molecular composition matrices. This method is based on the principle that the molecular composition of a petroleum fraction can be obtained by treating this stream as a blend of several oil streams of known molecular compositions. Saine Aye (2003) generated sample matrices, i.e. composition matrices representative of available chemical analysis information, of various refinery product streams to serve as a database for MTHS matrix generation with interpolation method. The interpolation method for generation of molecular type and homologous series matrices relies on the availability of experimental data from chemical analysis of petroleum fractions. This dependence on experimental data limits the application of this method to only those petroleum fractions for which molecular level chemical analysis is available in literature.
2.3.2 Estimation of physical properties

The aim of molecular modelling of refinery processes is to predict more accurately the performance of hydrocarbon conversion processes and the properties of the resulting product streams. Therefore, methods for estimating physical properties of mixtures are needed for MTHS matrix framework. Zhang (1999) developed a strategy for predicting bulk properties of petroleum streams from the molecular information using molecular structure-property correlations for normal boiling point and density of matrix components. The individual component boiling points and densities are used to estimate the bulk density and boiling point curve of the petroleum mixture. Once the bulk density and boiling point curve of the mixture is obtained desired physical properties are estimated with standard correlations available in the literature.

2.3.2.1 Estimation of component properties

The strategy developed by Zhang (1999) for estimation of bulk properties employs two key properties of components i.e. the normal boiling temperature and density. This section discusses the approach followed by Zhang (1999) for developing molecular structure-property correlations for estimation of normal boiling temperature and density of individual components of petroleum mixtures.

Fisher (1982) developed correlations for boiling temperature of normal paraffins based on the chain length (carbon number) of the molecules:

\[
\frac{C}{T_p} = 0.0116492 + 0.00106924 \cdot C \quad \text{Carbon number 9 – 14} \quad (2.1)
\]

\[
\frac{C}{T_p} = 0.0135703 + 0.000938137 \cdot C \quad \text{Carbon number 15 – 27} \quad (2.2)
\]

\[
\frac{C}{T_p} = 0.0154703 + 0.000866235 \cdot C \quad \text{Carbon number 27 – 40} \quad (2.3)
\]
where \( C \) is the carbon number of n-paraffin and \( T_p (K) \) is the boiling temperature. Another such correlation for estimating boiling temperatures is proposed by Kudchadker and Zwolinski (1966):

\[
\log (1078 - T_p) = 3.03191 - 0.0499901 \times C^{2/3}
\]  

(2.4)

Korsten (1997) extended this approach to other hydrocarbon species based on excess temperature concept. Korsten (1997) observed that the normal boiling points of various hydrocarbon compound classes fall on parallel lines when plotted against the molecular weights. The distance between these lines is expressed as a function of structural parameters such as number of olefinic double bonds as shown in Figure 2.3.

**Figure 2.3 Normal boiling temperatures of hydrocarbons plotted against the molecular weights (Korsten, 1997)**

Korsten (1997) describes hydrocarbon compounds by the structural formula \( \text{C}_n\text{H}_{2n} + Z \), where \( Z \) is the hydrogen deficiency used for classification of homologous series. The boiling temperature of hydrocarbon compounds is calculated using the equation:

\[
T = T_p + T_E
\]  

(2.5)
where $T_E$ is the excess temperature given by (Korsten, 1997):

$$T_E = (2.450 \cdot DBE + 0.53163 \cdot DBE^2) \cdot \Theta_T \quad (2.6)$$

$$\Theta_T = DBE - 2 \cdot DB_O / |DBE - 2 \cdot DB_O| \quad (2.7)$$

where $DB_O$ is the number of olefinic double bonds and $DBE$ denotes double bond equivalent, another structural parameter, given by:

$$DBE = 1 - Z / 2 \quad (2.8)$$

Based on the boiling temperatures estimated using the above equations, Zhang (1999) correlated the boiling points of hydrocarbon homologous series with the associated carbon number. The molecular structure-property correlations developed are of the form:

$$\frac{C}{T} = a + b \cdot C \quad (2.9)$$

where $a$ and $b$ are the coefficients for each homologous series, as shown in Table 2.2.
The molecular structure-property correlations for density developed by Zhang (1999) are of the form:

\[ d - d_0 = a/(b + C) \]  

(2.10)

where \( d \) is the density of the hydrocarbon (g/ml at 20°C), \( a \) and \( b \) are the coefficients for different molecular types, \( d_0 \) is the limiting value of density, and \( C \) is the carbon number. These correlations are based on the approach developed by

<table>
<thead>
<tr>
<th>Molecular type</th>
<th>Coefficients</th>
<th>Carbon number range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>nP</td>
<td>0.0116492</td>
<td>0.00106924</td>
</tr>
<tr>
<td></td>
<td>0.0135703</td>
<td>0.000938137</td>
</tr>
<tr>
<td></td>
<td>0.0154703</td>
<td>0.000866235</td>
</tr>
<tr>
<td>iP</td>
<td>0.010565789</td>
<td>0.001231172</td>
</tr>
<tr>
<td>O</td>
<td>0.01179746</td>
<td>0.00106943</td>
</tr>
<tr>
<td></td>
<td>0.013701933</td>
<td>0.00093431</td>
</tr>
<tr>
<td>1N</td>
<td>0.01150372</td>
<td>0.00106897</td>
</tr>
<tr>
<td></td>
<td>0.013440561</td>
<td>0.000936825</td>
</tr>
<tr>
<td></td>
<td>0.015350833</td>
<td>0.000864554</td>
</tr>
<tr>
<td>2N</td>
<td>0.01131937</td>
<td>0.00106781</td>
</tr>
<tr>
<td></td>
<td>0.013267521</td>
<td>0.000935016</td>
</tr>
<tr>
<td></td>
<td>0.015190967</td>
<td>0.000862273</td>
</tr>
<tr>
<td>3N</td>
<td>0.012992552</td>
<td>0.000935349</td>
</tr>
<tr>
<td></td>
<td>0.014992624</td>
<td>0.000859394</td>
</tr>
<tr>
<td>1A</td>
<td>0.01100208</td>
<td>0.00106741</td>
</tr>
<tr>
<td></td>
<td>0.012988684</td>
<td>0.00093196</td>
</tr>
<tr>
<td></td>
<td>0.014932077</td>
<td>0.000858504</td>
</tr>
<tr>
<td>1A1N</td>
<td>0.01036686</td>
<td>0.00106119</td>
</tr>
<tr>
<td></td>
<td>0.012377015</td>
<td>0.000924613</td>
</tr>
<tr>
<td></td>
<td>0.014358493</td>
<td>0.000849808</td>
</tr>
<tr>
<td>1A2N</td>
<td>0.011549258</td>
<td>0.000917387</td>
</tr>
<tr>
<td></td>
<td>0.013638978</td>
<td>0.000838189</td>
</tr>
<tr>
<td>2A</td>
<td>0.01006504</td>
<td>0.00105827</td>
</tr>
<tr>
<td></td>
<td>0.012089615</td>
<td>0.000920842</td>
</tr>
<tr>
<td></td>
<td>0.014086224</td>
<td>0.000845507</td>
</tr>
<tr>
<td>3A</td>
<td>0.010638163</td>
<td>0.000903088</td>
</tr>
<tr>
<td></td>
<td>0.012758921</td>
<td>0.000822816</td>
</tr>
</tbody>
</table>

Table 2.2 Coefficients for molecular structure-property correlations for boiling temperature (Zhang, 1999)
Smittenberg and Mulder (1948) who proposed to express the physical properties of hydrocarbons belonging to a homologous series in the following form:

\[ X = X_\infty + k l(C + Z) \]

where \( X \) represents the physical constant of a hydrocarbon containing \( C \) carbon atoms, \( X_\infty \) is the limiting value of this physical constant at an infinite number of carbon atoms, \( k \) and \( Z \) are empirical constants characteristic of the homologous series. The coefficients of the molecular structure-property correlations for density of hydrocarbons are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Molecular type</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>nP</td>
<td>-1.31</td>
</tr>
<tr>
<td>iP</td>
<td>-1.3794</td>
</tr>
<tr>
<td>O</td>
<td>-1.1465</td>
</tr>
<tr>
<td>N5</td>
<td>-0.5984</td>
</tr>
<tr>
<td>N6</td>
<td>-0.5248</td>
</tr>
<tr>
<td>2N</td>
<td>0.3072</td>
</tr>
<tr>
<td>3N</td>
<td>1.2827</td>
</tr>
<tr>
<td>1A</td>
<td>0.0535</td>
</tr>
<tr>
<td>1A1N</td>
<td>1.104</td>
</tr>
<tr>
<td>1A2N</td>
<td>1.9403</td>
</tr>
<tr>
<td>2A</td>
<td>1.6746</td>
</tr>
<tr>
<td>3A</td>
<td>2.6937</td>
</tr>
</tbody>
</table>

Table 2.3 Coefficients for molecular structure-property correlations for density of hydrocarbons (Zhang, 1999)

The above molecular structure-property correlations can be used for estimation of normal boiling temperature and density of individual components of a mixture. The estimation of bulk properties of mixtures is discussed in the next section.

2.3.2.2 Estimation of bulk properties

Bulk properties of a mixture can be calculated from boiling point curve and bulk density. The boiling point curve and bulk density of a mixture is estimated from the boiling points and densities of individual components.
The bulk density can be calculated as a weighted average using component densities assuming an ideal mixing rule for petroleum fractions (Jabr et al., 1992; Riazi and Al-Sahhaf, 1995). The true-boiling point (TBP) curve of a mixture is a plot of the individual boiling points of pure hydrocarbon compounds in increasing order against the cumulative volume percentage (Nelson, 1958). Based on this definition the true-boiling point curve of a petroleum fraction can be developed by plotting the normal boiling temperatures of matrix elements against the corresponding cumulative volume composition in an ascending order. This TBP curve can be conveniently converted to other forms such as ASTM D86 curve using the standard methods described in American Petroleum Institute (API) technical data book as physical property correlations commonly employ ASTM D86 temperatures as parameters.

Bulk density and boiling point curve are used to estimate other bulk properties such as aniline point, cetane number, cloud point and pour point, which are specified for various petroleum products and serve as performance indicators for refinery processes. Lee and Kesler (1975) correlated critical properties and acentric factor with specific gravity and boiling points of mixtures of non-polar and slightly polar substances. Kinetic viscosity, and refractive index can also be calculated using available correlations (Twu, 1985; Riazi and Daubert, 1987).

Cookson et al. (1995) developed composition-property correlations for diesel fuels of different boiling ranges. The correlations are of the form:

\[ P = a_1 \cdot C_n + a_2 \cdot C_{ar} + b_1 \cdot T_{10} + b_2 \cdot T_{90} + k \]  

(2.12)

where \( C_n \) is the fraction of n-alkyl carbon, \( C_{ar} \) is the fraction of aromatic carbon, \( T_{10} \) and \( T_{90} \) are the temperatures at which 10 and 90 weight % of the fuel is vaporised, \( P \) is the physical property of the mixture and \( a_1, a_2, b_1, b_2, k \) are the coefficients determined by regression given in Table 2.4.
<table>
<thead>
<tr>
<th>Property</th>
<th>a1</th>
<th>a2</th>
<th>b1</th>
<th>b2</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline point (°C)</td>
<td>55.6</td>
<td>-67.7</td>
<td>0.078</td>
<td>0.073</td>
<td>18.7</td>
</tr>
<tr>
<td>Cetane number</td>
<td>49.1</td>
<td>-32.4</td>
<td>0.061</td>
<td>0.025</td>
<td>24.3</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>33.2</td>
<td>-12.3</td>
<td>0.154</td>
<td>0.422</td>
<td>-189.4</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>-0.157</td>
<td>0.0655</td>
<td>0.0003</td>
<td>0.0001</td>
<td>0.7652</td>
</tr>
<tr>
<td>Hydrogen content (wt %)</td>
<td>2.41</td>
<td>-5.62</td>
<td>-0.003</td>
<td>-0.002</td>
<td>14.48</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>29.3</td>
<td>-24.5</td>
<td>0.192</td>
<td>0.389</td>
<td>-186.4</td>
</tr>
</tbody>
</table>

Table 2.4 Coefficients of composition-property correlations for diesel fuels (Cookson et al., 1995)

These correlations hold for diesel fuels with initial and final boiling point ranges of 190 – 230 °C and 320 – 370 °C respectively (Cookson et al., 1995). The carbon fractions and boiling temperatures required in these correlations can be easily obtained from the molecular type and homologous series matrix representation of the composition of a diesel stream.

2.3.3 Limitations of previous work on MTHS matrix characterisation approach

The molecular type and homologous series matrix representation of petroleum fractions forms the basis of the molecular modelling approach followed in this work for hydrotreating process design. However, the previous work on the MTHS matrix characterisation approach, presented in Sections 2.3.1 and 2.3.2, has some limitations which are discussed in this section and addressed in this work.

The interpolation method (Zhang, 1999) for generation of MTHS matrices requires a database of sample matrices of the same range of boiling point and properties as the desired petroleum fraction. Such sample composition matrices are available in the literature for gasoline range. However, such data is scarcely available in literature, for higher boiling petroleum fractions, for generation of molecular type and homologous series matrices by the interpolation method.
The strategy followed in previous work for estimation of properties of petroleum fractions using the matrix framework has a limited scope of application. The main reason for this shortcoming is that the molecular structure-property correlations developed by Zhang (1999) do not account for hydrocarbons with hetero-atoms such as sulphur and nitrogen compounds. The hydrocarbons with hetero-atoms have significant importance in fuel products especially in diesel product specifications, e.g. maximum sulphur content, due to environmental concerns regarding emissions from transport vehicles. The molecular structure-property correlations are available only for low boiling hydrocarbons fractions, i.e. gasoline range, and not for compound classes existing in middle distillates and heavy petroleum fractions, such as 4A, 1A3N, 2A1N, 2A2N, 3A1N and 4N.

2.4 Proposed improvements to MTHS matrix characterisation approach

This section addresses the limitations of previous work on generation of molecular type and homologous series matrices and estimation of physical properties of petroleum fractions. The strategy and methods developed in this section aim to extend the scope of molecular type and homologous series matrix representation to middle distillate and heavier petroleum fractions.

2.4.1 New strategy for estimation of properties

The strategy employed in this work for estimation of bulk properties of petroleum streams is to estimate the individual component properties and then using appropriate mixing rules to estimate the properties of the mixture. The new methods used for estimation of individual component properties are discussed in this section.

2.4.1.1 Estimation of component properties with group contribution methods

Group contribution methods are based on the principle that the properties of a compound are function of the atoms and structural groups combining to form the compound. Group contribution methods estimate the physical properties of a species by using the contributions that have been assigned to different atoms and atomic groups for each type of physical constant (Prausnitz et al., 2001).
One of the first group contribution methods for estimation of critical properties was developed by Lydersen (1955). Since then extensive research has been carried out for experimental and statistical determination of group contributions. A detailed discussion can be found elsewhere (Prausnitz et al., 2001). Joback and Reid (1987) modified Lydersen’s group contribution scheme by adding several new functional groups and determined new contribution values. The method of Joback and Reid (1987) is adapted in this work as it covers a broad range of compounds and functional groups and is simple in application.

The normal boiling point i.e. the temperature for phase transition at standard atmospheric pressure is estimated as (Joback and Reid, 1987):

\[ T_b(K) = 198 + \sum_k N_k(tb_k) \]  \hspace{1cm} (2.13)

where \( tb_k \) is the contribution of each group for normal boiling temperature, present in the compound.

Critical properties of individual components are of great importance in phase equilibrium calculations and experimental determination of these can be challenging for heavy components that tend to degrade at high critical temperatures (Prausnitz et al., 2001). The relations for critical properties are (Joback and Reid, 1987):

\[ T_c(K) = T_b \left[ 0.584 + 0.965 \left( \sum_k N_k(tck) \right) - \left( \sum_k N_k(tck) \right)^2 \right]^{-1} \]  \hspace{1cm} (2.14)

\[ P_c(bar) = \left[ 0.113 + 0.0032 N_{\text{Atoms}} - \sum_k N_k(pck) \right]^{-2} \]  \hspace{1cm} (2.15)

\[ V_c(cm^3/mol) = 17.5 + \sum_k N_k(vck) \]  \hspace{1cm} (2.16)
where \( tck \), \( pck \) and \( vck \) represent the contributions of each group for critical temperature, critical pressure and critical volume respectively. The average absolute error in critical temperature estimation of compounds, using group contribution method of Joback and Reid (1987), with three or more carbon atoms is 6.68 K; The average percent error for critical pressure (bar) calculation is 4.59 % while for critical volume (cm\(^3\)/mol) it is 3.11 % (Prausnitz et al., 2001).

An example to illustrate the application of group contribution method of Joback and Reid (1987) is presented here in which critical constants are estimated for ethyl benzene (C\(_8\)H\(_{10}\)). The structure of ethyl benzene is shown in Figure 2.4.

![Molecular structure of ethyl benzene](image)

**Figure 2.4 Molecular structure of ethyl benzene**

The structural groups present in the component under consideration are shown in Table 2.5 along with their contributions for calculating normal boiling temperature, critical temperature, critical pressure and critical volume.

<table>
<thead>
<tr>
<th>Group ( k )</th>
<th>( N_k )</th>
<th>( N_k(tbk) )</th>
<th>( N_k(tck) )</th>
<th>( N_k(pck) )</th>
<th>( N_k(vck) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)-</td>
<td>1</td>
<td>23.58</td>
<td>0.0141</td>
<td>-0.0012</td>
<td>65</td>
</tr>
<tr>
<td>CH(_2)-</td>
<td>1</td>
<td>22.88</td>
<td>0.0189</td>
<td>0</td>
<td>56</td>
</tr>
<tr>
<td>CH=(ds)</td>
<td>5</td>
<td>133.65</td>
<td>0.041</td>
<td>0.0055</td>
<td>205</td>
</tr>
<tr>
<td>C=(ds)</td>
<td>1</td>
<td>31.01</td>
<td>0.0143</td>
<td>0.0008</td>
<td>32</td>
</tr>
<tr>
<td>( \sum N_k F_k )</td>
<td></td>
<td>211.12</td>
<td>0.0883</td>
<td>0.0051</td>
<td>358</td>
</tr>
</tbody>
</table>

**Table 2.5 Group contribution values, for ethyl benzene, group contribution method (Joback and Reid, 1987)**

The summation of the product of contribution value of each group and the number of times the group occurs in the molecular structure of a particular compound is the value used in above equations for estimation of physical properties. A comparison
of the estimated physical properties with the values obtained from HYSYS is made in Table 2.6 and shows good agreement.

<table>
<thead>
<tr>
<th></th>
<th>Group contribution method</th>
<th>HYSYS</th>
<th>Absolute Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_b (°C)</td>
<td>135.97</td>
<td>136.2</td>
<td>0.23</td>
</tr>
<tr>
<td>T_c (°C)</td>
<td>345.405</td>
<td>343.9</td>
<td>1.505</td>
</tr>
<tr>
<td>V_c (m³/kgmol)</td>
<td>0.3755</td>
<td>0.374</td>
<td>0.40%</td>
</tr>
</tbody>
</table>

Table 2.6 Comparison of estimated properties of Ethyl benzene with HYSYS results

2.4.1.2 Estimation of acentric factor

The reduced vapour pressures of noble gases are about 0.1 at reduced temperatures of \( T_r = 0.7 = T/T_c \) (Pitzer and Curl, 1958). Acentric factor describes the deviation of the reduced vapour pressure of a particular substance from that of simple molecules (Stanley, 1985) given by the following equation:

\[
\omega = \left( \log P_c / 10 P_{sat} \right) @ T_r = 0.7 \tag{2.17}
\]

The most common way of estimation of unknown acentric factor is to obtain critical temperature and critical pressure and use one or more experimentally determined vapour pressure values. Acentric factor can then be calculated using the equations (Praunitz et al., 2001):

\[
\omega = -\ln\left( P_c / 1.01325 \right) + \frac{f^{(0)}(T_{br})}{f^{(1)}(T_{br})} \tag{2.18}
\]

\[
f^{(0)} = -5.97616\tau + 1.2987\tau^{1.5} - \frac{0.60394\tau^5}{T_r} \tag{2.19}
\]

\[
f^{(1)} = -5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - \frac{7.46628\tau^5}{T_r} \tag{2.20}
\]

\[
\tau = (1 - T_r) \text{ with } T_r = T_{br} = T_b/T_c \tag{2.21}
\]
where $P_c$ is in bar while $T_b$ and $T_c$ are both absolute temperatures. $f^{(0)}(T_{br})$ and $f^{(1)}(T_{br})$ are both functions of $T_{br}$. The average percentage deviation in $\omega$ is reported to be 2.4% (Prausnitz et al., 2001).

### 2.4.1.3 Estimation of saturated liquid volume

There are several techniques available for estimation of saturated liquid volume or specific volume as a function of temperature. In this work the modified Rackett equation proposed by Yamada and Gunn (1973) is used. In this modified equation $Z_c$, i.e. the critical compressibility is correlated with acentric factor:

$$Z_c = \frac{V_s}{V_c} = \frac{1}{1 - 0.08775(T - T_c)^{7/2} - 0.008775\omega}$$

where $V_s$ is the saturated liquid volume and $V_c$ is the critical volume.

### 2.4.1.4 Estimation of solubility parameter

The solubility parameter is estimated using the following relations (Prausnitz et al., 2001):

$$\delta_i = \left(\frac{AU_i}{V_i^L}\right)^{1/2}$$

where $AU_i$ is the energy required to isothermally evaporate liquid $i$ from the saturated liquid to the ideal gas. $AU_i$ is calculated using the following equation which holds for temperatures well below the critical point:

$$\Delta U_i \approx \Delta H_{vi} - RT$$

where $V_i^L$ is the liquid molar volume of pure liquid $i$ at temperature $T$, $R$ is the gas constant and $\Delta H_{vi}$ is the molar enthalpy of vaporisation. The molar enthalpy of vaporisation is calculated using the group contribution method of Joback (1987):

$$\Delta H_{vi} (kJ/mol) = 15.30 + \sum N_k (hv_k)$$

where $hv_k$ is the group contribution factor for molar enthalpy of vaporisation. Here it is worth mentioning that as the molar enthalpy of vaporisation is calculated using...
the relationship at normal boiling temperature therefore the molar liquid volume also needs to be estimated at the same temperature for consistency in estimation of solubility parameter (Prausnitz et al., 2001).

The above methods for estimation of various physical properties of individual components are used in this work for estimating bulk properties of petroleum fractions using established mixing rules. The bulk properties estimated this way are employed in the approach, presented in next section, for generation of sample MTHS matrices.

### 2.4.2 New approach for generation of molecular type and homologous series matrix

As discussed in the Section 2.3.1, the molecular composition by interpolation method for generation of the molecular type and homologous series matrix is limited to low boiling petroleum fractions, e.g. gasoline, and not used for middle distillate and heavy petroleum fractions due to the insufficient molecular composition data. In this work the approach developed by Saine Aye (2003) for generation of sample matrices is modified by accounting for the carbon number distribution, i.e. the distribution of amounts of individual components with different number of carbon atoms in molecules, in various compound classes existing in the middle distillate petroleum streams.

It is observed, based on chemical analysis of petroleum fractions (Amorelli et al., 1992; Teng et al., 1994; Mushrush et al., 1999; Georgina et al., 2001; Laredo et al., 2002; Bacha et al., 2007) that various compound classes existing in petroleum mixtures exhibit characteristic distributions. For example, the carbon number distribution for middle distillate fractions based on the measurements of Bacha et al., (2007) are shown in Figure 2.5.
Figure 2.5 Typical carbon number distribution for No.2 diesel fuel (Bacha et al., 2007)

Sun (2004) identified and quantified the distribution of sulphur and nitrogen species in middle distillates. The carbon number distribution shown in Figure 2.5 for the compound classes existing in diesel range petroleum streams is taken into account for modifying the approach developed by Saine Aye (2003) for generation of molecular type and homologous series matrices of diesel hydrotreating process streams.

The mathematical formulation of the model proposed for generation of molecular type and homologous series matrix without the use of sample matrices is as follows:

The objective function is to minimise the least squares difference of the measured and calculated properties (Zhang, 1999) of the middle distillate stream under consideration.

\[
F = \sum \left( \frac{p_{\text{measured}} - p_{\text{calculated}}}{p_{\text{measured}}} \right)^2
\]  

(2.26)

The bulk properties of the stream are calculated using individual component properties and established mixing rules:

\[
p_{\text{calculated}} = \sum_j \sum_i x_{i,j} \cdot p_{i,j}
\]  

(2.27)
where \( x_{i,j} \) is the mole fraction and \( p_{i,j} \) is the physical property of the matrix entry in the \( i \)th row and \( j \)th column of the molecular type and homologous series matrix. For some physical properties such as density and specific gravity volume fraction is used in the above equation or alternately the following mixing rule is used:

\[
P_{\text{calculated}} = \sum_{j} \sum_{i} w_{i,j} p_{i,j}
\]  

(2.28)

where \( w_{i,j} \) is the weight fraction of each component. The total fraction of a compound class existing in the stream is used to obtain a composition matrix representative of the mixture under consideration, using information available from chemical analysis.

\[
LWB \leq C_j \leq UPB
\]  

(2.29)

where \( LWB \), and \( UPB \) are the lower and upper limits for the fraction of a homologous series existing in the stream, \( C_j \) is the composition of a homologous series i.e. the cumulative fraction of components of a column of the matrix given by:

\[
C_j = \sum_i x_{i,j}
\]  

(2.30)

The characteristic carbon number distribution of petroleum fractions is incorporated in this modified approach to limit the search space to realistic solutions resulting in improved representation of petroleum fractions in matrix framework. The schematic of the modified molecular type and homologous series matrix generation approach is shown in Figure 2.6.
2.5 Illustrative example on MTHS matrix generation

In this section an example illustrates the new approach for generating molecular type and homologous series matrices developed in this work. A molecular composition matrix is generated for a synthetic crude distillate fraction from Canadian oil sands (Kimbara et al., 1996). The information available for the crude distillate fraction regarding the physical properties and composition is shown in Table 2.7.
<table>
<thead>
<tr>
<th>Properties of synthetic crude distillate</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>density g/cm³ (15 °C)</td>
<td>0.87</td>
</tr>
<tr>
<td>ASTM D86 distillation (wt% distilled) °C</td>
<td></td>
</tr>
<tr>
<td>Initial boiling point</td>
<td>147</td>
</tr>
<tr>
<td>10%</td>
<td>196</td>
</tr>
<tr>
<td>30%</td>
<td>239</td>
</tr>
<tr>
<td>50%</td>
<td>265</td>
</tr>
<tr>
<td>90%</td>
<td>312</td>
</tr>
<tr>
<td>Final boiling point</td>
<td>354</td>
</tr>
<tr>
<td>Compositional mass spectrometric analysis (Mass %)</td>
<td></td>
</tr>
<tr>
<td>paraffins</td>
<td>20.1</td>
</tr>
<tr>
<td>total cycloparaffins</td>
<td>40.4</td>
</tr>
<tr>
<td>monocycloparaffins</td>
<td>21.7</td>
</tr>
<tr>
<td>dicycloparaffins</td>
<td>12.3</td>
</tr>
<tr>
<td>tricycloparaffins</td>
<td>6.4</td>
</tr>
<tr>
<td>total aromatics</td>
<td>39.4</td>
</tr>
<tr>
<td>alkylbenzenes</td>
<td>15.3</td>
</tr>
<tr>
<td>benzocycloparaffins</td>
<td>11.7</td>
</tr>
<tr>
<td>benzodicycloparaffins</td>
<td>4.4</td>
</tr>
<tr>
<td>naphthalenes</td>
<td>5.1</td>
</tr>
<tr>
<td>acenaphthenes</td>
<td>1.6</td>
</tr>
<tr>
<td>fluorenes</td>
<td>0.5</td>
</tr>
<tr>
<td>triaromatics</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2.7 Physical properties and composition analysis of synthetic crude distillate (Kimbara et al., 1996)

The molecular type and homologous series matrix generated using the previous approach of Zhang (1999) is shown in Table 2.8. In this approach, the composition matrix was proposed by interpolating between matrices of known composition while minimising the least squares difference between measured and calculated bulk properties of the synthetic crude distillate.
The matrix entries shown in Table 2.8 are in weight %; * represents matrix components that do not exist. For example, matrix components in the column for di-aromatic compounds cannot exist for carbon numbers less than 10.
<table>
<thead>
<tr>
<th>P</th>
<th>1N</th>
<th>2N</th>
<th>3N</th>
<th>1A</th>
<th>1A1N</th>
<th>1A2N</th>
<th>2A</th>
<th>2A1N</th>
<th>3A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>0.59</td>
<td>0</td>
<td>0.92</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>0.7</td>
<td>0</td>
<td>1.84</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td>1.17</td>
<td>12.33</td>
<td>3.7</td>
<td>11.73</td>
<td>5.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>2.83</td>
<td>0</td>
<td>3.51</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C12</td>
<td>4.7</td>
<td>0</td>
<td>2.58</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C13</td>
<td>5.87</td>
<td>0</td>
<td>1.84</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14</td>
<td>20.15</td>
<td>5.87</td>
<td>6.32</td>
<td>0.92</td>
<td>4.41</td>
<td>2.1</td>
<td>0</td>
<td></td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2.8 Matrix composition of synthetic diesel fraction (Zhang, 1999)
In the previous work on molecular type and homologous series matrix representation, the estimation of bulk properties is carried out using the bulk density and true boiling point curve of the mixture. A comparison of these calculated properties, from the matrix generated using the method of Zhang (1999), with measured properties is shown in Table 2.9.

<table>
<thead>
<tr>
<th>Property</th>
<th>Measured</th>
<th>Calculated</th>
<th>Absolute Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.87</td>
<td>0.87</td>
<td>0.0</td>
</tr>
<tr>
<td>T10 °C</td>
<td>196</td>
<td>194.2</td>
<td>1.8</td>
</tr>
<tr>
<td>T90 °C</td>
<td>312</td>
<td>282.5</td>
<td>29.5</td>
</tr>
</tbody>
</table>

Table 2.9 Comparison of properties calculated using the previous approach (Zhang, 1999)

The two boiling temperatures T10 and T90 are chosen for comparison as these values have been used in numerous correlations available in literature for estimation of other bulk properties (Cookson et al., 1995). It can be seen from Table 2.9 that there is large discrepancy in the true boiling point curve of the mixture estimated using the composition matrix generated with the approach of Zhang (1999). The reason behind this discrepancy is that in the previous work for generation of molecular type and homologous series matrix the characteristic carbon number range of petroleum fractions and the distribution of various compound classes is not considered.

As discussed in the Section 2.4.2, the characteristic carbon number range and distribution of compound classes in petroleum fractions is taken into account in the new approach for matrix generation. The carbon number distribution used in this example is based on the measurements of Bacha et al., (2007) as already shown in Figure 2.5. The molecular type and homologous series matrix for the synthetic crude distillate using the approach developed in this work is shown in Table 2.10.
<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>1N</th>
<th>2N</th>
<th>3N</th>
<th>1A</th>
<th>1A1N</th>
<th>1A2N</th>
<th>2A</th>
<th>2A1N</th>
<th>3A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>0.509</td>
<td>0.473</td>
<td>*</td>
<td>*</td>
<td>0.351</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>C9</td>
<td>0.018</td>
<td>2.723</td>
<td>*</td>
<td>*</td>
<td>1.699</td>
<td>0.155</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>C10</td>
<td>1.600</td>
<td>1.977</td>
<td>0.318</td>
<td>*</td>
<td>0.749</td>
<td>0.331</td>
<td>*</td>
<td>0.010</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>C11</td>
<td>1.562</td>
<td>1.450</td>
<td>0.457</td>
<td>*</td>
<td>1.077</td>
<td>0.575</td>
<td>*</td>
<td>0.015</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>C12</td>
<td>2.088</td>
<td>1.938</td>
<td>0.611</td>
<td>*</td>
<td>1.440</td>
<td>0.819</td>
<td>*</td>
<td>0.020</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>C13</td>
<td>2.581</td>
<td>2.395</td>
<td>0.756</td>
<td>*</td>
<td>1.779</td>
<td>1.250</td>
<td>*</td>
<td>1.635</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>C14</td>
<td>3.209</td>
<td>2.978</td>
<td>5.903</td>
<td>1.942</td>
<td>2.212</td>
<td>2.132</td>
<td>2.050</td>
<td>2.210</td>
<td>1.670</td>
<td>0.304</td>
</tr>
<tr>
<td>C15</td>
<td>2.663</td>
<td>2.483</td>
<td>1.013</td>
<td>1.307</td>
<td>1.908</td>
<td>1.621</td>
<td>0.551</td>
<td>0.854</td>
<td>0.450</td>
<td>0.113</td>
</tr>
<tr>
<td>C16</td>
<td>2.281</td>
<td>2.145</td>
<td>0.805</td>
<td>1.264</td>
<td>1.575</td>
<td>1.297</td>
<td>0.537</td>
<td>0.798</td>
<td>0.233</td>
<td>0.112</td>
</tr>
<tr>
<td>C17</td>
<td>1.609</td>
<td>1.504</td>
<td>0.701</td>
<td>0.918</td>
<td>1.229</td>
<td>0.476</td>
<td>0.359</td>
<td>0.840</td>
<td>0.075</td>
<td>0.103</td>
</tr>
<tr>
<td>C18</td>
<td>1.249</td>
<td>1.075</td>
<td>0.855</td>
<td>0.642</td>
<td>0.854</td>
<td>0.404</td>
<td>0.337</td>
<td>0.312</td>
<td>0.071</td>
<td>0.095</td>
</tr>
<tr>
<td>C19</td>
<td>0.509</td>
<td>0.558</td>
<td>0.695</td>
<td>0.201</td>
<td>0.351</td>
<td>0.298</td>
<td>0.341</td>
<td>0.025</td>
<td>0.064</td>
<td>0.072</td>
</tr>
<tr>
<td>C20</td>
<td>0.221</td>
<td>0.000</td>
<td>0.185</td>
<td>0.125</td>
<td>0.077</td>
<td>0.290</td>
<td>0.226</td>
<td>0.015</td>
<td>0.051</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 2.10 MTHS matrix (wt %) generated for synthetic crude distillate using the new approach for matrix generation
It can be seen from Table 2.10 that the molecular type and homologous series matrix generated to represent the composition of the petroleum fraction under consideration consists of the carbon number range characteristic of diesel streams. The carbon number distribution of compound classes existing in the mixture under consideration is shown in Figure 2.7 and is in good agreement with the experimental findings of Fafet and Magne-Drisch (1995).

Figure 2.7 Carbon number distribution for synthetic crude distillate using the matrix generated with new approach for matrix generation

A comparison of the calculated key bulk properties of the mixture with the measured bulk properties is shown in Table 2.11.

<table>
<thead>
<tr>
<th>Property</th>
<th>Measured</th>
<th>Calculated</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.87</td>
<td>0.861</td>
<td>0.009</td>
</tr>
<tr>
<td>T10  °C</td>
<td>196</td>
<td>192.694</td>
<td>3.306</td>
</tr>
<tr>
<td>T90  °C</td>
<td>312</td>
<td>309.310</td>
<td>2.690</td>
</tr>
<tr>
<td>M.Wt (g/gmol)</td>
<td>190.9</td>
<td>187.410</td>
<td>3.490</td>
</tr>
</tbody>
</table>

Table 2.11 Comparison of calculated bulk properties with measured bulk properties of Kimbara et al., (1996)
It can be seen from Table 2.11 that the calculated bulk properties are consistently in good agreement with the measured properties. It can be concluded here that other bulk properties for the mixture can be calculated using correlations available in the literature more accurately using these estimated key properties compared to the prediction using approach of Zhang (1999).

2.6 Conclusions

The conventional characterisation methods that are widely used in refinery process modelling cannot provide detailed information at the molecular level. Such information is needed for modelling of refinery processes satisfying cleaner fuel specifications. The molecular type and homologous series matrix characterisation approach developed by Peng (1999) is a systematic representation of detailed molecular information that can be obtained using modern analytical techniques. In order to avoid expensive and time consuming chemical analysis of petroleum fractions previous researchers (Zhang, 1999; Saine Aye, 2003) developed methods for generation of molecular type and homologous series matrices by minimising the difference between calculated and measured bulk properties of streams.

The previous work on generation of molecular type and homologous series matrix representation is limited to low boiling petroleum fractions i.e. gasoline range. Another shortcoming of previous work is that the methods developed for estimation of physical properties of individual components of a mixture are limited to hydrocarbon compounds only.

A new strategy is developed in this work for estimation of bulk properties of petroleum fractions from the molecular composition matrix using group contribution methods to estimate properties of individual components, of not only hydrocarbon components but also hydrocarbons with hetero-atoms. Given these properties of individual components allows one to estimate the bulk properties of the mixture using mixing rules and correlations available in the literature.
It has been shown that the new approach for matrix generation developed in this work can provide molecular composition information in the absence of detailed chemical analysis. The methods developed in this work extend the scope of molecular type and homologous series matrix characterisation approach to middle distillate and heavy petroleum fractions and thus facilitate molecular modelling of heavy hydrocarbon conversion processes such as diesel hydrotreating process.
Chapter 3 Modelling of separation system of diesel hydrotreating process

3.1 Introduction

This chapter focuses on the application of molecular type and homologous series matrix representation of petroleum fractions in modelling of separation processes. In particular, the separation system of diesel hydrotreating process consists of high and low pressure flash units and a distillation column (See Figure 1.1 for diesel hydrotreating process flow sheet). The high pressure flash separators recover hydrogen, to be recycled back to the reactor after purification, and make a rough split between light and heavy reaction products. The liquid from the high pressure separators is sent to the low pressure separator, the liquid product of which feeds the distillation column. Naphtha is produced as the overhead product of distillation while the bottom product is the hydrotreated diesel product (Meyers, 1997). A detailed description of the separation system of diesel hydrotreating process is presented in the Section 1.1.

In this chapter the strategy developed for modelling of separation processes within the framework of molecular type and homologous series matrix representation of petroleum fractions is presented. The methods discussed here allow modelling of single-stage flash separation and distillation using molecular matrix representation of streams consistent with the molecular model of diesel hydrotreater (See Section 4.2). The modelling of reaction and separation system of diesel hydrotreating
process on a consistent basis using MTHS matrix representation provides the foundation for integrated design and optimisation of the overall process.

3.2 Previous work on separation modelling with MTHS matrix representation

The conventional lumped models for reaction and separation processes employ different lumping strategies (Peng, 1999), i.e. compounds belonging to a compound class are lumped together in lumped reaction models while the lumping for separation modelling is in terms of pseudo-components using physical properties such as boiling temperatures. These different lumping strategies make the conventional lumped models for reaction and separation processes incompatible for refinery optimisation. Peng (1999) explored the application of molecular type and homologous series matrix representation in separation modelling to provide a consistent modelling framework for refinery processes. In this section the work of Peng (1999) is reviewed and shortcomings are identified.

3.2.1 Application of matrix characterisation in separation modelling

Peng (1999) developed two approaches for employing MTHS matrix representation in modelling of separation processes:

1. Lumping strategy to allow incorporation of matrix information into commercial simulation tools.

2. Shortcut approach to predict distillate and bottom products of a distillation column, of fixed configuration, for varying feed composition.

The lumping strategy proposed by Peng (1999) applies a set of cut-points to a true boiling point (TBP) curve, generated from the matrix representing the petroleum fraction feeding the separation unit, to obtain pseudo-components. The pseudo-component properties may be estimated as weighted average of the properties of constituent elements. These pseudo-components can then be specified as input to
commercial process simulation softwares. In this approach the distribution of compounds, combining to form pseudo-components, is assumed to remain constant even after undergoing separation. The information from simulation in terms of pseudo-components is delumped, using the constant distribution assumption, to obtain matrix composition for product streams.

The shortcut approach for prediction of performance of a distillation column of fixed configuration requires the composition of distillate and bottom product of the distillation column to be measured (Peng, 1999) and the product matrices, based on this measured information, can be generated. The feed matrix is the summation of product matrices in terms of molar flows (Peng, 1999):

$$ F = D + B $$

(3.1)

The recovery ratios, $R$, of matrix elements are calculated as (Peng, 1999):

$$ R_{ij} = \frac{d_{ij}}{f_{ij}} $$

(3.2)

where $d_{ij}$ is the molar flow of the element in $i^{th}$ row and $j^{th}$ column of the matrix of distillate flow, $f_{ij}$ is the molar flow of the component in feed stream. In this approach the recovery ratios of components given by equation 3.2 are assumed to remain constant for small changes in the composition of the stream feeding the distillation column. When the feed composition changes slightly, the molar flow of component $ij$ in the new distillate stream $D'$ is calculated as (Peng, 1999):

$$ d'_{ij} = R_{ij} \cdot f'_{ij} $$

(3.3)

Where $d'$ and $f'$ represent the molar flow of components in the new feed and distillate streams. The molar flow of the new bottom product matrix $B'$ is found by simple matrix subtraction (Peng, 1999):

$$ B' = F' - D' $$

(3.4)
3.2.2 Limitations of previous work

The application of lumping strategy for generating pseudo-components from MTHS matrix representation and employing commercial process simulation software requires a delumping methodology to retain molecular composition information of product streams in matrix form. The strategy developed by Peng (1999) for delumping the products of a distillation column assumes that the distribution of chemical species within each pseudo-component remains unchanged if the number of pseudo-components is large (i.e. small boiling point intervals are used in lumping). This assumption does not hold for multi-stage separation processes such as distillation where, the overhead product becomes richer in lower boiling components and the bottom product in higher boiling components (Smith, 2005). Therefore a delumping methodology is required for the application of molecular type and homologous series matrix representation in separation modelling.

The shortcut approach, for prediction of performance of a distillation column of fixed configuration, developed by Peng (1999) is based on the assumption of constant recovery ratios of components. This approach can only be used to predict products of an existing column for changes in the composition of the feed stream of the order of less than 10% (Peng, 1999) and does not provide a framework for design scenarios.

3.3 Proposed strategy for separation modelling with matrix representation

This section discusses the models employed in this work for distillation and flash separation. Distillation column models can be classified as rigorous and short-cut models. Rigorous models take into account mass and energy balance and equilibrium relationship at every stage and solve these non-linear equations simultaneously. These models provide more accurate results compared to short-cut models but the calculations are time-consuming and dependant on good initialisation. Short-cut distillation models do not have convergence problems, so
consume less computation time. However, the results are less accurate. Short-cut models offer the opportunity to explore various design scenarios and are thus more suitable for design and optimisation at the conceptual design stage (Smith, 2005).

The application of molecular type and homologous series matrix representation of petroleum fractions in modelling of separation systems is not straightforward as the increased number of components, compared to representation of a mixture in terms of pseudo-components, requires more computational time (Peng, 1999). The strategy followed in this work is to generate pseudo-components, from the molecular type and homologous series matrix of a petroleum fraction, and make use of the models for distillation and flash separation that will be discussed in this section.

In order to retain the detailed molecular information we require a methodology for delumping the products of separation processes modelled using pseudo-components. The methodology employed for delumping the products of flash separation is discussed in the Section 3.3.4.

3.3.1 Short-cut model for distillation

The short-cut model for distillation employed in this work is the Fenske-Underwood-Gilliland (FUG) method based on the models developed by Fenske (1932), Gilliland (1940), and Underwood (1948). This method assumes constant molar overflow and constant relative volatilities throughout the column. For simple column design i.e. a distillation column with one feed, one top product, and one bottom product the key components and their recoveries are specified first. The light key is the component to be kept out of the bottom product according to some specification while the heavy key is the component to be kept out of the top product according to some specification (Smith, 2005). The Underwood equation describes minimum reflux condition, i.e. the minimum allowable reflux for a specified separation (King, 1980) and is used to find all the roots between the relative volatilities of light and heavy key components:
\[ \sum \frac{\alpha_i x_{F,i}}{\alpha_i - \theta} = 1 - q \]  \hfill (3.5)

where \( \alpha_i \) is the relative volatility of component \( i \).

\( x_{F,i} \) is the mole fraction of the component \( i \) in the feed stream.

\( q \) is the liquid fraction of feed stream.

\( \theta \) is the root of Underwood equation.

The minimum vapour flow in the top section and distribution of components between the two key components is determined by the following equation:

\[ \sum \frac{\alpha_i d_i}{\alpha_i - \theta} = V_{\text{min}} \]  \hfill (3.6)

Where \( d_i \) is the molar flow of the component \( i \) in the top product.

\( V_{\text{min}} \) is the minimum vapour flow in the top section.

The minimum reflux ratio \( (R_{\text{min}}) \) is calculated as:

\[ R_{\text{min}} = \frac{V_{\text{min}}}{D} - 1 \]  \hfill (3.7)

where \( D \) is the molar flow rate of the top product. The minimum vapour flow in the bottom section \( (V'_{\text{min}}) \) is calculated using the following equation:

\[ V'_{\text{min}} = V_{\text{min}} - (1 - q)F \]  \hfill (3.8)

where \( F \) is the molar flow rate of the feed.
The total reflux condition is described by the Fenske equation which determines the minimum number of stages:

\[
N_{\text{min}} = \ln \left[ \frac{R_{LK} / (1 - R_{LK})}{(1 - R_{HK} / R_{HK})} \right] \ln \left[ \frac{\alpha_{LK}}{\alpha_{HK}} \right]
\]

(3.9)

where \( N_{\text{min}} \) is the minimum number of stages at total reflux condition,

\( R_{LK} \) is the recovery of light key component in top product,

\( R_{HK} \) is the recovery of heavy key component in bottom product.

\( \alpha_{LK}, \alpha_{HK} \) are the relative volatilities of the light and heavy key components, respectively.

The distribution at total reflux condition is estimated using the following equation, derived from Fenske equation (Seader and Henley, 1998):

\[
d_i = \frac{\alpha_i^{N_{\text{min}}} f_i \left( \frac{d_{HK}}{b_{HK}} \right)}{1 + \alpha_i^{N_{\text{min}}} \left( \frac{d_{HK}}{b_{HK}} \right)}
\]

(3.10)

where \( f_i \) is the molar flow of component \( i \) in the feed stream, \( d_{HK} \) and \( b_{HK} \) are the molar flows of the heavy key in distillate and bottom products respectively.

The Underwood equation tends to underestimate the value of minimum reflux ratio because of the simplifying assumption of constant molar overflow (Smith, 2005). Suphanit (1999) proposed a modification for compensating the variation in molar overflow. In this proposed modification enthalpy balance is carried out around the top section of the column to estimate the condenser duty and the minimum vapour flow. An overall enthalpy balance is carried out to obtain the reboiler duty and finally an enthalpy balance around the reboiler calculates the minimum vapour flow in the bottom section.
The distribution of components at finite reflux may be approximated by linear interpolation between their distributions at minimum reflux and total reflux conditions as suggested by Treybal (1968).

The theoretical number of stages can be estimated from $N_{\text{min}}$ and $R_{\text{min}}$ using the graphical, empirical relationship of Gilliland (1940). This correlation may be represented analytically by (Molokanov et al. 1972):

$$\psi = 1 - \exp \left( \frac{1 + 54.4\zeta}{11 + 117.2\zeta} \times \frac{\zeta - 1}{\zeta^{0.5}} \right) \tag{3.11}$$

where

$$\zeta = \frac{R - R_{\text{min}}}{R + 1} \tag{3.12}$$

$$\psi = \frac{N - N_{\text{min}}}{N + 1} \tag{3.13}$$

The feed stage location can be determined by empirical equation of Kirkbride (1944):

$$\ln \left( \frac{N_R}{N_S} \right) = 0.206 \times \ln \left[ \frac{B}{D} \left( \frac{x_{f,\text{HK}}}{x_{f,\text{LK}}} \right) \left( \frac{x_{b,\text{LK}}}{x_{d,\text{HK}}} \right)^2 \right] \tag{3.14}$$

where $N_R$ and $N_S$ are the number of theoretical stages in the rectifying and stripping sections respectively.

### 3.3.2 Flash calculation model

The model for flash calculations employed in this work is based on the method for calculation of vapour-liquid equilibrium from Sandler (1989). The flash model is used for estimation of vapour and liquid fraction of a mixture of known composition for a given temperature and pressure. The overall material balance and component material balances can be represented by the following equations (Smith, 2005):
\[ F = V + L \quad (3.15) \]

\[ F \cdot z_i = V \cdot y_i + L \cdot x_i \quad (3.16) \]

where \( F \) is the molar flow rate of the feed, \( V \) and \( L \) are the molar flow rates of the vapour and liquid from the flash unit respectively, \( z \), \( y \), and \( x \) represent the mole fraction of component \( i \) in the feed, vapour and liquid stream of the flash unit respectively.

The vapour-liquid equilibrium relationship for each component is given by the equation (Smith, 2005):

\[ y_i = K_i \cdot x_i \quad (3.17) \]

where \( K \) represents the vaporisation equilibrium ration of component \( i \). The composition of the vapour and liquid streams of the flash unit are estimated using the following equations (Smith, 2005):

\[ y_i = \frac{z_i}{\frac{V}{F} + \left(1 - \frac{V}{F}\right) \frac{1}{K_i}} \quad (3.18) \]

\[ x_i = \frac{z_i}{(K_i - 1) \frac{V}{F} + 1} \quad (3.19) \]

where \( V/F \) is the fraction of the feed vapourised. The vapour fraction of the feed is calculated by an iterative search using the following objective function (Rachford and Rice, 1952):

\[ f(V/F) = \sum_i^N \frac{z_i (K_i - 1)}{V \left(\frac{V}{F} (K_i - 1) + 1\right)} = 0 \quad (3.20) \]

where \( N \) is the number of components in the mixture. A detailed account of flash calculations can be found elsewhere (e.g. Rachford and Rice, 1952; Walas, 1985; Sandler, 1989; Smith, 2005).
The component properties required for flash calculations are normal boiling temperature (K), critical temperature (K), critical pressure (bar), acentric factor, molar volume (cm$^3$/gmol) and solubility parameter (Joule/cm$^3)^{1/2}$. These component properties are estimated using the methods discussed in Chapter 2. In this work Grayson-Streed, and Peng-Robinson equation of state have been employed for vapour-liquid equilibrium calculation. A detailed discussion of these property packages can be found elsewhere (Grayson and Streed, 1963; Peng and Robinson, 1976). The Grayson-Streed correlation is recommended for systems having high hydrogen concentrations, such as hydrotreating processes (HYSYS version 1.1 manual, 1996).

The Grayson-Streed correlation is an extension of the correlation of Chao and Seader (1961) to temperatures of up to 800°F with emphasis on systems with high hydrogen partial pressures. This correlation applies to a wide range of hydrocarbon systems, temperatures and pressures (Grayson and Streed, 1963). In the Chao-Seader correlation, the vaporisation equilibrium ratio (K-value) is calculated through a combination of three factors:

\[
K = \frac{y}{x} = \frac{\Phi^L}{\Phi^V}
\]

(3.21)

where \( x \) and \( y \) are equilibrium mole fractions of a component in liquid and vapour phase respectively. The quantity \( \Phi^L \) is the fugacity coefficient of a component in the liquid phase, \( \gamma \) is the activity coefficient of component in the liquid phase and \( \Phi^V \) the fugacity coefficient in the vapour phase.

Chao and Seader (1961) proposed an empirical correlation for the liquid fugacity coefficient of components in terms of three constants that are critical temperature, critical pressure and acentric factor:

\[
\log \Phi^L = \log \Phi^{L(0)} + \omega \log \Phi^{L(1)}
\]

(3.22)
The two quantities $\Phi^{L(0)}$ and $\Phi^{L(1)}$ are dependent on reduced temperature and reduced pressure only:

\[
\log \Phi^{L(0)} = A_0 + A_1/T_r + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 + (A_5 + A_6 T_r + A_7 T_r^2)P_r \\
+ (A_8 + A_9 T_r)P_r^2 - \log P_r
\]

(3.23)

\[
\log \Phi^{L(1)} = -4.23893 + 8.65808 T_r - 1.22060/T_r - 3.15227 T_r^3 - 0.025(P_r - 0.6)
\]

(3.24)

The coefficients of the above equation are shown in Table 3.1 (Grayson and Streed, 1963). For reduced temperatures above 1.00 the values of $\Phi^{L(1)}$ are set equal to the values at $T_r = 1.00$. 
Table 3.1 Coefficients for equations of liquid fugacity coefficient calculation  
(Grayson and Streed, 1963)

The vapour fugacity coefficient $\Phi_i^v$ of a component $i$, at temperature $T$ is calculated using Redlich-Kwong (RK) equation of state (Redlich and Kwong, 1948):

$$\Phi_i^v = \exp\left[ (Z-1)\frac{b}{b} - \ln(Z-B) - \frac{A}{B} \left(2\sqrt{(a_i/a)} - \frac{b}{b} \right) \ln\left[1 + (B/Z)\right] \right]$$  \hspace{1cm} (3.25)

where

$$A = \frac{aP}{RT^2}$$ \hspace{1cm} (3.26)

$$B = \frac{bP}{RT}$$ \hspace{1cm} (3.27)
\[ a_i = 0.42748R^2 T_{ci}^{2.5} / P_{ci} T^{0.5} \]  \hspace{1cm} (3.28)

\[ b_i = 0.08664RT_{ci} / P_{ci} \]  \hspace{1cm} (3.29)

The following mixing rules are used to obtain the constants for the mixture:

\[ a = \sum_{i=1}^{N} \left[ \sum_{j=1}^{N} y_i y_j (a_i a_j)^{0.5} \right] \]  \hspace{1cm} (3.30)

\[ b = \sum_{i=1}^{N} y_i b_i \]  \hspace{1cm} (3.31)

where \( N \) is the total number of components in the mixture. The compressibility factor \( Z \) is calculated by analytically solving the following cubic equation:

\[ Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \]  \hspace{1cm} (3.32)

Three roots for the value of \( Z \) are obtained when the above equation is solved at a temperature below the critical point, where vapour and/or liquid phases can exist. The largest root corresponds to the vapour compressibility factor while the smallest corresponds to the liquid phase compressibility factor. The intermediate root does not hold any significance (Smith, 2005).

Liquid activity coefficients of components are calculated using the following equation (Hildebrand, 1950):

\[ \ln \gamma_i = \frac{V_i (\delta_i - \overline{\delta})^2}{RT} \]  \hspace{1cm} (3.33)

where \( \delta_i \) is the solubility parameter and \( V_i \) is the liquid molar volume of component \( i \). The quantity \( \overline{\delta} \) is the average value of the solubility parameter for the solution given by the equation:

\[ \overline{\delta} = \frac{\sum_i x_i V_i \delta_i}{\sum_i x_i V_i} \]  \hspace{1cm} (3.34)
The short-cut model for distillation and flash calculation model discussed are employed in this work for predicting the performance of flash units and distillation column for separation of diesel hydrotreating process streams. The computational time required for solving these models depends on the size of the problem, i.e. the number of components in the mixture (Leibovici et al., 1997). In order to reduce the computational time for optimisation purposes the components of mixtures, i.e. matrix entries of MTHS matrix representation of a stream, are lumped into pseudo-components. The pseudo-component generation method is discussed in the next section.

3.3.3 Pseudo-component generation

The strategy followed in this work for pseudo-component generation is based on the breakdown of true boiling point curve into cut-points (PRO/II version 3.02 manual, 1991). The percentage of the mixture volume assigned to a pseudo-component is the difference between the values of cumulative volume percentage of mixture at adjacent cut-points. This procedure is illustrated in Figure 3.1. The first pseudo-component is assigned the volume % of mixture boiling between the initial boiling point (IBP), i.e. 90 °F in this case as an example, and 125 °F. The normal boiling point of this pseudo-component (110 °F in this case) is determined by integrating the curve from initial boiling point to 125 °F point with respect to the cumulative volume percentage of the mixture. The second pseudo-component is assigned the material boiling from 125 °F to 150 °F and is integrated to get a boiling point of 138 °F. This procedure is then applied over the whole boiling curve. The specific gravity of each pseudo-component is calculated such that the resulting average agrees with bulk specific gravity of the mixture.
Figure 3.1 True boiling point (TBP) curve breakdown into pseudo-components

The physical properties for each pseudo-component are estimated using boiling points and specific gravities as correlating parameters. For example, molecular weight and critical properties have been correlated with normal boiling temperature and specific gravity by Lee and Kesler (1976):

\[
M.Wt = -122726 + 94864 \cdot SG + (4.6523 - 3.3287 \cdot SG) \cdot T_b + \left(1 - 0.77084 \cdot SG - 0.02058 \cdot SG^2\right)
\left[1.3437 - \frac{720.79}{T_b}\right] 10^\frac{T}{T_b} + \left[1 - 0.80882 \cdot SG + 0.02226 \cdot SG^2\right] \left[1.8828 - \frac{181.98}{T_b}\right] 10^{\frac{10^5}{T_b}}
\]

(3.35)

where \(M.Wt\) is the molecular weight,

\(SG\) the specific gravity at 60 °F relative to water,

\(T_b\) the normal boiling temperature (°R).

\[
T_c = 341.7 + 811 \cdot SG + (0.4244 + 0.1174 \cdot SG) \cdot T_b + (0.4669 - 3.2623 \cdot SG) \cdot 10^\frac{5}{T_b}
\]

(3.36)
where $T_c$ is the critical temperature (°R).

$$
\ln P_c = 8.3634 - 0.0566 \frac{SG}{SG} - \left( 0.24244 + \frac{2.2898}{SG} + \frac{0.11857}{SG^2} \right) \cdot 10^7 \cdot T_b + \left( 1.4685 + \frac{3.648}{SG} + \frac{0.47227}{SG^2} \right) \cdot 10^5 \cdot T_b^3
$$

where $P_c$ is the critical pressure (psia).

The correlation for acentric factor is based on reduced boiling temperature (Lee and Kesler, 1975):

$$
\omega = \frac{\ln P_{br} - 5.92714 + \frac{6.09648}{T_{br}} + 1.28862 \cdot \ln T_{br} - 0.169347 \cdot T_{br}^6}{15.2518 - \frac{15.6875}{T_{br}} - 13.4721 \cdot \ln T_{br} + 0.43577 \cdot T_{br}^6}
$$

(3.38)

For $T_{br} > 0.8$.

$$
\omega = -7.904 + 0.1352 \cdot K - 0.007465 \cdot K^2 + 8.359 \cdot T_{br} + \frac{1.408 - 0.01063 \cdot K}{T_{br}}
$$

(3.39)

An example is presented to illustrate the application of pseudo-component generation method by comparing the results of estimated physical properties with HYSYS. A mixture of normal alkanes from carbon number 7 to 12 has been lumped into two pseudo-components using the approach discussed above. The composition of the mixture of normal alkanes is shown in Table 3.2.
<table>
<thead>
<tr>
<th>Components</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Heptane</td>
<td>0.0909</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.0909</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>0.0909</td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.0909</td>
</tr>
<tr>
<td>n-C11</td>
<td>0.0909</td>
</tr>
<tr>
<td>n-C12</td>
<td>0.5455</td>
</tr>
</tbody>
</table>

Table 3.2 Composition of mixture of normal alkanes from C$_7$ to C$_{12}$

Table 3.3 presents the absolute error for the normal boiling temperature and critical temperature estimation, while for critical pressure and acentric factor the percentage error is shown.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Pseudo-components</th>
<th>HYSYS results</th>
<th>Calculated properties</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBP (K)</td>
<td>PC1</td>
<td>395.25</td>
<td>396.4</td>
<td>1.15 K</td>
</tr>
<tr>
<td></td>
<td>PC2</td>
<td>483.75</td>
<td>480.1</td>
<td>3.65 K</td>
</tr>
<tr>
<td>Critical temperature (K)</td>
<td>PC1</td>
<td>561.77</td>
<td>564.2</td>
<td>2.43 K</td>
</tr>
<tr>
<td></td>
<td>PC2</td>
<td>647.31</td>
<td>644.8</td>
<td>2.51 K</td>
</tr>
<tr>
<td>Critical pressure (bar)</td>
<td>PC1</td>
<td>23.467</td>
<td>23.81</td>
<td>1.46 %</td>
</tr>
<tr>
<td></td>
<td>PC2</td>
<td>17.297</td>
<td>17.72</td>
<td>2.45 %</td>
</tr>
<tr>
<td>Acentric factor</td>
<td>PC1</td>
<td>0.38878</td>
<td>0.3889</td>
<td>0.03 %</td>
</tr>
<tr>
<td></td>
<td>PC2</td>
<td>0.58086</td>
<td>0.5701</td>
<td>1.85 %</td>
</tr>
</tbody>
</table>

Table 3.3 Comparison of estimation of physical properties for pseudo-components with HYSYS results
Table 3.3 shows that the pseudo-component generation approach and estimation of physical properties for pseudo-components is in good agreement with results obtained using standard commercial simulation packages for mixtures of real components.

### 3.3.4 Pseudo-component delumping

In order to retain the molecular level information of hydrotreating process streams while modelling the separation processes using pseudo-components a delumping strategy is needed to obtain the composition information of mixtures in terms of the original components from the information available for the pseudo-components generated to represent the mixtures. Leibovici et al., (1996) proposed a delumping procedure for prediction of detailed composition of phases resulting from a flash calculation performed on a lumped mixture. The delumping approach proposed by Leibovici et al., (1996) assumes that the component fugacities can be expressed as a linear combination of pure component parameters with coefficients depending on mixture properties. This can be expressed mathematically as (Leibovici et al., 1996):

\[
\ln \left[ \frac{f_i}{x_i \cdot P} \right] = C_0 + \sum_{k=1}^{kn} C_k \cdot p_{i,k} \tag{3.40}
\]

where \(f_i\) is the fugacity of component \(i\).

\(x_i\) is the component mole fraction of component \(i\).

\(p_{i,k}\) is the component parameter for any equation of state \(P = f (T, V)\) involving \(n\) parameters.

\(C_k\) are the coefficients of above equation.

The isofugacity criterion has to be fulfilled for all components of a system at equilibrium:

\[
f_i^V = f_i^L \tag{3.41}
\]
The equilibrium constant ($K_i$) can therefore be expressed by (Leibovici et al., 1996):

$$\ln[K_i] = \Delta C_0 + \sum_{k=1}^{k=n} \Delta C_k \cdot p_{i,k}$$

(3.42)

where

$$\Delta C_k = C_k^L - C_k^V$$

(3.43)

For two-parameter equation of states such as Peng-Robinson equation of state (Peng and Robinson, 1976) the values of $p_{i, 1}$ and $p_{i, 2}$ are $\sqrt{a_i}$ and $b_i$, respectively.

For the Peng-Robinson equation of state the analytical expressions for $\Delta C_0$, $\Delta C_1$ and $\Delta C_2$ are (Leibovici et al., 1996):

$$\Delta C_0 = \ln \left[ \frac{v^V - b^V}{v^L - b^L} \right]$$

(3.44)

$$\Delta C_1 = \frac{\sqrt{a^V}}{\sqrt{2b^V} RT} \ln \left[ \frac{v^V + (1 + \sqrt{2})b^V}{v^V + (1 - \sqrt{2})b^V} \right] - \frac{\sqrt{a^L}}{\sqrt{2b^L} RT} \ln \left[ \frac{v^L + (1 + \sqrt{2})b^L}{v^L + (1 - \sqrt{2})b^L} \right]$$

(3.45)

$$\Delta C_2 = \frac{Z^L - 1}{b^L} + \frac{a^L}{2\sqrt{2}b^{L2} RT} \ln \left[ \frac{v^L + (1 + \sqrt{2})b^L}{v^L + (1 - \sqrt{2})b^L} \right] - \frac{Z^V - 1}{b^V} - \frac{a^V}{2\sqrt{2}b^{V2} RT}$$

(3.46)

\[ \cdot \ln \left[ \frac{v^V + (1 + \sqrt{2})b^V}{v^V + (1 - \sqrt{2})b^V} \right] \]

where $a$ and $b$ are the parameters of Peng-Robinson equation of state, $R$ represents the universal gas constant, $T$ is the temperature, $v$ is the molar volume, $Z$ is the compressibility factor, and the superscripts $L$ and $V$ represent the liquid and vapour phase respectively.
The delumping procedure is summarised into the following steps (Leibovici et al., 1996):

1. Lump a mixture of $N$ components into $M$ pseudo-components.
2. Perform flash calculation with the pseudo-components.
3. Determine $\Delta C_k$ values from the lumped system using the above equations.
4. Calculate $K_i$ values using equation 3.42 for all the $N$ components of the full system.
5. Calculate the vapour fraction, using the K-values in equation 3.20, and the vapour and liquid mole fractions of all $N$ components of the full system using equation 3.18 and 3.19 respectively.

This delumping procedure can be employed to derive composition information for the full system while performing a flash calculation on pseudo-components. However, this methodology has been developed by Leibovici et al., (1996) for single-stage separation and therefore not applicable directly for predicting detailed product distribution for distillation columns using short-cut models.

A new approach is developed for predicting detailed product distribution for distillation columns using the short-cut model, discussed in section 3.3.1, and is presented in the next section.

### 3.4 Prediction of detailed product distribution for distillation

Distillation columns are an extension of single equilibrium stage separation using a cascade of stages in which the more volatile components are transferred to vapour phase and the less- volatile components to liquid phase. The liquid needed to feed the cascade at the top is produced by condensation of the vapour leaving the top stage by a condenser. The vapour needed to feed the cascade at the bottom is produced by a reboiler. It is assumed that the liquid and vapour streams leaving
each stage in the cascade are in equilibrium (Smith, 2005). A methodology for prediction of the detailed product distribution for simple distillation columns is developed in this work. The proposed methodology uses Fenske-Underwood-Gilliland method for performing short-cut calculations of distillation using pseudo-components. The information, in terms of pseudo-components, for the products of distillation is delumped to obtain detailed information in terms of the MTHS matrix representation of streams by employing the delumping procedure discussed in the Section 3.3.4.

In order to be able to make reasonable prediction of product distribution in distillation columns we need to take into account the two operating limits for distillation process (Treybal, 1968). The first is the total reflux condition where the entire overhead vapour is refluxed back to the column and corresponds to the minimum number of stages required to achieve the desired separation. The second limiting operating condition is the minimum reflux condition which corresponds to minimum internal flows in the column and an infinite number of stages. Once the product distribution at these limiting operating conditions is predicted, the distribution of components at any actual reflux ratio $R$ may be estimated by linear interpolation between the distribution at minimum and total reflux conditions according to $R/(R + 1)$ (Treybal, 1968). The interpolation is carried out using $R/(R + 1)$ as a co-ordinate because the total reflux condition if used directly is an asymptotic limit while $R/(R + 1)$ at total reflux condition corresponds to a value of 1.

3.4.1 Estimation of detailed product distribution at total reflux condition

At total reflux conditions the minimum number of stages required to achieve desired separation can be estimated using the Fenske equation (Fenske, 1932). The Fenske equation assumes constant relative volatilities which is not the case in practice. The change in relative volatilities may result from changes in composition, temperature and pressure through the column. An average value of relative volatilities needs to be taken (Smith, 2005). The distribution of
components at total reflux conditions is estimated using Hengstebeck-Geddes method. The distribution ratio of a component \( i \) \((d_i/b_i)\) is given by the equation:

\[
\ln \left( \frac{d_i}{b_i} \right) = A + C \cdot \ln \left( \frac{\alpha_i}{\alpha_{HK}} \right)
\]  

(3.47)

where \( \alpha_i \) is the relative volatility of component \( i \) with respect to heavy key. The coefficients of the above equation are calculated using the light and heavy key components:

\[
A = \ln \left( \frac{d_i}{b_i} \right)
\]  

(3.48)

\[
C = \frac{\ln \left( \frac{d_{LK}}{b_{LK}} \right) - \ln \left( \frac{d_{HK}}{b_{HK}} \right)}{\ln \left( \frac{\alpha_{LK}}{\alpha_{HK}} \right)}
\]  

(3.49)

The distillate flows can be calculated using the distribution ratios using the following equation:

\[
d_i = \frac{\frac{d_i}{b_i} \cdot x_{f,i} \cdot F}{\frac{d_i}{b_i} + 1}
\]  

(3.50)

where \( F \) is the molar flow of the feed, \( x_{f,i} \) the mole fraction of component \( i \) in the feed.
The stepwise approach proposed for prediction of detailed distribution of components at total reflux conditions based on the distribution of pseudo-components is as follows:

1. Calculate the minimum number of stages, required for desired separation based on the lumped system, and the coefficients of Hengstebeck-Geddes equation.

2. Calculate the K-values of the full system, i.e. the mixture before lumping, using the delumping procedure explained in Section 3.3.4.

3. Calculate the relative volatilities of the full system using K-value of the heavy key from the calculation for the lumped system.

4. Estimate the distribution of components of the full system at total reflux conditions with Hengstebeck-Geddes method using the relative volatilities calculated in step 3.

3.4.2 Estimation of detailed product distribution at minimum reflux conditions

The Underwood equations (3.5 and 3.6) are most widely applied for estimation of minimum reflux, and distribution of key components at minimum reflux conditions. The Underwood equations assume that the relative volatility of components and molar over flow remain constant between the pinches, i.e. zones of constant composition (Smith, 2005). The relative volatilities at feed conditions are generally recommended over average values based on distillate and bottoms compositions because of the location of pinches is often close to the feed stage (Smith, 2005).

In order to estimate the distribution at minimum reflux it may be assumed that components lighter than the light key end up almost completely in the overhead product and components heavier than the heavy key in bottoms product (Hengstebeck, 1961). Equation 3.5 is solved for \( \theta \) values. Each \( \theta \) value lies between an adjacent pair of relative volatilities. For the case with non-adjacent key
components the number of \( \theta \) values required is one than the number of components between the light and heavy key (Smith, 2005). The equation 3.6 is then written for each \( \theta \) value and this set of equations is solved simultaneously to obtain minimum reflux and the mole fraction of components between the key components in the overhead product at minimum reflux condition.

Leibovici et al., (1996) observed that if lumping does not affect, or only slightly affects, the phase parameters then the delumping coefficients \( (\Delta C_k) \) are the same for the lumped system and full system. The approach developed for the estimation of distribution of components at minimum reflux conditions is based on the analogy to this observation. If a given petroleum fraction is lumped into pseudo-components appropriately i.e. satisfying the above criterion. It can be observed that the distribution curve (plot of distribution ratios of components vs. the relative volatilities) of pseudo-components matches closely with the distribution curve of the original mixture.

The stepwise procedure proposed for prediction of detailed distribution of components at minimum reflux conditions based on the distribution of pseudo-components is as follows:

1. Calculate the minimum reflux and distribution of lumped system at minimum reflux condition.

2. Calculate the distribution ratios for the distributing components as well as key components.

3. Plot distribution curve for pseudo-component system.

4. Calculate the K-values of full system using delumping procedure explained in Section 3.3.4.

5. Calculate relative volatilities of components of full system using K-value of heavy key from the calculation for the lumped system.
6. Interpolate for distribution ratios of components of full system which are distributing.

7. Calculate the distillate flows of components using equation 3.50.

Once the molecular composition information of the products of distillation is obtained using the proposed methodology the distribution of components at any actual reflux ratio is estimated using linear interpolation between the distribution at minimum and total reflux conditions. An example is presented to illustrate the application of the proposed methodology for predicting detailed product distribution for distillation.

### 3.4.3 Illustrative example for prediction of detailed product distribution for distillation

A mixture of normal alkanes from C₁ to C₁₂ is used to illustrate the application of proposed approach for predicting detailed distribution of components in distillation using short-cut model. The components and composition of the mixture under consideration is shown in Table 3.4 (Leibovici et al., 1996).
<table>
<thead>
<tr>
<th>Components</th>
<th>mole fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.7</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.1</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.05</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>0.02</td>
</tr>
<tr>
<td>n-C$<em>5$H$</em>{12}$</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C$<em>6$H$</em>{14}$</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C$<em>7$H$</em>{16}$</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C$<em>8$H$</em>{18}$</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C$<em>9$H$</em>{20}$</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C$<em>{10}$H$</em>{22}$</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C$<em>{11}$H$</em>{24}$</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C$<em>{12}$H$</em>{26}$</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 3.4 Composition of mixture of normal alkanes from C$_1$ to C$_{12}$ (Leibovici et al., 1996)

The mixture is lumped by generating two pseudo-components containing components from C$_7$ to C$_{12}$. The composition of the lumped system is shown Table 3.5.
Components mole fractions

<table>
<thead>
<tr>
<th>Components</th>
<th>mole fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.7</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.1</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.05</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>0.02</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C₆H₁₄</td>
<td>0.01</td>
</tr>
<tr>
<td>Pseudo-com1</td>
<td>0.03</td>
</tr>
<tr>
<td>Pseudo-com2</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 3.5 Composition of lumped system

The shortcut model calculations are carried out at $T = 100{^\circ}C$, $P_{\text{Condenser}} = 2$ bar and $P_{\text{Reboiler}} = 3$ bar. $n$-C₅H₁₂ is the light key and $n$-C₈H₁₈ is the heavy key in the full system while Pseudo-com1 is the heavy key in the lumped system simulation. The degree of separation is specified by specifying recoveries of both keys as 95%.

The results of the delumping approach proposed for short-cut distillation modelling, are validated using COLOM software (Version 2.1). The strategy followed is simulation of lumped system and prediction of detailed distribution at total and minimum reflux conditions using the proposed delumping approach. The results of the detailed prediction are then compared with simulation of the original mixture in COLOM. The results of the prediction of the detailed distribution of components at total reflux condition from pseudo-components are shown in Table 3.6.
<table>
<thead>
<tr>
<th>Components</th>
<th>F(kmol/sec)</th>
<th>Predicted distillate flows (kmol/s)</th>
<th>Distillate flow using COLOM (kmol/s)</th>
<th>Absolute Error</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>7</td>
<td>6.999971</td>
<td>6.99997</td>
<td>8.7E-07</td>
<td>0.000</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1</td>
<td>0.999924</td>
<td>0.99991</td>
<td>1.4E-05</td>
<td>0.001</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.5</td>
<td>0.499647</td>
<td>0.49962</td>
<td>2.7E-05</td>
<td>0.005</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>0.2</td>
<td>0.198728</td>
<td>0.19867</td>
<td>5.8E-05</td>
<td>0.029</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>0.1</td>
<td>0.095164</td>
<td>0.095</td>
<td>1.6E-04</td>
<td>0.173</td>
</tr>
<tr>
<td>n-C₆H₁₄</td>
<td>0.1</td>
<td>0.071678</td>
<td>0.071697</td>
<td>1.9E-05</td>
<td>0.027</td>
</tr>
<tr>
<td>n-C₇H₁₆</td>
<td>0.1</td>
<td>0.026215</td>
<td>0.02659</td>
<td>3.7E-04</td>
<td>1.408</td>
</tr>
<tr>
<td>n-C₈H₁₈</td>
<td>0.1</td>
<td>0.004625</td>
<td>0.005</td>
<td>3.7E-04</td>
<td>7.496</td>
</tr>
<tr>
<td>n-C₉H₂₀</td>
<td>0.1</td>
<td>0.000705</td>
<td>0.000794</td>
<td>8.9E-05</td>
<td>11.212</td>
</tr>
<tr>
<td>n-C₁₀H₂₂</td>
<td>0.1</td>
<td>0.000107</td>
<td>0.000124</td>
<td>1.7E-05</td>
<td>13.625</td>
</tr>
<tr>
<td>n-C₁₁H₂₄</td>
<td>0.1</td>
<td>1.88E-05</td>
<td>2.002E-05</td>
<td>1.2E-06</td>
<td>6.141</td>
</tr>
<tr>
<td>n-C₁₂H₂₆</td>
<td>0.6</td>
<td>1.77E-05</td>
<td>2.189E-05</td>
<td>4.2E-06</td>
<td>19.127</td>
</tr>
</tbody>
</table>

Table 3.6 Comparison of prediction of detailed distribution at total reflux conditions

Table 3.6 shows a good agreement for distillate flows of components except for the heavier components where the percentage error is greater than 10 % because of the very small amounts of these components in the overhead product. The comparison at minimum reflux conditions is shown in Table 3.7.
Components & F(kmol/sec) & Predicted distillate flows (kmol/s) & Distillate flows using COLOM (kmol/s) & Absolute Error & % Error

| Components | 7 | 7 | 7 | 0 | 0 |
| CH₄ | 1 | 1 | 1 | 0 | 0 |
| C₂H₆ | 0.5 | 0.5 | 0.5 | 0 | 0 |
| n-C₄H₁₀ | 0.2 | 0.2 | 0.2 | 0 | 0 |
| n-C₆H₁₂(LK) | 0.1 | 0.095 | 0.095 | 0 | 0 |
| n-C₆H₁₄ | 0.1 | 0.089 | 0.087 | 0.002 | 2.312 |
| n-C₇H₁₆ | 0.1 | 0.073 | 0.070 | 0.003 | 3.781 |
| n-C₈H₁₈(HK) | 0.1 | 0.005 | 0.005 | 0 | 0 |
| n-C₉H₂₀ | 0.1 | 0 | 0 | 0 | - |
| n-C₁₀H₂₂ | 0.1 | 0 | 0 | 0 | - |
| n-C₁₁H₂₄ | 0.1 | 0 | 0 | 0 | - |
| n-C₁₂H₂₆ | 0.6 | 0 | 0 | 0 | - |

Table 3.7 Comparison of prediction of detailed distribution at minimum reflux conditions

Table 3.7 shows a good agreement for results of delumping products of distillation column using short-cut model at minimum reflux conditions. The percentage error for components heavier than the heavy key could not be calculated as they end up completely in the bottoms product.

The results of the illustrative example show that the proposed delumping methodology predicts the detailed product distribution for distillation within reasonable accuracy. The proposed delumping methodology provides the
framework for retaining molecular level information while modelling distillation process with short-cut distillation model using pseudo-components.

3.5 Conclusions

The application of molecular type and homologous series matrix representation of petroleum fractions in modelling of separation processes such as flash separation and distillation is addressed in this work to provide a consistent modelling framework for overall process design and optimisation. Peng (1999) developed a strategy to allow incorporation of MTHS matrix information into commercial simulation tools by lumping matrix entries into pseudo-components. The delumping methodology developed by Peng (1999) assumes constant distribution of components lumped together as pseudo-components. However, the assumption of constant distribution of components does not hold for flash separation and distillation as vapour-liquid equilibrium considerations are neglected.

A new delumping methodology has been developed for predicting detailed product distribution for distillation using Fenske-Underwood-Gilliland short-cut method. The lumping and delumping methods developed in this work retain molecular level information from separation processes such as flash separation and distillation modelled using pseudo-components to represent petroleum fractions. The overall process design and optimisation for diesel hydrotreating process, using the models presented in this chapter for separation processes, is discussed in the next Chapter.
Chapter 4 Integrated design of hydrotreating processes

4.1 Introduction

Process design is conventionally carried out sequentially due to its hierarchical nature i.e. the design calculations start with the reactor moving out to the separation system. The reaction and separation system, along with recycle, establish the material and energy balance of the process thereby defining the heating and cooling duties for the heat recovery system (Smith, 2005). The overall process design is evolved in this step-by-step approach. However, the design and operating conditions of individual components of a process may influence each other and contribute to the overall performance of the process. This interaction is not accounted for fully if a sequential design strategy is followed. A novel approach is developed in this work for integrated hydrotreating process design with molecular type and homologous series matrix representation of petroleum fractions.

In this proposed framework the individual sub-systems of hydrotreating process namely the reaction, separation and heat recovery systems are handled simultaneously in order to capture the overall picture and achieve optimal hydrotreating process design. The heart of the hydrotreating process is the reactor and therefore, the molecular model of diesel hydrotreater is discussed first before the integrated hydrotreating process design approach is introduced.
4.2 Molecular model of diesel hydrotreater

Modern analytical measurements indicate the existence of $O \left(10^{15}\right)$ unique molecules in petroleum feedstocks (Klein et al., 2006). The reactions in diesel hydrotreating process are very complex due to this enormous number of compounds. Several classes of reactions occur simultaneously in hydrotreating processes and need to be taken into account for an understanding of the reactivity patterns of commercial feedstocks. The three main reaction groups in diesel hydrotreating process are aromatics hydrogenation, hydrodesulphurisation (HDS), and hydrodenitrogenation (HDN) (Sun, 2004). Other reaction classes in hydrotreating processes are hydrodeoxygenation (HDO), hydrodemetallation (HDM) and olefins hydrogenation (HO). Girgis and Gates (1991) have presented a comprehensive literature review of catalytic hydروprocessing chemistry and discuss the reaction networks for various species belonging to diesel hydrotreating feeds. Pure compound data available in the literature is considered to be the best source available for developing a sound understanding of the chemistry of hydروprocessing and provides a quantitative foundation for process modelling (Girgis and Gates, 1991).

The molecular pathways level model for diesel hydrotreater employed in this work is developed by Sun (2004) based on the molecular type and homologous series matrix representation for middle distillate fractions. This diesel hydrotreater model makes use of the reaction family concept. A reaction family can be defined, in the context of petroleum mixtures, as a specific rearrangement of molecular structure by the molecules (Sun, 2004). Each of the three main reaction groups of diesel hydrotreating process include reaction families that show similar reactions and the molecular level pathways of these reaction families are expressed as inter-conversions of the matrix elements (Sun, 2004). The overall reaction network obtained in this way accounts for detailed process chemistry, i.e. in terms of observable molecular species in reactions excluding reaction intermediates, and is convenient for computation (Klein et al., 2006).
This section introduces the major features of the molecular model of Sun (2004) for diesel hydrotreaters, identifies its limitations, and proposes some modifications to enable improved prediction of products of diesel hydrotreating reactions.

4.2.1 Aromatic hydrogenation

The aromatic hydrogenation reactions consist of the addition reactions of hydrogen with aromatic species existing in a petroleum feedstock. Aromatic hydrogenation reactions are reversible and exothermic with equilibrium conversions of hydrocarbons often less than 100% under practical processing conditions (Girgis and Gates, 1991). The extent of these reactions at equilibrium decreases with increase in temperature. Aromatic hydrogenation (AH) is different from hydrodesulphurisation and hydrodenitrogenation owing to thermodynamic equilibrium limitations, so a clear understanding of the effects of catalyst type, and process variables on the chemistry and thermodynamic equilibria of different types of aromatic compounds present in petroleum feedstock is necessary for determination of optimum operating strategies.

Analysis of petroleum fractions shows that the aromatic compounds in petroleum mixtures mainly fall into four groups, namely monoaromatics, diaromatics, triaromatics and polycyclic aromatics (Stanislaus and Cooper, 1994). The polycyclic aromatics with four or more condensed benzene rings are usually present in high-boiling fractions (Boiling range > 350°C), while the first three types are present in middle distillates. It is seen that diaromatics (mainly alkyl naphthalenes) constitute a major portion of the total aromatic content in straight-run gas oil (Stanislaus and Cooper, 1994). Therefore the MTHS matrix representation, of middle distillate fractions, excludes polycyclic aromatic compounds in this work.

The reaction networks for the above mentioned aromatic compounds of diesel hydrotreating feedstocks are obtained from the literature (Girgis and Gates, 1991; Korre et al., 1994; Korre et al., 1995) and presented in Figure 4.1.
The aromatic hydrogenation reactions shown in Figure 4.1 can be expressed in terms of inter conversions of matrix elements as (Sun, 2004):

\[
(C_n, \text{AAA}) + 3(C_0, \text{P}) \rightarrow (C_n, \text{AAN}) \tag{4.1}
\]

\[
(C_n, \text{AA}) + 3(C_0, \text{P}) \rightarrow (C_n, \text{AN}) \tag{4.2}
\]

\[
(C_n, \text{A}) + 3(C_0, \text{P}) \rightarrow (C_n, \text{N}) \tag{4.3}
\]

\[
(C_n, \text{AAN}) + 3(C_0, \text{P}) \rightarrow (C_n, \text{ANN}) \tag{4.4}
\]

\[
(C_n, \text{ANN}) + 3(C_0, \text{P}) \rightarrow (C_n, \text{NNN}) \tag{4.5}
\]

\[
(C_n, \text{AN}) + 3(C_0, \text{P}) \rightarrow (C_n, \text{NN}) \tag{4.6}
\]
Korre et al., (1994) observed several qualitative trends in the hydrogenation of aromatic compounds on the basis of their experimental results. For polynuclear aromatics (PNA) hydrogenation proceeds in a ring-by-ring manner and the reactivity increases with the number of rings. For groups with same number of aromatic rings, the presence of alkyl substituents and/or naphthenic rings enhances reactivity, and hydrogenation of the rings located at the end of molecules is faster than hydrogenation of the rings in the middle. The aromatic hydrogenation reactions can be generalised as (Stanislaus and Cooper, 1994):

\[ A + nH_2 \leftrightarrow AH \quad (4.7) \]

The equilibrium concentrations can be represented by (Stanislaus and Cooper, 1994):

\[ \frac{Y_A}{(Y_A + Y_{AH})} = \frac{1}{1 + K_P P_{H_2}^{np}} \quad (4.8) \]

Where \( A \) and \( AH \) represent the aromatic and hydrogenated aromatic species respectively, \( Y_A \) and \( Y_{AH} \) are the mole fractions, \( K_P \) the equilibrium constant, \( P_{H_2}^{np} \) the partial pressure of hydrogen and \( np \) is the number of moles of hydrogen required for saturation. Data on equilibrium constants of aromatic compounds present in middle distillate fractions is available in the literature (Frye, 1962; Frye and Weitkamp, 1969; Stull et al., 1969).

The rate of aromatic hydrogenation reactions may be expressed in a simplified form of Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate expression to account for reactivity, equilibrium and competitive adsorption of all aromatic hydrocarbons (Korre et al., 1994):

\[ r_{op} = k_{op} (C_o - C_p / K_{op}) / (1 + \sum_m K_m C_m) \quad (4.9) \]

Where, \( r_{op} \) (mol kg\textsubscript{cat}\textsuperscript{-1}s\textsuperscript{-1}) is the rate of reaction of aromatic molecule \( o \) to naphthenic molecule \( p \); \( C_o, C_p, C_m \) (mol L\textsuperscript{-1}) are the concentrations of molecules \( o, p \) and \( m \), respectively; \( k_{op} \) (L kg\textsubscript{cat}\textsuperscript{-1}s\textsuperscript{-1}) is the combined rate parameter; \( K_{op} \) is the equilibrium ratio and \( K_m \) (L mol\textsuperscript{-1}) is the adsorption constant of molecule \( m, m \).
represents molecule in the MTHS matrix. Reaction rate parameters for aromatic hydrogenation reactions of the aromatic species existing in middle distillate fractions are also available in the literature (Aubert et al., 1988; Moreau et al., 1990; Korre et al., 1995).

4.2.2 Hydrodesulphurisation

The sulphur compounds in diesel fuel can be classified into four groups based on reactivities namely alkyl benzothiophenes, dibenzothiophenes and alkyl dibenzothiophenes without substituents at the 4- and 6-positions, alkyl dibenzothiophenes with only one of substituents at either the 4- or 6-position, and alkyl dibenzothiophenes with two of the alkyl substituents at the 4- and 6-positions (Ma et al., 1994). The hydrodesulphurisation reactions of organo-sulphur compounds are exothermic and essentially irreversible under the reaction conditions employed industrially (Girgis and Gates, 1991).

The sulphur compounds in middle distillates may be classified into five groups in molecular type and homologous series matrix representation (Sun, 2004): SI to SV. SI homologous series includes mercaptans and similar compounds while the other four groups account for the above mentioned groups. Increasing quality regulations and interest in hydroprocessing of high boiling petroleum fractions have led research efforts to be focused on chemistry of thiophenic compounds which are the least reactive ones (Gates et al., 1979).

The reaction networks and rate expressions for hydrodesulphurisation reactions have been investigated extensively, based on model compounds such as thiophene, benzothiophene, dibenzothiophene, and isomers of benzonaphthothiophene, and are available in the literature (Houalla et al., 1978; Gates et al., 1979; Nag et al., 1979; Vrinat, 1983; Aubert et al., 1986; Van Parijis et al., 1986; Moreau et al., 1987; Sauer et al., 1989).
A detailed reaction network for hydrodesulphurisation of dibenzothiophene (Houalla et al., 1978) is shown in Figure 4.2 as an example. Literature studies show that the hydrodesulphurisation pathways consist of hydrogenation and hydrogenolysis reactions occurring on two different types of sites on the catalyst. These sites are denoted by $\sigma$ for hydrogenolysis and $\tau$ for hydrogenation reactions (Van Parijs and Froment, 1986).

The hydrodesulphurisation reaction pathways for sulphur compounds in diesel hydrotreating feedstocks can be expressed in terms of interconversions of matrix elements as (Sun, 2004):

$$ (C_n, \text{SI}) + (C_0, \text{P}) \rightarrow (C_n, \text{P}) + (C_0, \text{SI}) $$  \tag{4.10} 

$$ (C_n, \text{SII}) + 3(C_0, \text{P}) \rightarrow (C_n, \text{A}) + (C_0, \text{SI}) $$  \tag{4.11}
where mercaptans \((C_n, SI)\) are converted to paraffins \((C_n, P)\), and benzothiophenes \((C_n, SII)\) to aromatics \((C_n, A)\). SII, SIII, SIV, SV compounds react through hydrogenolysis and hydrogenation reaction pathways to produce biphenyls \((C_n, AA)\) and cyclohexylbenzenes \((C_n, A_N)\).

A model for hydrodesulphurisation reactions proposed by Hidalgo-Vivas (1999) is incorporated in the diesel hydrotreater molecular model. The model for hydrodesulphurisation reactions proposed by Hidalgo-Vivas (1999) is derived from the LHHW formalism, assuming the surface reaction is the rate determining step. The hydrodesulphurisation model assumes non-competitive adsorption of sulphur containing compounds and hydrogen, and molecular adsorption of hydrogen:
\[ r_g = k_{g,\sigma} \frac{K_{g,\sigma}C_gK_{H2,\sigma}C_{H2}}{\left(1 + \sum_g K_{g,\sigma}C_g + K_{H2S}C_{H2S}\right)^2} \left(1 + K_{H2}C_{H2}\right) + k_{g,\tau} \frac{K_{g,\tau}C_gK_{H2,\tau}C_{H2}}{\left(1 + \sum_g K_{g,\tau}C_g + K_{Aro}C_{Aro}\right)} \]  

(4.18)

\[ \dot{k}_g = k_g^0 \exp\left(-\frac{E_{a,g}}{RT}\right) \]  

(4.19)

\[ K_g = K_g^\infty \exp\left(-\frac{\Delta H_{a,g}}{RT}\right) \]  

(4.20)

where \( r_g \) is the rate of reaction of sulphur compound \( g \), \( C_g \), \( C_{H2} \), \( C_{H2S} \), \( C_{Aro} \), are the concentrations; \( k_g \) is the rate constant; \( E_{a,g} \) is the activation energy; \( K_{g}, K_{H2}, K_{Aro} \), \( K_{H2S} \) are the adsorption constants and \( \Delta H_{a,g} \) is the heat of adsorption.

### 4.2.3 Hydrodenitrogenation

Nitrogen compounds in middle distillate fractions are present as heterocyclic aromatic compounds and nonheterocyclic organonitrogen compounds (Girgis and Gates, 1991). Nonheterocyclic organonitrogen compounds such as anilines, aliphatic amines and nitriles are usually in very minute quantities and are denitrogenated very rapidly. Thus they are of very little importance in hydroprocessing of heavy feeds (Girgis and Gates, 1991). The nitrogen heterocyclic compounds are classified as basic nitrogen compounds such as pyridine, quinoline and non-basic nitrogen compounds e.g. indole, and carbazole (Klein et al., 2006).

Nitrogen removal from heterocyclic organonitrogen compounds requires hydrogenation of the ring containing the nitrogen atom before hydrogenolysis of carbon-nitrogen bond (Girgis and Gates, 1991). This requirement implies that equilibrium of hydrogenation reactions can affect the rate of hydrodenitrogenation. Hydrodenitrogenation reaction rates can be increased using high hydrogen partial pressure to increase the equilibrium concentrations of saturated heteroring compounds (Girgis and Gates, 1991). The hydrodenitrogenation reactions in
industrial hydroprocessing are virtually irreversible under high hydrogen partial pressure conditions (Girgis and Gates, 1991).

The mechanism of hydrodenitrogenation involves saturation of heterocyclic and aromatic ring followed by C-N bond scission. Mathur et al., (1982) observed that the hydrogenation rates are higher than the C-N bond scission rates and that the overall hydrodenitrogenation rates are similar to the rates of bond scission. Thus the simplified hydrodenitrogenation reaction network is based on hydrogenolysis as the rate determining step (Sun, 2004). The hydrodenitrogenation reaction pathways for indole are shown in Figure 4.3 as an example. A detailed account of the hydrodenitrogenation reaction mechanism for nitrogen compounds can be found elsewhere (Cocchetto and Satterfield, 1976).

\[
\begin{align*}
\text{Indole} & \quad \text{Indole} & \quad \text{Othoethylaniline} & \quad \text{Ethylbenzene} \\
\text{\includegraphics[width=0.8\textwidth]{indoleReactionNetwork.png}}
\end{align*}
\]

**Figure 4.3 Hydrodenitrogenation reaction network for Indole (Zhang and Ozkan, 1997)**

The hydrodenitrogenation reaction pathways for nitrogen compounds in diesel hydrotreating feedstocks can be expressed in terms of interconversions of matrix elements as (Sun, 2004):

Indole:

\[
\text{Indole} + \text{H}_2 \rightarrow \text{Ethyl aniline}
\]
Mathur et al., (1982) determined the hydrodenitrogenation rates of several basic nitrogen heterocyclic compounds. The hydrodenitrogenation reaction rate can be expressed as:
\[ r_{ni} = \frac{k_{ni} C_{ni}}{1 + \sum_{ni} K_{ni} C_{ni}} P_{H2}^{\beta_{ni}} \]  
(4.28)

where \( r_{ni} \) is the rate of hydrodenitrogenation reaction, \( k_{ni} \) is the rate constant, \( C_{ni} \) is the concentration of nitrogen species \( ni \), \( K_{ni} \) is the adsorption constant, \( P_{H2}^{\beta_{ni}} \) is the hydrogen partial pressure with \( \beta_{ni} \) as a coefficient (Sun, 2004).

### 4.2.4 Cracking reactions

The molecular model of the diesel hydrotreater also takes into account the formation of light gases due to cracking of molecules apart from the main reaction groups of the diesel hydrotreating process. The model employed in this work for prediction of light gas formation is proposed by Hidalgo-Vivas (1999) and assumes that light gas is formed mainly due to the cracking reactions of paraffins. The contribution from the cracking of aromatic and naphthenic compounds is assumed to be small. The production of light gases is correlated with the concentration of \( H2S \) and is given as (Hidalgo-Vivas, 1999):

\[
\ln\left(\frac{1}{1 - X_{cracking}}\right) = 4.603 \times 10^{-6} \cdot P_{H2S} 
\]  
(4.29)

where \( X_{cracking} \) is the yield of light gas, and \( P_{H2S} \) is the partial pressure of hydrogen sulphide. The composition of light gas is assumed to be constant in previous work due to mild operating conditions generally employed in diesel hydrotreating process. A detailed account of the cracking model can be found elsewhere (Hidalgo-Vivas, 1999; Sun, 2004).

The reaction groups discussed above have been considered in the molecular model for diesel hydrotreaters by Sun (2004). A detailed account of the reaction mechanisms, estimation of kinetic parameters, and validation of reaction models can be found elsewhere (Korre et al., 1994; Korre et al., 1995; Hidalgo-Vivas, 1999; Sun, 2004).
4.2.5 Reactor modelling of diesel hydrotreater

A one-dimensional pseudo homogeneous reactor model of Sun (2004) is employed in this work based on the following assumptions (Sun, 2004):

1. The reactor operates isothermally under isobaric and steady-state conditions.
2. There is no radial profile of concentration within the reactor.
3. The reactor behaves like a plug-flow reactor.
4. Evaporation of diesel oil occurs instantaneously only at the entrance of the reactor, liquid volume in the reactor remains constant.
5. The catalyst particles are completely wetted.

The rate of mass transfer between gas, liquid and solid phases has been ignored as the hydrogenation reaction is kinetically controlled (Cooper and Donnis, 1996). Also, adequate gas and liquid distribution is assumed for complete wetting of the catalyst particles as is commonly accepted for commercial hydroprocessing units (Shah, 1975). A detailed account of modelling techniques can be found elsewhere (Froment and Bischoff, 1990). Both mass and energy balance are considered:

\[
\frac{dC_s}{dz} = r_s \rho_B / U_s \\
\frac{dT}{dz} = \sum (-\Delta H_r), r_s \sum C_{Ps} C_s
\]

where \( r_s \) is the rate of reaction of molecule \( s \), \( \rho_B \) is the catalyst bulk density, \( U_s \) is the superficial velocity, \( C_{Ps} \) is the heat capacity, \( C_s \) is the concentration, \( z \) is the reactor length, \( T \) is the temperature of the bed, \( \Delta H_r \) is the heat of reaction. The differential equations of pseudo-homogeneous model are integrated numerically.
using fourth order Runge-Kutta method (NAG, D02PCF) for the purpose of simulating concentration profiles along the length of an existing reactor or the design of a new reactor (Sun, 2004).

4.2.6 Catalyst de-activation model and run length calculation

The catalyst de-activation model and the strategy for run length calculation, i.e. the estimation of catalyst life, followed in this work are the ones adopted by Sun (2004). The catalysts in diesel hydrotreating processes are primarily de-activated due to carbon containing deposits. Therefore, the deactivation model estimates the catalyst activity based on the amount of coke, deposited on the catalyst, calculated as a function of time and process conditions.

The de-activation model is based on the coke formation model and reactivity-coke content relationship developed by De Jong (1994a, b). Aromatic compounds are assumed to be the precursor to coke formation and the rate of coke deposition \( r_{\text{coke}} \) is based on the thermal and catalytic coke generation (De Jong, 1994b):

\[
    r_{\text{coke}} = r_c + r_t
\]

\[
    r_t = k_t C_p^2 / P_{H_2}
\]

\[
    r_c = \frac{k_c K_{\text{ads}} C_p}{1 + K_{\text{ads}} C_p}
\]

\[
    k_c = k_{c,0} \left(1 - \frac{W_c}{W_{c,\text{max}}} \right)
\]

where \( k_t \) is the rate constant for thermal coke formation, \( P_{H2} \) is the hydrogen partial pressure, \( W_c \) is the amount of coke deposited on the catalyst, \( W_{c,\text{max}} \) is the maximum amount of catalytic coke deposited on the catalyst, \( k_c \) is the rate constant for coke catalytic coke formation, \( k_{c,0} \) is the initial reactivity for catalytic coke formation, \( K_{\text{ads}} \) is the adsorption constant of coke precursor i.e. the aromatic content of the feedstock, and \( C_p \) is the concentration of coke precursor.
Catalyst de-activation is represented with a de-activation coefficient calculated from the total coke content deposited on the catalyst (Dong et al., 1997):

\[ \alpha = 1 - a \cdot (W_c)^b \]  
\[ W_c = \int_0^t r_{\text{coke}} dt \]

where \( \alpha \) is the de-activation coefficient, and \( a \) and \( b \) are the coefficients of the de-activation relation. This de-activation coefficient, which is a fraction, represents the inhibition, to the rate of diesel hydrotreating reactions, due to the loss of catalyst activity as a function of coke formation.

The run length calculation for the diesel hydrotreater operation, i.e. the estimation of catalyst life, is carried out using dynamic programming approach for optimisation of catalyst life of fixed bed reactors (Gary, 2002). The strategy is based on the breakdown of catalyst life into fixed interval operating periods, e.g. two weeks. The molecular model of the diesel hydrotreater calculates the reactor temperature needed to satisfy the product specifications, such as the sulphur content, for each operating period, starting with a new catalyst. Based on the reactor temperature and the aromatic content of the feedstock, the de-activation model predicts the coke formation and the de-activation coefficient. The catalyst activity for the consecutive period is updated based on the de-activation coefficient and the calculations are repeated sequentially until the termination criterion for shutting down the process is satisfied (Sun, 2004). The termination criterion may be based on an upper limit of the reactor temperature and/or a lower limit on the catalyst activity.

Sun (2004) illustrated through industrial case studies that the molecular model of diesel hydrotreater predicts the conversion for sulphur and nitrogen compounds with reasonable accuracy. The maximum percentage error in estimation of temperatures of boiling point curve (ASTM D86) is 4.92%. The molecular model also predicts the run-length, i.e. catalyst life, with reasonable accuracy (Sun, 2004).
4.3 Proposed modifications to molecular model of diesel hydrotreater

The molecular model for diesel hydrotreaters discussed in Section 4.2 provides a framework for prediction of product properties and operating conditions for achieving desired product specifications based on detailed reaction chemistry and reaction kinetics at the level of molecular pathways. This section presents the improvements proposed in this work to the molecular model of Sun (2004) for diesel hydrotreaters. As this research work focuses on the design of the overall diesel hydrotreating process and not just the reactor, the incorporation of proposed improvements into the molecular model for diesel hydrotreaters is considered to be beyond the scope of this work.

4.3.1 Equilibrium constant calculations for aromatic hydrogenation

The equilibrium constant calculations for the aromatic hydrogenation reactions of Section 4.2.1 are based on experimental data available for benzene, alkyl benzenes and the products of their hydrogenation reactions (Stull et al., 1969). The equations for calculating equilibrium constants employed by Sun (2004) estimate the equilibrium constants of aromatic compound classes at various temperatures and are in the following form:

\[ \log K = \frac{a}{T} - b \]  \hspace{1cm} (4.38)

where \( K \) is the equilibrium constant, \( T \) is the temperature in Kelvin, and \( a \) and \( b \) are the coefficients for a given homologous series. Experimental data shows that the equilibrium constants are dependent not only on temperature but also on the molecular structure. Therefore, we need a relationship to reflect how equilibrium constants depend on molecular structure, i.e. carbon number and homologous series, as well as temperature.

The equations, for calculation of equilibrium constants, of the above form are corrected in this work using data generated with group contribution method of Joback (1987), to account for the change in equilibrium constant values with respect to the number of alkyl substituent carbon atoms, to the base structure, and
the temperature. The proposed modification is illustrated with an example for the hydrogenation reaction of equation 4.3 i.e. the hydrogenation of single ring aromatic compounds to naphthenes. The original equation for calculation of equilibrium constants for this reaction is (Sun, 2004):

\[
\ln K = 25758 \left( \frac{1}{T(K)} \right) - 46.657
\]  
(4.39)

The modified equation with correction for influence of molecular structure is:

\[
\ln K = (25758 - 294.07 \cdot C_{AS}) \times \frac{1}{T(K)} - (46.657 + 0.2 \cdot C_{AS}) \quad \text{For } C_{AS} \leq 4
\]  
(4.40)

where \( C_{AS} \) represents the number of alkyl substituent carbon atoms. This equation may be applied to molecules with four or less substituted carbon atoms. For molecules with higher number of substituted carbon atoms, it is observed that the change in equilibrium constants becomes negligible with respect to the change in number of substituent carbon atoms (Sun, 2004). Table 4.1 shows experimental values of equilibrium constants for the hydrogenation reaction of single ring aromatic compounds. A range of carbon numbers and temperatures are presented.
<table>
<thead>
<tr>
<th>T (K)</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
<th>C10</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>39.541</td>
<td>38.257</td>
<td>36.888</td>
<td>36.313</td>
<td>35.638</td>
</tr>
<tr>
<td>300</td>
<td>39.026</td>
<td>37.733</td>
<td>36.357</td>
<td>35.803</td>
<td>35.115</td>
</tr>
<tr>
<td>400</td>
<td>18.078</td>
<td>16.945</td>
<td>15.912</td>
<td>15.409</td>
<td>14.893</td>
</tr>
<tr>
<td>500</td>
<td>5.207</td>
<td>4.230</td>
<td>3.374</td>
<td>2.911</td>
<td>2.508</td>
</tr>
<tr>
<td>600</td>
<td>-3.516</td>
<td>-4.373</td>
<td>-5.094</td>
<td>-5.522</td>
<td>-5.866</td>
</tr>
</tbody>
</table>

Table 4.1 Experimental values of equilibrium constants for single ring aromatic hydrogenation reactions (Stull et al., 1969)

A comparison of the results of calculation of equilibrium constants using the equation 4.39 from previous work, i.e. of Sun (2004), with the experimental data is shown in Table 4.2.
Table 4.2 Comparison of equilibrium constant values calculated using equation 4.39, from previous work (Sun, 2004), with experimental results

A comparison of the equilibrium constant values calculated using the equation 4.40, proposed in this work, with the experimental data is shown in Table 4.3.
Table 4.3 shows that the estimation of equilibrium constants is in good agreement with the experimental data for various carbon numbers and a wide range of temperatures, and is significantly improved compared to the previous work. Other aromatic classes are assumed to have the similar trends and the differences between equilibrium constants in single ring aromatic compounds can be used in the calculations for other aromatic compound classes (Sun, 2004).

The proposed correction in the estimation of equilibrium constants takes into account the effect of temperature as well as molecular structure on the equilibrium constants of aromatic hydrogenation reactions. The prediction of conversion of aromatic hydrogenation reactions with molecular model for diesel hydrotreaters
may be improved using this proposed correction in the estimation of equilibrium constants.

### 4.3.2 Estimation of rate constants for hydrodesulphurisation

The hydrodesulphurisation model of Section 4.2.2 represents the thiophenic sulphur compound classes with model compounds, namely benzothiophene, dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene. The representation of various components of a homologous series with one model compound neglects the effect of molecular structure on the reactivity of a species.

In order to reflect the effect of molecular structure on reactivity of a species quantitative structure-reactivity correlations (QSRCs) can be explored to relate the reactivity of components with their molecular properties for a homologous series of reactions (Klein et al., 2006):

\[
\ln k_i = a + b \cdot RI_i
\]  

(4.41)

where \( k \) is the rate constant, \( RI \) is the reactivity index such as heat of reaction of species \( i \), and \( a \) and \( b \) are constants for various homologous series that may be regressed using experimental data. The quantitative structure-reactivity correlations concept is exploited to account for the effect of substituent carbon atoms on reactivity using representative model compounds as base structures. The quantitative structure-reactivity correlation developed in this work for the SI compound class of the molecular type and homologous series matrix, consisting of benzothiophene and alkylbenzothiophenes, is:

\[
\ln k = a + b \cdot \Delta H_{rxn} + c \cdot C_{AS}
\]  

(4.42)

where \( \Delta H_{rxn} \) is the standard heat of reaction, \( C_{AS} \) represents the number of alkyl substituent carbon atoms to the representative base compound i.e. benzothiophene in this case. The coefficients are regressed based on the experimental data available in the literature (Ma et al., 1994). The coefficients for equation 4.42 are:

\[ a = -7.788 \]
The heat of reaction is calculated as follows (Smith, 2005):

\[
\Delta H_{\text{rxn}} = \Delta H_{T_0}^0 + \int_{T_0}^T \Delta C_p \, dT
\]  

(4.43)

where \( \Delta H_{T_0}^0 \) is the standard enthalpy of formation at \( T_0 \), \( \Delta C_p \) is the difference of heat capacity of reaction products and reactants as a function of temperature (Smith, 2005). A comparison of the results of the proposed correlation, for estimation of rate constants for desulphurisation of benzothiophenes, with the experimental data from literature (Ma et al., 1994) is shown in Table 4.4.

<table>
<thead>
<tr>
<th>Alkyl benzothiophenes</th>
<th>( C_{AS} )</th>
<th>( \ln k ) Experimental</th>
<th>( \ln k ) Calculated</th>
<th>% Error</th>
<th>Absolute Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{10}H_{10}S )</td>
<td>2</td>
<td>-1.347</td>
<td>-1.558</td>
<td>15.664</td>
<td>0.211</td>
</tr>
<tr>
<td>( C_{14}H_{18}S )</td>
<td>6</td>
<td>-1.609</td>
<td>-1.542</td>
<td>4.164</td>
<td>0.067</td>
</tr>
<tr>
<td>( C_{15}H_{20}S )</td>
<td>7</td>
<td>-1.609</td>
<td>-1.538</td>
<td>4.413</td>
<td>0.071</td>
</tr>
</tbody>
</table>

Table 4.4 Comparison of estimated rate constants for desulphurisation of benzothiophenes at 340 °C with experimental data (Ma et al., 1994)

Table 4.4 compares natural log of rate constants for benzothiophenes with two, six and seven substituent carbon atoms (\( C_{AS} \)) at 340°C on commercial CoMo/Al₂O₃ catalyst. This comparison indicates that the representation of sulphur compound classes with model compounds may result in discrepancies in prediction of rate of conversion of individual sulphur components and the proposed form of quantitative structure-reactivity correlations may improve the desulphurisation model.
4.4 Integrated approach for process design

This section introduces a novel approach for integrated design of hydrotreating processes using the molecular type and homologous series matrix representation of petroleum fractions. Previous research studies using MTHS matrix representation (Peng, 1999; Zhang, 1999; Sun, 2004) have been focused on individual subsystems of refinery processes such as modelling of reaction or separation systems. However, the interaction between hierarchical levels of process design, namely the reaction, separation and heat recovery system have not been explored in previous studies employing the molecular type and homologous series matrix representation. Integrated design and optimisation framework developed in this work is presented in the light of the individual subsystems, i.e. the reaction, separation and heat recovery system, as well as the optimisation algorithm. Each is addressed in turn here.

4.4.1 Reactor design for diesel hydrotreating processes

The molecular model of the diesel hydrotreater discussed in Section 4.2 is employed in the integrated design and optimisation framework. The cost data for the reactor and catalyst are taken from Sun (2004) and presented in Appendix A. The annualised catalyst cost is estimated, depending on the size of the reactor and the catalyst life:

\[
\text{Cat. Cost} (\$/yr) = a \times \pi R^2 \times Z \times \left( \frac{1}{\text{Cat. life} (\text{yr})} \right)
\]

(4.44)

where \( R \) is the radius of the reactor, \( Z \) is the length of reactor, and \( a = 62018.452 \) $/m^3 is the catalyst cost coefficient. A linear correlation is developed for estimation of catalyst life from the simulation results of the molecular model for run-length calculation using the method discussed in Section 4.2.6:

\[
\text{Cat. life} (\text{yr}) = 9.843 - 0.01172 \times T (K)
\]

(4.45)

where \( T \) is the operating temperature of the diesel hydrotreater at the start-of-run, i.e. when the catalyst is 100% active. The catalyst life depends on the start-of-run
temperature of the reactor, which influences the rate of catalyst de-activation, and
the aromatic content of feedstock.

4.4.2 Separation system design for diesel hydrotreating process

The separation system of a diesel hydrotreating process may consist of high and low pressure flash units and a distillation column. In this work the flash separation is modelled using the flash model discussed in Section 3.3.2. However, the size and cost of these units have not been taken into account in this framework. The reason for this simplification is that the operating conditions of flash separation units have been assumed to remain constant while comparing the proposed integrated design approach with conventional sequential design approach. The amount of diesel feedstock to be treated in the design calculations also remains constant. Therefore, this simplification may be justified for comparing the integrated design approach developed in this work with sequential approach for design of overall diesel hydrotreating process.

The distillation column is modelled using the short-cut model discussed in Section 3.3.1. The column capital cost and operating costs are accounted for using the methods and data presented in Appendix B. The short-cut model discussed in Section 3.3.1 requires key components and their recoveries to be specified for a desired separation. However, in refinery processes, such as diesel hydrotreating process, the products of distillation process are specified in terms of the boiling range and bulk physical properties (Watkins, 1979). In order to model the distillation column of a diesel hydrotreating process, using the short-cut model discussed in Section 3.3.1, the product specifications in terms of boiling curve temperatures need to be translated in terms of key components and their recoveries. Chen (2008) developed a methodology for specifying boiling curve temperatures, and flow rates for products of a distillation column. This methodology employs Levenberg-Marquardt algorithm (Gill et al., 1978). The methodology developed by Chen (2008) treats key components and recovery of key components as optimisation variables, i.e. degrees of freedom, and not as specifications for a desired separation. A detailed account of the methodology for specifying boiling
curve temperatures of products of distillation can be found elsewhere (Chen, 2008). This methodology is employed along with the short-cut model for distillation so that the diesel product, i.e. bottom product of distillation column may be specified in terms of boiling range and flow rate.

4.4.3 Heat recovery system design for diesel hydrotreating process

Heat exchanger networks provide a means of recovering the heat available from hot process streams and transferring to cold process streams, thereby reducing the heating and cooling duties of external utilities such as steam and cooling water. The heating and cooling duties of the heat recovery system depend on the design and operating conditions of reactor and separation system.

Capital and operating costs may be estimated for a given heat recovery system using the material and energy balance of process streams. These targets, i.e. estimates, provide an opportunity to screen design options conveniently without the actual design of heat exchanger networks (Smith, 2005). Pinch analysis is a widely used tool for estimation of minimum hot and cold utility demand, minimum number of units and minimum investment cost for a given set of process streams, pinch analysis is discussed in Chapter 5. In this section, capital and energy cost targeting for a heat recovery system is briefly introduced for the benefit of understanding the integrated approach for design of diesel hydrotreating process.

The stream data for hot and cold process streams of a heat recovery system depends on the reactor and separation system design. This stream data, i.e. stream temperatures, flow rates and enthalpies, are used to estimate the minimum hot and cold utility requirement using the pinch analysis. In order to estimate the capital cost of the heat recovery system, the number of heat exchangers and the heat transfer area required for the heat recovery system needs to be estimated. The minimum number of heat exchangers required for the heat recovery system is estimated from the number of process streams and pinch point (Hohman, 1971; Linnhoff et al., 1979). The heat transfer area required for a heat recovery system is
estimated assuming vertical heat transfer (Townsend and Linnhoff, 1984; Linnhoff and Ahmad, 1990).

The integrated approach for design of diesel hydrotreating processes developed in this work is the first of its kind using the molecular type and homologous series matrix representation. Therefore, a methodology is needed to translate the detailed molecular level information employed in the molecular model of a diesel hydrotreater to bulk macroscopic thermal properties, such as heat capacities of process streams, required in design and cost estimation for heat recovery system. The heat capacities of diesel hydrotreater streams are calculated using the heat capacities and mole fractions of individual components:

\[ Cp = \sum_{i=1}^{n} x_i \cdot Cp_i \]  

(4.46)

where \( Cp \) is the heat capacity of the stream, \( x_i \) and \( Cp_i \) represent the mole fraction and heat capacity of component \( i \), respectively. The individual component heat capacities are estimated using group contribution methods, as discussed in Section 2.4.1. Pinch analysis is based on the assumption of constant thermal properties. Therefore, mean molar heat capacity is calculated for diesel hydrotreater streams:

\[ \bar{Cp} = \frac{\int_{T_i}^{T_2} CpdT}{T_2 - T_i} \]  

(4.47)

where \( \bar{Cp} \) is the mean molar heat capacity of a stream.

**4.4.4 Optimisation framework for integrated process design**

The optimisation of design of diesel hydrotreating processes is a complex problem due to the simultaneous handling of different non-linear models i.e. the molecular model of the diesel hydrotreater, short-cut distillation model, and flash model for high pressure and low pressure flash separation. Stochastic optimisation methods may be applied for optimisation of design of diesel hydrotreating processes due to the non-linear nature and complexity of the problem. Stochastic optimisation
techniques have higher probability of escaping local optima and finding solutions in the vicinity of the global optimum for complex non-linear and non-convex problems compared to deterministic methods (Chen, 2008).

Simulated annealing is a widely applied stochastic optimisation algorithm due to its robustness and simplicity to be implemented (Rodriguez, 2005). Simulated annealing is implemented in this framework for optimisation of the integrated design of diesel hydrotreating process. In the simulated annealing algorithm, the problem is treated as a black-box. A black-box may be defined as a system that provides output for a given input and the information about internal calculations is not required (Chen, 2008). The optimisation algorithm makes use of the values of the objective function at randomly chosen points in the search space. The black-box treatment decouples the simulation and optimisation of the design problem and improves the performance of optimisation algorithm for complex problems (Chen, 2008). Simulated annealing algorithm is discussed in detail in Section 4.5.

4.5 Simulated annealing

Simulated annealing algorithm has been developed using the analogy to the physical annealing of metals where a metal in molten state at a very high temperature is cooled down very slowly. This analogy was observed and applied to the optimisation of combinatorial problems for the first time by Kirkpatrick et al., (1983). In molten state the metal atoms are distributed randomly. When the system, i.e. the metal, is cooled it reaches the state of minimum energy. If the annealing process is carried out slowly such that at any point in time the system is close to thermodynamic equilibrium then the system may reach stable crystalline structure with minimum energy. However, if the metal is not cooled sufficiently slowly or the initial temperature of the system is not high enough, then a glassy metastable structure, with energy higher than the desired minimum level, is formed.
The simulated annealing algorithm of Kirkpatrick et al., (1983) is represented in Figure 4.4. The simulated annealing process starts with an initial trial solution at an appropriate high value of the annealing temperature. The annealing temperature serves as a control parameter for the optimisation. The initial trial solution is modified by a random change, known as a random move; the objective function for this new prospective solution is evaluated against that of previous trial solution. The modification made to the current trial solution may be accepted or rejected based on the acceptance criterion employed. This process of modification, simulation and evaluation is repeated a number of times (N) determined by the parameter known as the Markov chain length ($N_{\text{max}}$), to obtain a decent set of sample solutions. Once several candidate solutions have been obtained, the annealing temperature is reduced. This cycle is continued until the termination criterion is satisfied. The annealing temperature, acceptance criterion, Markov chain length and termination criterion constitute the simulated annealing parameters. These parameters will be discussed briefly in this work; details can be found elsewhere (Rodriguez, 2005).
4.5.1 Simulated annealing parameters

The performance of the simulated annealing algorithm is dictated by simulated annealing parameters; therefore a brief introduction to the parameters involved in a simulated annealing optimisation is presented here.
4.5.1.1 Annealing temperature

The initial value of the annealing temperature and its cooling schedule i.e. the way it is reduced, have a strong impact on the performance of an optimisation run. If the initial annealing temperature is too low or the cooling is not slow enough, then the solution could end up trapped in a local optimum. However, a very high initial annealing temperature or very slow cooling would unnecessarily increase the computation time (Rodriguez, 2005).

4.5.1.2 Acceptance criterion

Any modifications made by the simulated annealing algorithm to trial solutions are accepted or rejected depending on the acceptance criterion chosen. Usually an acceptance criterion accepts a random move made by the algorithm if it improves the objective function (downhill move) and accepts an uphill move, i.e. modifications to the current trial solution that deteriorate the objective function, with a probability that decreases as the search progresses. This feature helps the simulated annealing algorithm to avoid getting a solution trapped in a search space with a local optimum. Metropolis acceptance criterion (Metropolis et al., 1953) has been used throughout this work as this acceptance criterion has been observed to provide efficient performance in simulated annealing algorithm (Rodriguez, 2005; Chen, 2008).

4.5.1.3 Markov chain length

In the simulated annealing algorithm, a current trial solution is subjected to random moves a number of times. The number of times these random modifications are made at each annealing temperature is termed the Markov chain length. A short Markov chain length may lead the solution to a local optimum, while increasing this number improves the probability of the search leading to a global optimum at the expense of added computation time (Rodriguez, 2005).
4.5.1.4 Termination criterion

The decision to stop the search for optimal solution of an optimisation problem in the simulated annealing algorithm is made through the termination criterion being satisfied. Usually the search is terminated if the specified lower limit of the annealing temperature is reached or if no modifications to the current trial solution have been accepted even after a certain specified number of reductions in the annealing temperature.

4.5.2 Simulated annealing moves

The modifications or changes made by the simulated annealing algorithm to a current structure are known as random moves. The random moves made by the algorithm depend on the nature of the optimisation problem and the variables involved. Table 4.5 presents a list of simulated annealing moves for modifications to the integrated design of diesel hydrotreating process.

<table>
<thead>
<tr>
<th>Integrated design moves for diesel hydrotreating process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel hydrotreater move ( p )</td>
</tr>
<tr>
<td>Reactor operating temperature move</td>
</tr>
<tr>
<td>Hydrogen partial pressure move</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Table 4.5 Simulated annealing moves for integrated diesel hydrotreating process design

The integrated design problem consists of two sub-systems: the diesel hydrotreater and the separation system. The heat recovery system depends on the design of the diesel hydrotreater and the separation system, since only targeting of heat recovery
system is employed and not the actual heat exchanger network design. The move probabilities are classified into two groups based on these sub-systems with the probability $p$ for a diesel hydrotreater move and $1-p$ for distillation column move. The probabilities for random moves of individual optimisation variables provide flexibility to the optimisation procedure and are specified on the basis of the influence of a design variable on the overall performance of the process (Chen, 2008).

### 4.6 Case study

A case study is presented in this section to illustrate the application and benefits of the proposed integrated approach for design of diesel hydrotreating processes with molecular type and homologous series matrix representation. The objective of the case study is to design the diesel hydrotreating process for a given feedstock satisfying the commercial product specifications for diesel fuel with the conventional sequential design approach, the novel integrated design approach, and to analyse the new design framework against the conventional one.

The case study is taken from Sun (2004) for a diesel hydrotreating process using straight run gas oil (SRGO) as the diesel hydrotreater feed. The properties of the feedstock are shown in Table 4.6.
### Table 4.6 Properties of feedstock of diesel hydrotreater for case study on design of diesel hydrotreating process

The molecular type and homologous series matrix for composition of the feedstock is shown in Appendix A. The sulphur content of the diesel product is specified to be at most 10 ppm, i.e. ultra-low sulphur diesel. The specifications for the bottom product of the distillation column i.e. the diesel stream are shown in Table 4.7.
Table 4.7 Bottom product specifications for the distillation column of diesel hydrotreating process

<table>
<thead>
<tr>
<th>Flow rate specification (kmol/sec)</th>
<th>0.127</th>
</tr>
</thead>
<tbody>
<tr>
<td>True boiling point specification (°C)</td>
<td></td>
</tr>
<tr>
<td>T10</td>
<td>201.10</td>
</tr>
<tr>
<td>T50</td>
<td>251.70</td>
</tr>
<tr>
<td>T90</td>
<td>310.70</td>
</tr>
</tbody>
</table>

The cost data for the heat recovery system are taken from Verheyen and Zhang (2006) and is shown in Appendix B. The heat recovery system targeting is carried out for a minimum approach temperature of 20 °C. The operating conditions of the high pressure and low pressure flash separation units are fixed for both the design approaches and correspond to the range of operating conditions in commercial hydroprocessing units (Meyers, 1997). The operating conditions of the flash separation units are shown in Table 4.8.

<table>
<thead>
<tr>
<th>Operating conditions of flash separation units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>High pressure flash unit</td>
</tr>
<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Pressure (bar)</td>
</tr>
</tbody>
</table>

Table 4.8 Operating conditions of the flash separation units of diesel hydrotreating process

In conventional approach to process design, the design of diesel hydrotreating process may be carried out sequentially, starting with the reactor i.e. the diesel hydrotreater, followed by the separation system and heat recovery system. The sequential approach to process design is taken as the base case in this case study.
for evaluation and comparison of the novel integrated approach for design of diesel hydrotreating process developed in this work.

For the sequential design of diesel hydrotreating process a quadratic interpolation method is used to minimise the diesel hydrotreater cost (NAG, E04ABF). The separation system is designed for the reactor products using COLOM software version 2.1 minimising the capital cost of distillation column. Simulated annealing algorithm is used for optimisation of capital cost of distillation column. Finally the capital and energy costs are estimated using the methods discussed in Section 4.4.3. The major features of the overall diesel hydrotreating process design obtained from the sequential approach for the system under consideration are shown in Table 4.9. The process stream data of this design are shown in Table 4.10.

It can be seen from Table 4.9 that in sequential approach for design of diesel hydrotreating process the start-of-run temperature, i.e. the reactor operating temperature at the beginning of catalyst life, is as low as possible while satisfying the product specifications e.g. sulphur content. In this way a maximum catalyst life and consequently, a minimum catalyst cost is ensured. The capital cost of distillation column is then minimised while satisfying the flow rate and boiling range specification of diesel product. However this sequential approach of process design neglects the interactions of individual subsystems of the overall process. For example, the reactor operating temperature may effect the product composition, boiling range and enthalpies of the product streams. These factors in turn may influence the capital and operating costs of the distillation column and the heat recovery system.
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diesel hydrotreater</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Reactor operating temperature (°C)</strong></td>
<td>322.52</td>
</tr>
<tr>
<td><strong>Length of reactor (m)</strong></td>
<td>11.522</td>
</tr>
<tr>
<td><strong>Distillation column</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Column pressure (bar)</strong></td>
<td>5.926</td>
</tr>
<tr>
<td><strong>Reflux ratio</strong></td>
<td>1.795</td>
</tr>
<tr>
<td>Light key</td>
<td>Pseudo-component number 7</td>
</tr>
<tr>
<td>Heavy key</td>
<td>Pseudo-component number 8</td>
</tr>
<tr>
<td>Light key recovery (%)</td>
<td>86.95</td>
</tr>
<tr>
<td>Heavy key recovery (%)</td>
<td>61.09</td>
</tr>
<tr>
<td>Total number of stages</td>
<td>44</td>
</tr>
<tr>
<td>Column feed temperature (°C)</td>
<td>232.43</td>
</tr>
<tr>
<td>Feed pre-heat duty (kW)</td>
<td>2417</td>
</tr>
<tr>
<td>Total condenser duty (kW)</td>
<td>6090</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>7311</td>
</tr>
</tbody>
</table>

Table 4.9 Sequential design of diesel hydrotreating process
<table>
<thead>
<tr>
<th>Stream</th>
<th>Supply temperature (°C)</th>
<th>Target temperature (°C)</th>
<th>Enthalpy difference (kW)</th>
<th>Heat capacity flow rate (kW/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor feed</td>
<td>25.0</td>
<td>322.52</td>
<td>33240.9</td>
<td>111.729</td>
</tr>
<tr>
<td>Reactor product</td>
<td>322.52</td>
<td>50.0</td>
<td>-29724.6</td>
<td>109.075</td>
</tr>
<tr>
<td>Column feed</td>
<td>50.0</td>
<td>232.43</td>
<td>2416.93</td>
<td>13.248</td>
</tr>
<tr>
<td>Condenser stream</td>
<td>238.95</td>
<td>230.48</td>
<td>-6089.88</td>
<td>718.909</td>
</tr>
<tr>
<td>Distillate product</td>
<td>230.48</td>
<td>50.0</td>
<td>-764.782</td>
<td>4.237</td>
</tr>
<tr>
<td>Reboiler stream</td>
<td>328.50</td>
<td>340.57</td>
<td>7310.74</td>
<td>605.556</td>
</tr>
<tr>
<td>Bottom product</td>
<td>340.57</td>
<td>25.0</td>
<td>-3115.08</td>
<td>9.871</td>
</tr>
</tbody>
</table>

Table 4.10 Stream data of diesel hydrotreating process from sequential design approach

The cost breakdown of the design of diesel hydrotreating process obtained using the sequential design approach is shown in Table 4.11.
<table>
<thead>
<tr>
<th>Cost Item</th>
<th>Cost (£/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst cost (£/yr)</td>
<td>2,733,000</td>
</tr>
<tr>
<td>Column capital cost (£/yr)</td>
<td>366,000</td>
</tr>
<tr>
<td>Heat exchanger area cost (£/yr)</td>
<td>1,209,000</td>
</tr>
<tr>
<td>Energy cost (£/yr)</td>
<td>978,000</td>
</tr>
<tr>
<td>Total annualised cost (£/yr)</td>
<td>5,287,000</td>
</tr>
</tbody>
</table>

Table 4.11 Cost breakdown of design of diesel hydrotreating process obtained using sequential approach

The major features of the design, obtained using the proposed integrated approach for design of diesel hydrotreating process, are shown in Table 4.12. The process stream data of this design are shown in Table 4.13.
<table>
<thead>
<tr>
<th>Diesel hydrotreater</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor operating temperature (°C)</td>
<td>324.74</td>
</tr>
<tr>
<td>Length of reactor (m)</td>
<td>11.522</td>
</tr>
<tr>
<td>Distillation column</td>
<td></td>
</tr>
<tr>
<td>Column pressure (bar)</td>
<td>1.296</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>1.064</td>
</tr>
<tr>
<td>Light key</td>
<td>Pseudo-component number 7</td>
</tr>
<tr>
<td>Heavy key</td>
<td>Pseudo-component number 8</td>
</tr>
<tr>
<td>Light key recovery (%)</td>
<td>74.44</td>
</tr>
<tr>
<td>Heavy key recovery (%)</td>
<td>64.86</td>
</tr>
<tr>
<td>Total number of stages</td>
<td>16</td>
</tr>
<tr>
<td>Column feed temperature (°C)</td>
<td>152.56</td>
</tr>
<tr>
<td>Feed pre-heat duty (kW)</td>
<td>1322</td>
</tr>
<tr>
<td>Total condenser duty (kW)</td>
<td>5343</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>6294</td>
</tr>
</tbody>
</table>

Table 4.12 Design of diesel hydrotreating process obtained using integrated approach developed in this work
<table>
<thead>
<tr>
<th>Stream</th>
<th>Supply temperature (°C)</th>
<th>Target temperature (°C)</th>
<th>Enthalpy difference (kW)</th>
<th>Heat capacity flow rate (kW/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor feed</td>
<td>25.0</td>
<td>324.74</td>
<td>33528.9</td>
<td>111.859</td>
</tr>
<tr>
<td>Reactor product</td>
<td>324.74</td>
<td>50.0</td>
<td>-29999.7</td>
<td>109.192</td>
</tr>
<tr>
<td>Column feed</td>
<td>50.0</td>
<td>152.56</td>
<td>1321.66</td>
<td>12.887</td>
</tr>
<tr>
<td>Condenser stream</td>
<td>167.26</td>
<td>156.44</td>
<td>-5342.71</td>
<td>493.822</td>
</tr>
<tr>
<td>Distillate product</td>
<td>156.44</td>
<td>50.0</td>
<td>-409.193</td>
<td>3.844</td>
</tr>
<tr>
<td>Reboiler stream</td>
<td>238.41</td>
<td>251.48</td>
<td>6293.74</td>
<td>481.636</td>
</tr>
<tr>
<td>Bottom product</td>
<td>251.48</td>
<td>25.0</td>
<td>-2124.32</td>
<td>9.379</td>
</tr>
</tbody>
</table>

Table 4.13 Stream data of diesel hydrotreating process from integrated approach for design of diesel hydrotreating process

The cost breakdown of the design for diesel hydrotreating process obtained using the proposed integrated approach is shown in Table 4.14 in comparison with the design obtained using the sequential approach to process design.
Table 4.14 Comparison of cost breakdown of integrated design with sequential design for diesel hydrotreating process

The design obtained using the integrated approach developed in this work provides a saving of 0.16 MM £/yr corresponding to 3% reduction compared to the design obtained using sequential approach. It may be observed that with the proposed framework for integrated design of hydrotreating process the simulated annealing algorithm is able to search for a start-of-run reactor operating temperature which results in a lower total annualised cost for the overall diesel hydrotreating process. The diesel hydrotreater is operating at a slightly higher operating temperature compared to the sequential design. However, the distillation column satisfies the bottom product specification, i.e. the flow rate and boiling range of diesel product, operating at a lower pressure and reflux ratio. Therefore, the column capital cost and energy costs are lower compared to the design obtained using sequential approach to process design.

Another scenario may be analysed for the given system as it may be argued that the compression costs would be higher for downstream processing of the distillation column products for the design obtained using the novel integrated approach. The distillation column operates close to atmospheric pressure in the design obtained using the novel integrated approach. In order to account for this scenario, an additional constraint of minimum operating pressure for distillation column of 5 bar is enforced on the integrated design framework.
The major features of the design, obtained using the integrated approach with an additional constraint on the operating pressure of the distillation column, are shown in Table 4.15. The process stream data of the design for this new scenario are shown in Table 4.16.

<table>
<thead>
<tr>
<th>Diesel hydrotreater</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor operating temperature (°C)</td>
<td>324.74</td>
</tr>
<tr>
<td>Length of reactor (m)</td>
<td>11.522</td>
</tr>
<tr>
<td>Distillation column</td>
<td></td>
</tr>
<tr>
<td>Column pressure (bar)</td>
<td>5.0</td>
</tr>
<tr>
<td>Reflux ratio</td>
<td>1.428</td>
</tr>
<tr>
<td>Light key</td>
<td>Pseudo-component number 7</td>
</tr>
<tr>
<td>Heavy key</td>
<td>Pseudo-component number 8</td>
</tr>
<tr>
<td>Light key recovery (%)</td>
<td>60.53</td>
</tr>
<tr>
<td>Heavy key recovery (%)</td>
<td>63.18</td>
</tr>
<tr>
<td>Total number of stages</td>
<td>14</td>
</tr>
<tr>
<td>Column feed temperature (°C)</td>
<td>167.26</td>
</tr>
<tr>
<td>Feed pre-heat duty (kW)</td>
<td>1515</td>
</tr>
<tr>
<td>Total condenser duty (kW)</td>
<td>5254</td>
</tr>
<tr>
<td>Reboiler duty (kW)</td>
<td>7164</td>
</tr>
</tbody>
</table>

Table 4.15 Design results obtained using integrated approach with an additional constraint on distillation column operating pressure
<table>
<thead>
<tr>
<th>Stream</th>
<th>Supply temperature (°C)</th>
<th>Target temperature (°C)</th>
<th>Enthalpy difference (kW)</th>
<th>Heat capacity flow rate (kW/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor feed</td>
<td>25.0</td>
<td>324.74</td>
<td>33528.9</td>
<td>111.859</td>
</tr>
<tr>
<td>Reactor product</td>
<td>324.74</td>
<td>50.0</td>
<td>-29999.7</td>
<td>109.192</td>
</tr>
<tr>
<td>Column feed</td>
<td>50.0</td>
<td>167.26</td>
<td>1515.49</td>
<td>12.924</td>
</tr>
<tr>
<td>Condenser stream</td>
<td>228.66</td>
<td>219.87</td>
<td>-5254.02</td>
<td>598.023</td>
</tr>
<tr>
<td>Distillate product</td>
<td>219.87</td>
<td>50.0</td>
<td>-682.627</td>
<td>4.018</td>
</tr>
<tr>
<td>Reboiler stream</td>
<td>313.59</td>
<td>326.73</td>
<td>7164.14</td>
<td>545.022</td>
</tr>
<tr>
<td>Bottom product</td>
<td>326.73</td>
<td>25.0</td>
<td>-2992.05</td>
<td>9.916</td>
</tr>
</tbody>
</table>

Table 4.16 Stream data of diesel hydrotreating process from integrated approach with an additional constraint on distillation column operating pressure

The cost breakdown of the design for diesel hydrotreating process obtained using the proposed integrated approach for this new scenario is shown in Table 4.17 in comparison with the design obtained using the sequential approach to process design.
<table>
<thead>
<tr>
<th></th>
<th>Sequential design</th>
<th>Integrated design (Pressure constraint)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst cost (£/yr)</td>
<td>2,733,000</td>
<td>2,758,000</td>
</tr>
<tr>
<td>Column capital cost (£/yr)</td>
<td>366,000</td>
<td>198,000</td>
</tr>
<tr>
<td>Heat exchanger area cost (£/yr)</td>
<td>1,209,000</td>
<td>1,205,000</td>
</tr>
<tr>
<td>Energy cost (£/yr)</td>
<td>978,000</td>
<td>980,000</td>
</tr>
<tr>
<td>Total annualised cost (£/yr)</td>
<td>5,287,000</td>
<td>5,141,000</td>
</tr>
</tbody>
</table>

Table 4.17 Comparison of cost breakdown of integrated design, with an additional constraint on distillation column operating pressure, with sequential design for diesel hydrotreating process

The design obtained using the proposed integrated approach, for design of diesel hydrotreating process, with an additional constraint on the operating pressure of distillation column provides a saving of **0.15 MM £/yr** corresponding to **2.8 %** reduction compared to the design obtained using sequential approach to process design. It can be seen from Table 4.15 that the start-of-run temperature of the diesel hydrotreater is the same as in the design, obtained using integrated approach, without the pressure constraint for distillation column. However, the energy cost is increased due to higher reflux ratio resulting in slightly lower savings compared to the original integrated design.

### 4.7 Conclusions

The molecular model of diesel hydrotreater provides the composition of products of diesel hydrotreating reactions at molecular level and makes improved predictions of conversion of reactions, compared to conventional lumped models, taking into account detailed reaction chemistry, and kinetics using reaction family concept. The de-activation model coupled with the molecular model of the diesel hydrotreater helps estimate the run-length of the catalyst. The de-activation model along with molecular model of the diesel hydrotreater also provides a framework
for analysis of the performance of diesel hydrotreater at various operating conditions.

The capital and energy cost for the heat recovery system of the diesel hydrotreating process is estimated using pinch analysis. The estimation of capital and energy cost of the heat recovery system requires only the information about temperatures, and heat capacity flow rates of process streams. The heat capacity flow rates are estimated using the heat capacities and mole fractions of individual components of diesel hydrotreating streams. The heat capacities of individual components are calculated using group contribution methods.

The approach developed for integrated design of diesel hydrotreating processes helps obtain designs with lower total annualised costs as illustrated by the case study. The novel integrated approach developed in this work for design of diesel hydrotreating processes takes into account the interactions of individual subsystems, i.e. the diesel hydrotreater, the separation system, and the heat recovery system. The proposed approach to process design provides a framework to analyse the effects of modifications or changes to the operating conditions of individual subsystems, e.g. diesel hydrotreater, and distillation column, on the performance of the overall process.
5.1 Introduction

Heat exchanger networks are a means of utilising the heat available in a process by exchanging between hot and cold process streams, thereby decreasing energy demand and therefore utility costs, as well as capital investment in auxiliary equipment. Heat exchanger networks thus improve the economics of plant operation. Heat exchanger network design has long been the focus of research studies and remains an area of continuous development due to the current trend of increasing energy costs.

The operating conditions of a plant can vary with time. Firstly, unplanned and/or uncontrolled operational fluctuations in operating conditions around desired values or set points are inevitable. Secondly, planned periodic changes in operating conditions for enhancing performance is inherent to the nature of some processes. For example, the reactor operating temperature in processes such as hydrotreating and hydrocracking in refineries can be changed with time to compensate for catalyst deactivation; distillation column operating pressures can be varied to take advantage of seasonal variations in ambient temperatures. Heat exchanger networks that can remain operable in such varying operating conditions and
optimal over the time period of interest are termed flexible heat exchanger networks. Flexible heat exchanger networks are classified as resilient or multi-period respectively, depending on the nature of variation in the plant operating conditions (Verheyen and Zhang, 2006). The aim of this work is to review and analyse multi-period heat exchanger network design and propose a new robust and effective approach using simulated annealing for optimisation.

5.2 Review of heat exchanger network design methodologies

This section presents an overview of approaches for design of heat exchanger networks for fixed process operating conditions. A detailed discussion of these design methodologies can be found elsewhere (Nishida et al., 1980; Smith, 2005; Verheyen and Zhang, 2006). Since the pioneering work on heat exchanger network synthesis by Masso and Rudd (1969), based on heuristics, different strategies have been explored and developed. Heat exchanger network design methodologies have been classified based on the underlying approach; these are summarised here as background to the extension of conventional approaches to multi-period design.

5.2.1 Pinch analysis and heat exchanger network design

Pinch analysis is a thermodynamic tool for estimating minimum utility consumption, number of units and investment cost of a network for a given minimum approach temperature. Linnhoff and Hindmarsh (1983) proposed heuristic rules for heat exchanger network design based on the concept of the pinch temperature, i.e. the temperature where the net driving force for heat exchange is zero. This technique is based on the systematic methods introduced by Hohmann (1971) and further refined by Linnhoff and Flower (1978).

Pinch analysis provides estimates for minimum energy and capital costs based on the material and energy balance of process streams. The design of a heat exchanger network is carried out by dividing the problem at pinch temperature. The network is designed above and below the pinch by starting at the pinch and moving away as there is more freedom in the choice of matches away from the pinch. The matches between hot and cold process streams and the heat exchanger duties are determined
using heuristics to minimise the number of units and maximise the heat recovery. A maximum energy recovery design can be obtained in this way with the minimum approach temperature constraint satisfied for all heat exchangers, if heat is not exchanged across the pinch and if the utilities are placed appropriately i.e. cold utilities are only placed below the pinch and hot utilities above the pinch.

5.2.2 Sequential approaches for heat exchanger network design

The sequential design approaches using the pinch theory decompose the heat exchanger network design problem into sub-problems for minimising utility costs, number of units and investment costs. The most widely employed models for estimating minimum utility consumption and number of units are the transshipment models of Papoulias and Grossmann (1983). The linear programming (LP) formulation of the transshipment model predicts minimum utility cost for a given system while a mixed integer linear programming (MILP) formulation develops heat exchanger network designs with the minimum number of heat exchangers. Alternative formulations based on the same concept have been developed (e.g. Cerda et al., 1983).

The transshipment models are based on the flow of heat through temperature intervals. The hot process streams and hot utilities are the sources while the cold process streams and cold utilities are the sinks or destinations. The temperature intervals serve as the intermediate nodes of a transshipment model for the heat recovery problem. Within a temperature interval, heat flows from all hot streams to cold streams. The excess heat that cannot be utilised in a temperature interval is termed residual heat and flows down to the next temperature interval. Since the entire temperature range of the system is partitioned into temperature intervals the only variables are the residual heat flows from one temperature interval to the next lower temperature interval, and the flow rates of hot and cold utilities.
Floudas and Grossmann (1986) proposed a two-stage procedure using transshipment models to obtain the heat exchanger network configuration first with an MILP model and then the minimum total annualised cost using a non-linear programming (NLP) model. However, this decomposition of heat exchanger network design problem into sub-problems can lead to sub-optimal solutions. For example, heat exchanger networks with minimum total annualised costs but higher number of heat exchanger units are not considered in the search space. A later approach to sequential design of heat exchanger networks has been proposed by Zhu and co-workers (Zhu, 1995; Zhu et al., 1995; Zhu, 1997) where the problem is decomposed into enthalpy intervals.

5.2.3 Simultaneous approaches for heat exchanger network design

The simultaneous approaches make use of superstructures consisting of a variety of structural possibilities, and optimise them to remove the redundant features. When the level of heat recovery from a system is increased, the contribution of operating costs to the total annualised cost reduces. However, there is a corresponding increase in the investment costs. This trade-off between the capital cost (fixed costs of heat exchanger units and area costs) and operating cost (hot and cold utility costs) is considered in a single rigorous optimisation framework in the simultaneous design approach for heat exchanger networks.

Floudas and Grossmann (1986) proposed one such superstructure consisting of a wide range of structural features. Ciric and Floudas (1991) presented a simultaneous approach for systematically determining optimal heat exchanger network designs by solving a single MINLP model. Yee et al., (1990) developed a simplified stage-wise superstructure with the assumption of isothermal mixing to simplify the formulation. The simplified stage-wise superstructure is shown in Figure 5.1. In this superstructure all the hot streams are split and matched with all cold streams in each stage i.e. a section of the heat exchanger network. The number of stages is chosen by the designer and is normally equal to the number of hot and cold streams. The assumption of isothermal mixing specifies that the outlet temperature of a stream at every exchanger is the same as the outlet stage
temperature of that particular stream. Yee and Grossmann (1990) proposed an MINLP model based on this simplified stage-wise superstructure. The main drawback of the simultaneous heat exchanger network design approaches is the difficulty in solving these large size models.

Figure 5.1 Simplified stage-wise superstructure of Yee et al. 1990 for heat exchanger network optimisation

Bjork and Westerlund (2002) proposed a methodology based on the same simplified stage-wise superstructure but without the assumption of isothermal mixing.

5.2.4 Stochastic optimisation methods for heat exchanger network design

Stochastic optimisation methods address both structural and parametric variables simultaneously and do not rely on superstructures or decomposition of the design problem into smaller sub-problems. Some commonly used stochastic optimisation
methods for process design are simulated annealing, genetic algorithm and Tabu search method (Verheyen, 2005). Simulated annealing has been successfully applied for synthesis and optimisation of heat exchanger networks (Dolan et al. 1990; Nielsen et al. 1994; Athier et al. 1996; Athier et al. 1997; Rodriguez, 2005; Chen, 2008). Genetic algorithms based on the analogy with the process of natural evolution, have been applied for heat exchanger network design and optimisation by Androulakis et al. 1991; Lewin et al. (1998a, b); Ravagnani et al. 2005. Tabu search is an iterative improvement method for optimisation based with a characteristic feature of short-term memory to keep track of previously found solutions. Tabu search has been applied to heat exchanger network design (Lin et al., 2004). Some other hybrid strategies (Yu et al., 2000) have also been applied for optimisation of heat exchanger networks.

5.2.5 Critical analysis of heat exchanger network design methodologies

Pinch analysis has been widely applied in targeting stage of process design i.e. estimation of minimum hot and cold utility demand for a given system. Pinch analysis is also applied for screening of various design options. However, it can be misleading in some cases, as pinch analysis does not take into account heat transfer coefficients properly (Verheyen and Zhang, 2006). Sequential approaches decompose the problem into easy-to-solve sub problems. However this decomposition into sub-problems with different objectives may fail to account for trade-offs between capital and operating costs. Simultaneous approaches offer promising results in comparison to the sequential approaches. However the problem size, complexity and issues associated with local optima are drawbacks. Stochastic optimisation methods allow a thorough search of the solution space in order to obtain near optimal solutions, at the expense of computational time (Dolan et al., 1990).

5.3 Multi-period heat exchanger network design

A multi-period heat exchanger network is a heat exchanger network that would be operated in a series of different set of conditions, such as temperatures and heat loads. It should remain feasible, i.e. provide the heating and cooling requirements of the process streams, under these different operating modes and its design should
be optimal in terms of the overall costs. The operating conditions of a heat exchanger network may vary with process changes, such as feedstock, throughput and operating conditions, as a result the network of heat exchangers must satisfy different heat loads in different operating periods. Its design may include bypasses; furthermore, as the optimal solution may represent more than one value of required heat exchanger area for a given match in different operating periods, the maximum area out of these values must be considered for cost calculations. The design strategies introduced in the previous section are all based on fixed values of stream temperatures and heat capacity flow rates and therefore, cannot be employed directly for the design of flexible heat exchanger networks.

In multi-period design it is assumed that specified values of flow rates, temperatures and heat capacities are available for the different operating periods under consideration. The aim of multi-period design is to obtain a heat exchanger network that can satisfy the heating and cooling requirements of all the operating periods while minimising its total annualised cost i.e. utility costs and annualised heat exchanger capital costs.

**5.3.1 Sequential approach for multi-period heat exchanger network design**

Floudas and Grossmann (1986) proposed a sequential approach to address multi-period design of heat exchanger networks based on the transshipment models of Papoulias and Grossmann (1983). The approach employs the LP transshipment model to estimate the minimum utility consumption for each operating period, and then a multi-period formulation of the MILP transshipment model is used to obtain a configuration that has the fewest heat exchanger units and incurs the minimum utility cost for each period. The drawback of this approach is that heat exchanger network configurations with higher number of heat exchanger units but lower total annualised costs are neglected.
5.3.2 Simultaneous approach for multi-period heat exchanger network design

The simultaneous approaches for multi-period heat exchanger network design formulate the optimisation problem of heat exchanger network design by introducing variables such as the duties of all process-to-process and utility heat exchangers, flow rates and temperatures of streams for all the periods of operation under consideration. The binary variables representing the existence of both process-to-process and utility heat exchangers are independent of the operating periods (Aaltola, 2002).

The constraints for the multi-period HEN design problem are as follows:

- Overall heat balances for streams hold in each operating period
- Stage-wise heat balances for streams hold in each operating period
- The assignment and feasibility of stream temperatures, at each stage in all the operating periods, based on the inlet and outlet stream temperatures
- Logical constraints for existence of matches between streams.

Aaltola (2002) proposed a multi-period simultaneous approach to minimise the overall costs using an extension of the simplified stage-wise superstructure of Yee et al., (1990). A simplified illustration of this superstructure incorporating two hot streams and two cold streams is shown in Figure 5.2.
Figure 5.2 A simplified version of multi-period extension of the stage-wise superstructure (Verheyen and Zhang, 2006)

As can be seen in the Figure 5.2, for a system with two hot streams and two cold streams the superstructure consists of four heat exchangers per stage for a given operating period.

The multi-period optimisation model proposed by Aaltola (2002) is based on the MINLP formulation of Yee and Grossmann (1990). The MINLP model optimises the heat exchanger network structure with the assumption of iso-thermal mixing i.e. streams can only be mixed if they are at the same temperature. A multi-period NLP formulation in the second stage then adjusts the flow rates and duties of exchangers to improve the total annualised cost of the network.

The objective function of Aaltola (2002), i.e. the total annualised cost, is the sum of unit costs of all heat exchangers, mean area costs of all process and utility matches and mean hot utility costs and cold utility costs. The assumption of mean area costs in the MINLP model can lead to sub-optimal solutions (Verheyen and Zhang, 2006). Verheyen and Zhang (2006) modified this simultaneous approach.
for multi-period heat exchanger network design to account for the maximum area costs in the objective function.

5.3.3 Limitations of previous multi-period heat exchanger network design methodologies

The sequential approach proposed by Floudas and Grossmann (1986) has the inherent weakness of not taking into account the trade-offs between area, number of heat exchanger units, and energy costs rigorously, although the decomposition of the problem into stages helps reduce the size of the problem (Verheyen and Zhang, 2006). The simultaneous approaches of Aaltola (2002) and Verheyen and Zhang (2006) have addressed this issue but make use of a simplified superstructure, to keep the problem size manageable without decomposition. However the simplified stage-wise superstructure excludes some structural features of heat exchanger network configurations. For example, it does not include splitting streams with two or more heat exchangers in series on one branch, stream bypassing or any structural combination of these two features.

5.4 Proposed methodology for multi-period heat exchanger network design with simulated annealing

Simulated annealing is a multivariable combinatorial optimisation technique (Kirkpatrick et al., 1983), based on the Monte Carlo algorithm. Simulated annealing algorithm searches for the optimal solution of an optimisation problem based on the evaluation of objective function at randomly selected points within the search space. Section 4.5 in Chapter 4 presents a discussion on important features and characteristics of the simulated annealing algorithm.

Simulated annealing has been successfully applied for synthesis and optimisation of heat exchanger networks (Dolan et al., 1990; Nielsen et al., 1994; Athier et al., 1996; Athier et al., 1997; Rodriguez, 2005; Chen, 2008). The heat exchanger network structures generated by simulated annealing can involve stream splitting, mixing, bypass and multiple matches between same pairs of streams. The application of simulated annealing for multi-period optimisation of heat exchanger
networks has not been studied previously and shall be presented in this work for the first time.

5.4.1 Simulated annealing for multi-period heat exchanger network design

A new methodology for the design and optimisation of multi-period heat exchanger networks has been developed and is presented in this section. The application of simulated annealing for multi-period heat exchanger network design requires an understanding of multi-period operation and of the characteristic features of multi-period heat exchanger networks. For example, the maximum area consideration for heat exchangers based on all the operating periods of interest i.e. a given heat exchanger may have to satisfy different heat loads and thus the required heat transfer area may be different in different operating periods; however, the cost calculation would need to be based on the maximum area amongst these values. Figure 5.3 shows the algorithm for multi-period design of heat exchanger networks with simulated annealing.
Figure 5.3 Simulated annealing algorithm for multi-period heat exchanger network design
The proposed methodology employs simulated annealing to search for optimal heat exchanger network configurations starting from a feasible initial heat exchanger network. A feasible heat exchanger network is one that can satisfy the heating and cooling requirements of a given system and also satisfies the minimum approach temperature constraint for each heat exchanger unit. A very simple and convenient initial guess for a feasible heat exchanger network is to match all the hot process streams a cold utility and the cold process streams with a hot utility. The simulated annealing algorithm modifies this initial heat exchanger network configuration by making random moves (See section 4.5.2 in Chapter 4). Table 5.1 presents a list of possible simulated annealing moves for modifications to a heat exchanger network.

<table>
<thead>
<tr>
<th>Continuous Moves</th>
<th>Structural Moves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat duty change</td>
<td>Repipe a heat exchanger</td>
</tr>
<tr>
<td>Splitter flow fractions change</td>
<td>Resequence a heat exchanger</td>
</tr>
<tr>
<td></td>
<td>Add a new heat exchanger</td>
</tr>
<tr>
<td></td>
<td>Remove a heat exchanger</td>
</tr>
<tr>
<td></td>
<td>Add a splitter-mixer unit</td>
</tr>
<tr>
<td></td>
<td>Remove a splitter-mixer unit</td>
</tr>
</tbody>
</table>

Table 5.1 Simulated annealing moves for heat exchanger network design

The modifications made to the existing network configuration as shown in Table 5.1 are classified into two categories based on the nature of the variables involved. The continuous moves result in changes in duties of heat exchangers or flow fractions in various branches of a stream, while structural moves involve manipulation of binary variables and result in changes in the heat exchanger network configuration.

The modified structure is then simulated for all the operating period under consideration. The simulation of a heat exchanger network for multi-period operation is explained in the next section. The objective function is evaluated, i.e. the objective function value for the current configuration is compared to that of the previous configuration, and the modification may be accepted or rejected based on the acceptance criterion employed. This process is repeated a number of times, as governed by the Markov chain length, and the annealing temperature is
progressively reduced. In this way, the simulated annealing algorithm searches for the optimal heat exchanger network configuration for multi-period design. Once the termination criterion is satisfied, the best design obtained so far is reported as the optimal multi-period heat exchanger network.

5.4.2 Multi-period heat exchanger network simulation model

In the methodology proposed in this work, for multi-period heat exchanger network design using the simulated annealing algorithm, any modifications made to the heat exchanger network need to be simulated for all the operating periods under consideration. The multi-period simulation of heat exchanger network structure modified by the algorithm is shown in Figure 5.4. The heating and cooling requirements of the process streams may vary from one operating period to another, as a result the matches proposed by the simulated annealing algorithm may not satisfy the constraints of outlet temperatures of the hot and cold process streams in some operating periods. Therefore the hot and/or cold utility load is adjusted for each operating period. Once the modified structure has been simulated for all the operating periods under consideration and the corresponding utilities have been adjusted, the objective function can be evaluated by comparison with the previous best solution.
The multi-period model developed in this work is an extension of the heat exchanger network simulation model proposed by Rodriguez (2005). The heat exchanger network model for multi-period operation is based on the following assumptions:

- Mass flow rates of process streams are assumed to be constant.
- The physical properties of fluid streams such as the heat capacities are assumed to be constant and independent of temperature.
- Heat transfer coefficients are assumed to be constant throughout each heat exchanger.

Figure 5.4 Multi-period simulation of heat exchanger network
The following sets of variables have been used in the mathematical model:

Set of process heat exchangers:

\[
PHX = \{i \in [1, N_{PHX}] \}
\]  (5.1)

Set of utility heat exchangers:

\[
UHX = \{j \in [1, N_{UHX}] \}
\]  (5.2)

Set of heat exchangers:

\[
HX = \{k \in PHX \cup UHX \}
\]  (5.3)

Set of stream splitters:

\[
SP = \{\psi \in [1, N_{SP}] \}
\]  (5.4)

Set of hot streams:

\[
HS = \{m \in [1, N_{HS}] \}
\]  (5.5)

Set of cold streams:

\[
CS = \{n \in [1, N_{CS}] \}
\]  (5.6)

Set of all process streams:

\[
ST = \{\phi \in HS \cup CS \}
\]  (5.7)

Set of utilities:

\[
UT = \{u \in [1, N_{UT}] \}
\]  (5.8)

Set of operating periods:

\[
TP = \{p \in [1, N_{TP}] \}
\]  (5.9)
5.4.2.1 Process heat exchangers

This work focuses on the design of heat exchanger networks, where we need to calculate the heat exchanger area required for a given heat load. Thus for a heat exchanger, \( i \in PHX \) in a given operating period \( p \in TP \) as shown in the Figure 5.5, heat is transferred from the hot stream \( hs_i \in HS \), to the cold stream \( cs_i \in CS \).

![Diagram of a single heat exchanger for multi-period operation]

**Figure 5.5 A single heat exchanger for multi-period operation**

The temperature of the hot stream decreases from \( TH_{i,p}^{in} \) to \( TH_{i,p}^{out} \), while the temperature of the cold stream increases from \( TC_{i,p}^{in} \) to \( TC_{i,p}^{out} \). The thermal duty or heat load of the heat exchanger i.e. the heat transferred between the two streams is a function of the inlet temperatures of the streams and their heat capacity flow rates. This heat load is given by the equations:

\[
Q_{i,p} = CP_{hs,i,p} \left( TH_{i,p}^{in} - TH_{i,p}^{out} \right) \quad (5.10)
\]

\[
Q_{i,p} = CP_{cs,i,p} \left( TC_{i,p}^{out} - TC_{i,p}^{in} \right) \quad (5.11)
\]

The outlet temperature of the hot and cold stream can be calculated using the equations:

\[
TH_{i,p}^{out} = TH_{i,p}^{in} - \frac{Q_{i,p}}{CP_{hs,i,p}} \quad (5.12)
\]

\[
TC_{i,p}^{out} = TC_{i,p}^{in} + \frac{Q_{i,p}}{CP_{cs,i,p}} \quad (5.13)
\]
The area of the heat exchanger is calculated using the equation:

\[ A_{i,p} = \frac{Q_{i,p}}{U_{i,p} \times F_{T_{i,p}} \times LMTD_{i,p}} \]  \hspace{1cm} (5.14)

where

\[ LMTD_{i,p} = \frac{(TH_{i,p}^\text{in} - TC_{i,p}^\text{out}) - (TH_{i,p}^\text{out} - TC_{i,p}^\text{in})}{\ln \left( \frac{TH_{i,p}^\text{in} - TC_{i,p}^\text{out}}{TH_{i,p}^\text{out} - TC_{i,p}^\text{in}} \right)} \]  \hspace{1cm} (5.15)

The correction factor \( F_T \) depends on the type of heat exchanger used and can be calculated. For example, using the correlations presented in Smith (2005).

### 5.4.2.2 Utility heat exchangers

The heating and cooling duties of process streams that cannot be satisfied by process-to-process heat exchange are supplied by utility heat exchangers. The utility heat exchangers are specified in terms of the heat load and are modelled similarly to the process heat exchangers, except that only the process side of the utility heat exchangers is considered explicitly.

For a heater:

\[ T_{j,p}^\text{out} = T_{j,p}^\text{in} + \frac{Q_{j,p}}{CP_{cs_j,p}} \]  \hspace{1cm} (5.16)

For a cooler:

\[ T_{j,p}^\text{out} = T_{j,p}^\text{in} - \frac{Q_{j,p}}{CP_{hs_j,p}} \]  \hspace{1cm} (5.17)

The area of utility heat exchangers is calculated using the same equation as for process heat exchangers and the log mean temperature difference is given by the equation:
\[
LMTD_{j,p} = \frac{(T_{in,j,p} \, T_{out,j,p}^{in})}{\ln\left(\frac{T_{in,j,p}}{T_{out,j,p}}\right)}
\]

where \(TU_{in,j,p}\) and \(TU_{out,j,p}\) are the inlet and outlet temperatures of the utility stream in operating period \(p\).

### 5.4.2.3 Stream splitters and mixers

Stream splitting provides flexibility to heat exchanger networks by better utilisation of the temperature driving forces in heat exchangers and thus helps in reducing the required heat transfer area. The model assumes that each splitter has only two branches and all the branches of a stream are remixed before leaving the heat exchanger network. Therefore each splitter is associated with a mixer. Streams with more than two branches can be modelled by nesting splitters one inside the other. Figure 5.6 shows a splitter-mixer unit, \(l \in SP\) in a given operating period \(p \in TP\), which splits a stream, \(st_l \in ST\) into two branches.

![Figure 5.6 A splitter-mixer unit for multi-period heat exchanger network](image)

The branch flow rates depend on the split fraction and the flow rate of the inlet stream. The heat capacity flow rates of the branch streams are given by the equations:

\[
CP_{st,l,p}^{in} = SF_{l,p} \times CP_{st,l,p}
\]

(5.19)
\[ CP_{st,1,p} = (1 - SF_{1,p}) \times CP_{st,1,p} \] (5.20)

The temperatures of the branch streams are the same as the temperature of the inlet stream given by the equations:

\[ TSP_{1,p}^{\text{out1}} = TSP_{1,p}^{\text{in}} \] (5.21)

\[ TSP_{1,p}^{\text{out2}} = TSP_{1,p}^{\text{in}} \] (5.22)

The temperature of the mixer outlet stream is obtained by carrying out energy balance over the mixing point and is given by the equation:

\[ TMX_{1,p}^{\text{out}} = \frac{TMX_{1,p}^{\text{in1}} \times CP_{st,1,p}^{i} + TMX_{1,p}^{\text{in2}} \times CP_{st,1,p}^{j}}{CP_{st,1,p}} \] (5.23)

5.4.2.4 Stream Bypassing

Stream bypassing involves re-routing of a fraction of a stream upstream of the inlet to a heat exchanger to be mixed again at the outlet. Stream bypassing provides a degree of freedom to manipulate heat loads and stream temperatures. Heat exchangers with bypass streams are modelled using the equations:

\[ TH_{1,p}^{\text{out2}} = TH_{1,p}^{\text{in}} \frac{Q_{1,p} \left(1 - XBH_{1,p} \right)}{CP_{st,1,p}} \] (5.24)

\[ TC_{1,p}^{\text{out2}} = TC_{1,p}^{\text{in}} + \frac{Q_{1,p} \left(1 - XBC_{1,p} \right)}{CP_{st,1,p}} \] (5.25)

where \( XBH_{1,p} \) and \( XBC_{1,p} \) represent the fraction of the stream bypassed from a heat exchanger in a particular operating period. The variables \( TH_{1,p}^{\text{out2}} \) and \( TC_{1,p}^{\text{out2}} \) represent the temperatures of the hot and cold streams after the bypassed stream is re-mixed with the heat exchanger outlet stream.

5.4.2.5 Simulation of the overall heat exchanger network

The modelling equations presented in the previous sections describe the behaviour of individual units. However, the performance of the overall heat exchanger...
network depends on the connections and interactions between these components and can only be simulated by combining the individual component models and solving them simultaneously.

The framework developed for representation of the overall heat exchanger network operating in multiple periods of operation is an extension of the nodal representation presented by Rodriguez (2005). The individual network components such as heat exchangers, and splitter-mixer units, are connected to each other by specifying nodes on each stream of the heat exchanger network. Figure 5.7 shows a heat exchanger network and its network components and nodes on each stream. The location of any network component is identified by its inlet, \( nd_{\text{in}} \) and outlet node \( nd_{\text{out}} \). For example, the location of heat exchanger E2 in Figure 5.7 is represented by the inlet and outlet nodes of its hot side, \( nd_{\text{in}}^{E2} = 3 \) and \( nd_{\text{out}}^{E2} = 4 \), and the inlet and outlet nodes of its cold side, \( nd_{\text{in}}^{E2} = 10 \) and \( nd_{\text{out}}^{E2} = 11 \).

![Diagram of a heat exchanger network based on temperature nodes](image)

**Figure 5.7 Representation of a heat exchanger network based on temperature nodes**

The representation of a heat exchanger network in terms of temperature nodes requires that each node is associated with a unique temperature and that the temperatures of the network components sharing a common node are same. The total number of temperature nodes required for simulation of a heat exchanger network operating in multiple periods is given by the equation:

\[
N_{ND,p} = N_{ST,p} + 2N_{PHX,p} + N_{UHX,p} + 3N_{SP,p}
\]  

(5.26)
where $N_{ST,p}$ is the number of streams, $N_{PHX,p}$ the number of process heat exchangers, $N_{UHX,p}$ the number of utility heat exchangers and $N_{SP,p}$ the number of splitter-mixer units operating in a given period of operation.

The total number of equations, in the multi-period heat exchanger network model, is given by the equation:

$$N_{EQ,p} = N_{ST,p} + 2N_{PHX,p} + N_{UHX,p} + 3N_{SP,p}$$  \hspace{1cm} \text{(5.27)}$$

It can be observed here that the number of equations is equal to the number of variables and hence we can simulate the network by solving the equations simultaneously. The heat exchanger network shown in Figure 5.7 can be represented by the equations given in Table 5.2. This heat exchanger network consists of three process streams, two process heat exchangers, one utility heat exchanger and one splitter-mixer unit. It can be seen that there are eleven unknown node temperatures, for each operating period, which can be calculated by solving the same number of equations of the model.
Exchanger E1:

\[ T_{2,p} = T_{1,p} - \frac{Q_{E1,p}}{CP_{H1,p}} \]

\[ T_{9,p} = T_{7,p} + \frac{Q_{E1,p}}{CP_{C1,p}} \]

Exchanger E2:

\[ T_{4,p} = T_{3,p} - \frac{Q_{E2,p}}{CP_{H2,p}} \]

\[ T_{11,p} = T_{10,p} + \frac{Q_{E2,p}}{CP_{C1,p}} \]

Utility heat exchanger U1:

\[ T_{5,p} = T_{4,p} - \frac{Q_{U1,p}}{CP_{H2,p}} \]

Splitter-mixer unit:

\[ T_{7,p} = T_{6,p} \]

\[ T_{8,p} = T_{6,p} \]

\[ T_{10,p} = \frac{T_{9,p} \times CP_{C1,p}^I + T_{8,p} \times CP_{C1,p}^q}{CP_{C1,p}} \]

Boundary conditions:

\[ T_{1,p} = TS_{H1,p} \]

\[ T_{3,p} = TS_{H2,p} \]

\[ T_{6,p} = TS_{C1,p} \]
5.4.3 Objective function for multi-period heat exchanger network design

The objective function for the optimisation is the total annualised cost of the multi-period heat exchanger network. The total annualised cost for multi-period design is the sum of all annualised capital costs (heat exchanger unit costs and maximum area costs based on the consideration of multiple periods of operation) and operating costs (hot and cold utility costs). The hot and cold utility costs are calculated as the weighted sum of these costs for all the operating periods under consideration.

The objective function for multi-period heat exchanger network design is given by the equation:

\[
\text{min} TAC = AF \cdot \left[ \sum_{i \in \text{PHX}} C_f \cdot z_i + \sum_{j \in \text{UHX}} C_f \cdot z_{ut_j} \right] + AF \cdot \sum_{i \in \text{PHX}} C \cdot A_{\text{max}}^i + AF \cdot \sum_{j \in \text{UHX}} C \cdot A_{\text{max}}^j
\]

\[
+ \sum_{p \in \text{TP}} \frac{DOP_p \cdot \sum_{j \in \text{UHX}} C_{\text{ut}} \cdot Q_{ut,j,p}}{N_{TP}}
\]

\[(5.28)\]

The maximum area of heat transfer required for any heat exchanger is obtained using the equations:

\[
A_{\text{max},i} \geq \frac{Q_{i,p}}{U_{i,p} \cdot F_{r,i,p} \cdot LMTD_{i,p}}
\]

\[(5.29)\]

\[
A_{\text{max},ut} \geq \frac{Q_{ut,j,p}}{U_{j,p} \cdot F_{r,j,p} \cdot LMTD_{j,p}}
\]

\[(5.30)\]

The equations 5.29 and 5.30 are alternative representations of equation 5.14 to account for the maximum area consideration for multi-period heat exchanger network design.
5.5 Case study

In this section a case study is presented to allow the comparison of the new optimisation approach using simulated annealing, for multi-period heat exchanger network design, with existing deterministic methods.

This case study has been taken from Verheyen and Zhang (2006). The objective of the case study is to design a heat exchanger network for the vacuum gas oil hydrotreater unit of an oil refinery. Vacuum gas oil hydrotreating process is a heavy hydrocarbon conversion process for upgrading vacuum gas oil to gas oil, diesel, gasoline and light products. Error! Reference source not found. can be referred for a general view of a hydrotreating process flow sheet, a detailed of vacuum gas oil hydrotreating process can be found elsewhere (Meyers, 1997; Verheyen and Zhang, 2005). The heat exchanger network should remain feasible, i.e. satisfy the heating and cooling requirements of all process streams, for all the specified operating periods. The objective is to minimise the total annualised cost given by equation 5.28. The three operating periods under consideration correspond to different process conditions resulting from catalyst deactivation in the reactor:

- Start-of-run
- Middle-of-run
- End-of-run

The process streams to be considered for heat recovery are presented in Table 5.3.
<table>
<thead>
<tr>
<th>Stream name</th>
<th>Description of stream in flow sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>Reactor outlet stream</td>
</tr>
<tr>
<td>H2</td>
<td>Diesel stream from distillation side stripper</td>
</tr>
<tr>
<td>H3</td>
<td>Gas oil stream from reboiler</td>
</tr>
<tr>
<td>C1</td>
<td>Reactor inlet stream</td>
</tr>
<tr>
<td>C2</td>
<td>Stream from low pressure separator to H$_2$S stripper</td>
</tr>
<tr>
<td>C3</td>
<td>Stream from H$_2$S stripper to distillation inlet</td>
</tr>
<tr>
<td>C4</td>
<td>Side stripper reboiler</td>
</tr>
</tbody>
</table>

Table 5.3 Process streams considered in the design of heat exchanger network for vacuum gas oil hydrotreater unit of an oil refinery

Tables 5.4 to 5.6 provide the stream data for each of the three operating periods. All the three operating periods are assumed to have equal durations.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Inlet temperature (ºC)</th>
<th>Outlet temperature (ºC)</th>
<th>Heat capacity flow rate (kW/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>393</td>
<td>60</td>
<td>201.6</td>
</tr>
<tr>
<td>H2</td>
<td>160</td>
<td>40</td>
<td>185.1</td>
</tr>
<tr>
<td>H3</td>
<td>354</td>
<td>60</td>
<td>137.4</td>
</tr>
<tr>
<td>C1</td>
<td>72</td>
<td>356</td>
<td>209.4</td>
</tr>
<tr>
<td>C2</td>
<td>62</td>
<td>210</td>
<td>141.6</td>
</tr>
<tr>
<td>C3</td>
<td>220</td>
<td>370</td>
<td>176.4</td>
</tr>
<tr>
<td>C4</td>
<td>253</td>
<td>284</td>
<td>294.4</td>
</tr>
</tbody>
</table>

Table 5.4 Stream data for the first operating period i.e. start-of-run condition

<table>
<thead>
<tr>
<th>Stream</th>
<th>Inlet temperature (ºC)</th>
<th>Outlet temperature (ºC)</th>
<th>Heat capacity flow rate (kW/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>406</td>
<td>60</td>
<td>205.0</td>
</tr>
<tr>
<td>H2</td>
<td>160</td>
<td>40</td>
<td>198.8</td>
</tr>
<tr>
<td>H3</td>
<td>362</td>
<td>60</td>
<td>136.4</td>
</tr>
<tr>
<td>C1</td>
<td>72</td>
<td>365</td>
<td>210.3</td>
</tr>
<tr>
<td>C2</td>
<td>62</td>
<td>210</td>
<td>141.0</td>
</tr>
<tr>
<td>C3</td>
<td>220</td>
<td>370</td>
<td>175.4</td>
</tr>
<tr>
<td>C4</td>
<td>250</td>
<td>290</td>
<td>318.7</td>
</tr>
</tbody>
</table>

Table 5.5 Stream data for second operating period i.e. middle-of-run condition
<table>
<thead>
<tr>
<th>Stream</th>
<th>Inlet temperature (°C)</th>
<th>Outlet temperature (°C)</th>
<th>Heat capacity flow rate (kW/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>420</td>
<td>60</td>
<td>208.5</td>
</tr>
<tr>
<td>H2</td>
<td>160</td>
<td>40</td>
<td>175.2</td>
</tr>
<tr>
<td>H3</td>
<td>360</td>
<td>60</td>
<td>134.1</td>
</tr>
<tr>
<td>C1</td>
<td>72</td>
<td>373</td>
<td>211.1</td>
</tr>
<tr>
<td>C2</td>
<td>62</td>
<td>210</td>
<td>140.5</td>
</tr>
<tr>
<td>C3</td>
<td>220</td>
<td>370</td>
<td>174.5</td>
</tr>
<tr>
<td>C4</td>
<td>249</td>
<td>286</td>
<td>271.2</td>
</tr>
</tbody>
</table>

Table 5.6 Stream data for third operating period i.e. end-of-run condition

Heat exchanger costs are evaluated using the formula:

Heat exchanger cost = \( C_f + C \cdot (\text{Area})^B \).

Where \( C_f \) is the fixed cost of a heat exchanger = 8333.3 €.

\( C \) is the area cost coefficient for a heat exchanger = 641.7 €/m².

\( B \) is the area exponent = 1.

Annualisation factor used = 0.2.

Economic data for energy costs are also taken from Verheyen and Zhang (2006) and are as follows:

\( C_{cu} \) is the cost of cold utility = 1.3 €/kWy.

\( C_{hu} \) is the cost of hot utility = 115.2 €/kWy.

A single period comparison is made first to illustrate the strength of simulated annealing optimisation method in searching for optimal heat exchanger network configurations.
5.5.1 Single period comparison

In this section the overall cost of the heat exchanger network for a single period, i.e. the start-of-run condition, is optimised using simulated annealing, and is compared with the objective function value from the single period MINLP-NLP model of Verheyen and Zhang (2006). The minimum approach temperature ($\Delta T_{\text{min}}$) used in for this comparison is 25°C. The MINLP-NLP model is run a number of times with different values of maximum hot utility available as this can influence the solving path and can lead the search towards a set of different local minima. The design with lowest total annualised cost is chosen from this set of solutions to serve the purpose of comparing the design and optimisation methodologies. Table 5.7 shows the objective function values for the specified minimum approach temperature with various upper bounds for hot utility. The objective function is the total annualised cost (TAC) consisting of the capital cost (fixed and area costs for heat exchangers) and energy cost (hot and cold utility costs).

<table>
<thead>
<tr>
<th>$\text{HU}_{\text{up}}$ (kW)</th>
<th>Total annualised cost (€/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50,000</td>
<td>6,359,872</td>
</tr>
<tr>
<td>45,000</td>
<td>6,304,400</td>
</tr>
<tr>
<td>40,000</td>
<td>6,303,146</td>
</tr>
<tr>
<td>35,000</td>
<td>6,306,067</td>
</tr>
<tr>
<td>30,000</td>
<td>6,303,146</td>
</tr>
<tr>
<td>25,000</td>
<td>6,363,657</td>
</tr>
<tr>
<td>20,000</td>
<td>7,098,245</td>
</tr>
<tr>
<td>16,000</td>
<td>Infeasible</td>
</tr>
</tbody>
</table>

Table 5.7 Results from MINLP-NLP model of Verheyen and Zhang (2006) for single period heat exchanger network design

The heat exchanger network with lowest overall cost obtained using the simultaneous single period MINLP-NLP model of Verheyen and Zhang (2006) is shown in Figure 5.8. The total annualised cost of this network is 6.3 MM €/y.
Figure 5.8 Heat exchanger network for single period operation using the MINLP-NLP model of Verheyen and Zhang (2006)

The simulated annealing parameters used to obtain heat exchanger network for single period operation with minimum total annualised cost are shown in Table 5.8.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial annealing “temperature”</td>
<td>0.10E+10</td>
</tr>
<tr>
<td>Final annealing “temperature”</td>
<td>0.10E-07</td>
</tr>
<tr>
<td>Cooling parameter</td>
<td>0.50E-02</td>
</tr>
<tr>
<td>Markov chain length</td>
<td>50</td>
</tr>
<tr>
<td>Acceptance criterion</td>
<td>Metropolis</td>
</tr>
</tbody>
</table>

Table 5.8 Simulated annealing parameters used for optimisation of heat exchanger networks in this work

The total annualised cost obtained by simulated annealing for the single period heat exchanger network with the same minimum approach temperature is 6.13 MM €/y, corresponding to a 2.8 % (0.17 MM €/y) reduction to the minimum value of the objective function achieved from all of the various implementations of MINLP-NLP optimisation approach of Verheyen and Zhang (2006). The heat exchanger network configuration obtained by simulated annealing is presented in Figure 5.9.
It is evident from the comparison of the results for single period design using simulated annealing and deterministic optimisation approach that simulated annealing can be a more robust optimisation approach for heat exchanger network design and optimisation and can provide designs with bigger savings compared to those of deterministic optimisation strategies. The robustness of the proposed methodology is attributed to the strategy that only perturbations made by simulated annealing moves to the heat exchanger network that result in a feasible network configuration are accepted.

5.5.2 Multi-period comparison

In this section the results obtained using the proposed methodology for the design of multi-period heat exchanger networks are compared with those obtained by the multi-period MINLP-NLP approach of Verheyen and Zhang (2006). The objective is to design a heat exchanger network that remains operable in all the three specified periods of operation and has the minimum total annualised cost given by equation 5.28.
The objective function for multi-period heat exchanger network is the total annualised cost i.e. the sum of capital costs (heat exchanger unit costs and maximum area costs) and operating costs (hot and cold utility costs) for all the periods of operation under consideration. Table 5.9 shows the results obtained using the simultaneous multi-period model for a minimum approach temperature ($\Delta T_{\text{min}} = 25^\circ\text{C}$) and various upper bounds for hot utility (HU$_{\text{up}}$).

<table>
<thead>
<tr>
<th>HU$_{\text{up}}$ (kW)</th>
<th>TAC (€/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50,000</td>
<td>6,416,403</td>
</tr>
<tr>
<td>45,000</td>
<td>7,591,377</td>
</tr>
<tr>
<td>40,000</td>
<td>6,431,203</td>
</tr>
<tr>
<td>35,000</td>
<td>6,410,355</td>
</tr>
<tr>
<td>30,000</td>
<td>6,431,203</td>
</tr>
<tr>
<td>25,000</td>
<td>6,641,023</td>
</tr>
<tr>
<td>20,000</td>
<td>Infeasible</td>
</tr>
<tr>
<td>18,000</td>
<td>Infeasible</td>
</tr>
</tbody>
</table>

Table 5.9 Results from simultaneous multi-period approach by Verheyen and Zhang (2006)

It can be observed from Table 5.9 that the simultaneous multi-period model is strongly influenced by the constraints applied and may lead to different solutions or even infeasibility. The multi-period heat exchanger network with lowest total annualised cost is chosen from this set for testing the strengths and weaknesses of the proposed methodology for multi-period heat exchanger network design. The multi-period heat exchanger network with lowest total annualised cost is shown in Figure 5.10. The total annualised cost of this design is 6.41 MM €/y.
Figure 5.10 Heat exchanger network for multi-period operation using the MINLP-NLP model of Verheyen and Zhang (2006)

Figure 5.10 shows the maximum area of each heat exchanger based on the three operating periods under consideration.

The simulated annealing parameters used to obtain heat exchanger network for multi-period operation with minimum total annualised cost are the same as those used for single period design, as already presented in Table 5.8. The total annualised cost for multi-period heat exchanger network obtained using the proposed methodology for the same minimum approach temperature is 6.34 MM €/y and corresponds to a reduction of 1% (65,000 €/y) to the minimum value of the objective function obtained using multi-period MINLP-NLP model. The heat exchanger network configuration for multi-period operation obtained by simulated annealing is presented in Figure 5.11. Figure 5.11 shows the maximum area of each match from all the three operating periods under consideration.
An interesting feature that can be observed here is that the overall costs for multi-period designs are higher than the single period designs. The reason behind this increase in overall costs is that multi-period designs provide the flexibility to remain operable under different operating conditions at the expense of additional costs related to heat exchanger area.

5.6 Conclusions

A new methodology for multi-period heat exchanger network design using the simulated annealing algorithm has been developed in this work. The new approach promises to obtain optimal heat exchanger network designs that are flexible and can operate feasibly in multiple modes of operation. The main strengths of this approach are that simulated annealing does not rely on simplified superstructure and can explore a greater search area accounting for multiple time intervals. The proposed approach is not subject to decomposition of the main problem and therefore takes into account the trade-offs between energy costs, number of heat exchanger units and area costs simultaneously.
It can be concluded, based on the results of the case study presented, that this new approach for multi-period heat exchanger network design using the simulated annealing algorithm is robust unlike the previous simultaneous multi-period approaches that may lead to different local optima or even infeasible solutions depending on the constraints. The proposed approach develops cost-effective heat exchanger network designs for both single period and multi-period operation.
Chapter 6  Multi-period hydrogen management

6.1  Introduction

Petroleum refineries consist of many processes with complex reactions involving hydrogen consumption or production. Hydrogen management aims to achieve the optimal allocation of hydrogen resources in order to satisfy the demands of refinery processes. Research in the area of hydrogen management is developing methodologies and approaches for the design and optimisation of refinery hydrogen networks (e.g. Alves, 1999; Liu, 2002).

Hydrogen management is of interest to refiners as the cleaner fuel specifications require refineries to increase hydroprocessing capacities, and the severity of hydroprocessing operating conditions in order to produce environmentally more benign fuels such as ultra low sulphur diesel (ULSD) with sulphur contents of 10 ppm or lower. The product specifications for gasoline require reduction in the aromatics content of gasoline resulting in lesser hydrogen available from the catalytic reforming unit which has traditionally been the most cost efficient source of hydrogen. Hydrogen production plants can represent over one-third of the cost of hydrocarbon conversion processes for upgrading heavy petroleum fractions (Peramanu et al., 1999). Therefore, hydrogen management has become essential to ensure an optimum economic performance of refineries.
6.1.1 Hydrogen network and its components

A hydrogen network may be described as a system of refinery processes that interact with each other through distribution of hydrogen. The refinery processes, operating together with hydrogen as a shared commodity, constitute the hydrogen network. A typical refinery hydrogen network with its refinery processing units is shown in Figure 6.1.

These refinery processes may be classified into two categories based on their contribution to the hydrogen network.

6.1.1.1 Hydrogen producing processes

Hydrogen producers are units that supply hydrogen to the hydrogen distribution system, such as the hydrogen plant and catalytic reforming unit. The catalytic reforming process produces hydrogen as a by-product of cyclisation and dehydrogenation reactions of hydrocarbon molecules to increase the aromatic content and the octane number of naphtha products (Meyers, 1997). Hydrogen plants may employ steam reforming or partial oxidation for the production of high purity hydrogen through conversion of light hydrocarbon fractions such as refinery off-gases and light naphtha.
6.1.1.2 Hydrogen consuming processes

Hydrogen consumers are conversion processes, such as the hydrocracking process for upgrading heavy hydrocarbon fractions, hydrotreating processes to satisfy cleaner fuel specifications, lubricant plants, the isomerisation process, and the hydro de-alkylation unit. These processes employ hydrogen as a reactant to upgrade the quality of refinery products. Amongst all the hydrogen consuming processes, hydrocracking and hydrotreating processes are the major hydrogen consumers (Liu, 2002).

6.1.1.3 Other components of a hydrogen network

Apart from the above mentioned refinery processes, compressors and purification units also form part of a refinery hydrogen network. Purification processes help recover hydrogen from refinery off-gases, i.e. the purge streams from hydrogen consuming processes such as hydrotreaters and hydrocracker. Compressors do not influence a hydrogen network in terms of the demand and supply of hydrogen. However, are needed to ensure the pressure requirements of refinery processes are met.

6.2 Review of previous research on hydrogen management

Hydrogen management is of increasing importance because of the contribution of hydroprocessing operations to the overall performance of modern refineries. The need for hydrogen management strategies for the design and operation of refinery processes was first acknowledged by Simpson (1984). This section reviews the methodologies developed previously for refinery hydrogen management.

6.2.1 Cost and value composite curves for hydrogen management

The first systematic approach for the assessment of hydrogen resources of a hydrogen network was developed by Towler et al., (1996) by analogy to pinch analysis for design and optimisation of heat exchanger networks. In this approach, cost and value composite curves are generated for refinery processes that produce hydrogen or consume hydrogen. The driving force for hydrogen distribution, i.e. flow of hydrogen gas streams, between hydrogen sources and sinks is assumed to
be dependant on economics of individual refinery processes, where the cost of hydrogen available from the hydrogen plant is dependant on the price of the feedstock of hydrogen plant. The value added to refinery products in hydrogen consuming processes is the value of the products of a refinery process minus the cost of its feed. The cost of hydrogen recovery from a hydrogen source stream is calculated using the cost of purification. Using this concept of cost and value the driving force for hydrogen transfer may be defined as the difference between the cost of hydrogen available and the value added to refinery products (Towler et al., 1996).

The cost composite curve is generated by combining the cost curves for all the hydrogen sources i.e. the hydrogen plant and the streams from which hydrogen can be purified. The cost composite curve thus provides the amount of hydrogen available in each cost interval. The value composite curve is generated similarly using the information of value added in all the hydrogen consuming processes. A plot of cost and value composite curves, i.e. cost or value of hydrogen ($/kmol) plotted against the amount of hydrogen (kmol/s), can provide an overview of the economic performance of refinery processes within the hydrogen network. The cost and value composite curve provide a graphical method to estimate the demand of hydrogen utility, i.e. the amount of hydrogen needed from the hydrogen plant to satisfy the operation of refinery processes.

The cost and value composite curves may be used for the economic analysis of a refinery hydrogen distribution system. However, this approach does not provide any systematic rules or methodology for the retrofit or design of hydrogen networks. The analysis relies on the availability of economic data, such as the value added to refinery products per unit hydrogen consumption, as well as for purification processes which may not always be available, especially for design scenarios. Another major drawback of this approach is that it does not provide a systematic framework for screening design options such as the choice of streams to purify, the degree of purification, the selection of purification processes, and their
placement within the hydrogen network. All these factors may affect the performance of a hydrogen distribution system.

6.2.2 Hydrogen pinch analysis and design of hydrogen networks

Hydrogen pinch analysis was developed by Alves (1999) using the analogy to pinch analysis for heat exchanger networks (Linnhoff et al., 1979). Hydrogen pinch analysis is a tool for the estimation of the minimum hydrogen utility requirement of a hydrogen network before the system design.

Hydrogen pinch analysis is developed using the following assumptions (Alves, 1999):

- Constant operating conditions of the refinery processes constituting the hydrogen network
- Hydrogen streams in the hydrogen network are binary mixtures of hydrogen and methane.
- Any hydrogen source may supply any hydrogen sink if the hydrogen purity of source is higher than the sink. Pressure differences are ignored.

Hydrogen pinch analysis requires the flow rate and purity constraints of the network to be satisfied, i.e. the overall mass balance and the hydrogen mass balance, for a given hydrogen network. In hydrogen pinch analysis gas streams are treated as binary mixtures of hydrogen and methane. This simplification of representing all impurities in a hydrogen stream, e.g. light hydrocarbons, sulphur and nitrogen compounds, by methane may lead to discrepancies in calculations (Singh, 2004). For example, hydrocarbon compounds with different molecular weights have different vapour-liquid equilibrium characteristics which may affect the purity, and flow rate of recycle and purge streams from hydroprocessors (Singh, 2004). Another limitation of hydrogen pinch analysis is that pressure differences between source and sink streams are ignored. Hydrogen pinch analysis
assumes that any source may supply hydrogen to any sink if the purity of source is higher than the purity of sink. The estimated minimum amount of hydrogen utility required to satisfy the demands of a hydrogen network using this assumption may only be achieved at the expense of extra compression costs (Hallale and Liu, 2001).

6.2.2.1 Hydrogen sinks and sources

Alves (1999) defined the concepts of sink and source to classify components of a hydrogen distribution system. A sink is a stream that consumes hydrogen from the hydrogen distribution system while a source is defined as a stream supplying hydrogen to the system. The hydrogen producing processes form the sources of a hydrogen distribution system with given purity and pressure levels. The hydrogen consuming processes are represented in the framework of sinks and sources as shown in Figure 6.2.

![Figure 6.2 Simplified representation of a hydrogen consuming process in hydrogen pinch analysis](image)

A hydrogen consuming process is represented as a sink and a source in the hydrogen management framework (Alves, 1999). The net hydrogen-rich gas fed to the hydrogen consuming process, i.e. the mixture of the recycle stream from the process and the hydrogen make-up stream, is represented as the sink. While the stream that is partly recycled and partly purged, in order to prevent the build-up of hydrocarbons in the recycle stream, is represented as the source. The flow rate and purity of the process source and sink are calculated using the data available for the process purge, recycle and make-up streams. The flow rate and purity of the process sink are calculated using equations 6.1 and 6.2 (Alves, 1999):
The flowrate and purity of the process source are given by the following equations (Alves, 1999):

\[ F_{\text{Source}} = F_p + F_R \]  \hspace{1cm} (6.3)

\[ y_{\text{Source}} = y_p \]  \hspace{1cm} (6.4)

Apart from hydrogen producing and consuming processes, other components of a hydrogen network are also classified in terms of sources and sinks. Purification units consist of one hydrogen sink, i.e. the feed stream and two hydrogen sources, the product and residue streams. Compressors consist of one sink and one source, i.e. the inlet and outlet streams.

### 6.2.2.2 Purity profiles and hydrogen surplus diagram

In Hydrogen pinch analysis the source and sink data of a hydrogen distribution system are used to generate purity profiles (Alves, 1999). A purity profile is a plot of hydrogen purity against the stream flow rates. A source purity profile can be generated by plotting the purities of all the source streams, starting with the highest purity and continuing in decreasing order, against the flow rates. The sink purity profile is generated similarly using the flow rate and purity information of sinks. The purity profiles in hydrogen pinch analysis as shown in Figure 6.3 are analogous, to the hot and cold composite curves of heat recovery pinch analysis.
The purity profiles are a graphical representation of the required and available amount of hydrogen at various purity levels. When the purity profiles are plotted together, as shown in Figure 6.3, there are regions where the source profile lies above the sink profile indicating an excess of hydrogen available in that particular range of purity. On the other hand, if the source profile is beneath the sink profile then there is a deficit of available hydrogen in that purity range.

The availability of hydrogen at different purity levels is represented as the hydrogen surplus, defined as the net cumulative excess of hydrogen in the purity profile at a given flow rate (Alves et al., 2002). A hydrogen surplus diagram is a plot of the hydrogen surplus against different purity levels of a hydrogen network. Figure 6.4 shows a hydrogen surplus diagram generated by plotting the hydrogen surplus or deficit, from purity profiles, at different purity levels.
The hydrogen pinch is determined by moving this surplus curve towards the vertical axis, i.e. by minimising the surplus amount of hydrogen available in the hydrogen network. The hydrogen pinch, as shown in Figure 6.5, occurs at the point, i.e. the purity level, where the hydrogen surplus becomes zero. The amount of hydrogen supplied by the hydrogen plant, i.e. the hydrogen utility, when a hydrogen network is pinched is the minimum amount of hydrogen utility that can satisfy the requirement of the given hydrogen network (Alves, 1999).

Figure 6.4 Hydrogen surplus diagram (Alves, 1999)
6.2.2.3 Hydrogen purification analysis

The hydrogen pinch represents the minimum amount of hydrogen utility required for the feasible operation of a hydrogen network. Hydrogen pinch also represents a bottleneck to the savings that can be made in terms of reducing the hydrogen utility. One of the debottlenecking options discussed by Alves (1999) is the utilisation of purification processes to increase the purity of one or more hydrogen sources. The advantage of purifying a source stream is that the amount of hydrogen available at a given purity level increases thereby improving the allocation of hydrogen between sinks (Alves, 1999).

A purification unit in a given hydrogen network may be represented graphically on a hydrogen surplus diagram, as increasing purity of sources above the pinch, across the pinch or below the pinch resulting in three different scenarios (Alves, 1999). If a purification unit is placed above the hydrogen pinch in a hydrogen network than the required hydrogen utility may decrease as the hydrogen surplus lost to the purification feed stream is replaced by excess hydrogen surplus from high purity product stream of the purification unit. However, this saving depends on the amount of hydrogen lost to the residue stream of the purification unit. Purification

Figure 6.5 Hydrogen pinch shown on the hydrogen surplus diagram (Alves, 1999)
across the pinch provides the highest reduction in the required amount of hydrogen utility. In purification across the pinch a source stream with lower hydrogen surplus from an unconstrained region is purified to a purity level above the pinch. In this way an excess of hydrogen surplus is provided above the pinched region. The third placement of purification units, i.e. below the pinch has little benefit as this provides an excess hydrogen surplus below the pinch in a region that already has excess hydrogen surplus and therefore may result in no reduction in the hydrogen utility. The three options for placement of purification units in a hydrogen network are shown in Figure 6.6.

Figure 6.6 Placement of purification unit in a hydrogen network (Alves, 1999)

The purification analysis by Alves (1999) assumes that the placement of a purification unit would not create a new pinch and thus ignores the possibility of increase in the required amount of hydrogen utility if a new pinch is formed (Liu, 2002). Another limitation of the above purification analysis is that it does not identify which hydrogen sources would be most beneficial for purification or which purification processes would perform optimally for a given hydrogen network.

6.2.2.4 Hydrogen network design

The approach developed by Alves (1999) for design of hydrogen networks applies the same constraints, i.e. overall mass balance and hydrogen balance, as the
hydrogen pinch analysis. However, for network design these equality constraints are formulated for each hydrogen source and sink. The objective function is to minimise the total cost of the design of a given hydrogen network which consists of the cost of hydrogen from the sources, distribution cost and the value of the gas sent to the fuel gas system. The design problem is formulated as a linear programming problem using linear cost correlations (Alves, 1999).

Hydrogen pinch analysis provides insight to a hydrogen network, with the graphical representation of the sources and sinks, and can estimate the minimum hydrogen utility required for feasible operation of the system. However, the assumption that any hydrogen source can supply any hydrogen sink ignores pressure constraints. Therefore, the estimated reduction in the hydrogen utility may only be achieved at the expense of higher capital and operating costs for compressors (Hallale and Liu, 2001). Hallale et al., (2002) discussed some limitations of the hydrogen pinch analysis and design approach and observed that the approach does not take into account some practical constraints such as layout of the units, safety, piping, operability, and capital costs.

**6.2.3 Automated design of hydrogen networks**

Hallale and Liu (2001) developed a superstructure based optimisation approach for the design of hydrogen networks addressing the limitations of hydrogen pinch analysis such as incorporating pressure constraints and taking into account the existing compressors for retrofit scenarios. The automated design approach also provides a strategy for selection of purification processes and their integration with hydrogen networks. Liu (2002) developed shortcut models for compressors and purification units such as pressure swing adsorption and membrane separation for this purpose. The design problem is formulated as mixed integer non-linear programming and handles different objective functions, such as minimising the hydrogen utility, operating costs or the total annualised costs of the hydrogen network.
The approach developed for automated design of hydrogen networks (Hallale and Liu, 2001; Liu, 2002) addresses one of the limitations of hydrogen pinch analysis by taking into account pressure differences between sources and sinks of a given hydrogen network. However, this approach makes assumptions similar to hydrogen pinch analysis, e.g. the operating conditions of refinery processes constituting a hydrogen network are assumed to remain constant.

6.2.3.1 Superstructure based hydrogen network optimisation

In this approach, the components of a hydrogen network are represented as sources and sinks, and ranked in the order of decreasing hydrogen purity. A superstructure may be set up to allow connections between all the sources and all the sinks. In order to account for pressure constraints this superstructure is reduced by eliminating those connections where the source pressure is less than the sink pressure (Liu, 2002). Existing compressors are incorporated in the superstructure consisting of one sink, i.e. the compressor inlet and one source, i.e. the compressor outlet. The inlet and outlet pressures of existing compressors are fixed at their design values. New compressors may be included in the superstructure in a similar fashion. However, the inlet and outlet pressures of new compressors are not known in advance and become optimisation variables. The objective function is chosen to be the total annualised cost, i.e. the sum of annualised capital cost and annual operating cost, for optimum design of hydrogen networks (Liu, 2002).

6.2.3.2 Integration of purification processes in hydrogen network

Purification processes provide economical means of recovering hydrogen from refinery off-gases (Peramanu et al., 1999). An understanding of the basic separation principles and characteristics of different purification processes can provide physical insight for selection and integration of purification processes in hydrogen network design and optimisation (Liu, 2002). The purification processes integrated in approach developed by Liu (2002) for automated design of hydrogen networks are briefly introduced in this section. A detailed account of the purification processes employed in refinery hydrogen networks can be found elsewhere (Miller and Stoecker, 1989; Spillman, 1989; Winston and Sirkar, 1992; Ruthven et al., 1994).
In pressure swing adsorption, process impurities are removed from a hydrogen gas stream through a two stage cyclic process (Miller and Stoecker, 1989). The two stages of the separation process are: adsorption and desorption. The adsorption stage is operated at a higher pressure than the desorption stage. In the adsorption stage most of the impurities, along with a small amount of hydrogen, are adsorbed in the adsorbent. These impurities are then removed from the adsorbent in desorption stage by reducing the pressure. The relative adsorptivity of typical feed impurities is shown in Table 6.1.

<table>
<thead>
<tr>
<th>Non-Adsorbed</th>
<th>Light</th>
<th>Intermediate</th>
<th>Heavy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>O₂</td>
<td>CO</td>
<td>C₂H₆</td>
</tr>
<tr>
<td>He</td>
<td>N₂</td>
<td>CH₄</td>
<td>C₄H₁₀</td>
</tr>
<tr>
<td>Ar</td>
<td>C₂H₆</td>
<td>CO₂</td>
<td>C₅⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂S</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>BTX</td>
<td>H₂O</td>
</tr>
</tbody>
</table>

Table 6.1 Relative adsorptivity of typical components (Miller and Stoecker, 1989)

The product stream from a pressure swing adsorption unit has a pressure close to the feed stream pressure while the residue stream, i.e. the stream containing the removed impurities and lost hydrogen, is at lower pressure (Hallale et al., 2002).

In membrane separation, hydrogen is separated from impurities, by permeation into a membrane, due to the difference in permeability of hydrogen and impurities. The relative permeability of hydrogen and some typical feed impurities is shown in Table 6.2. Absolute permeation rates may vary depending on the type of membrane employed (Miller and Stoecker, 1989).
<table>
<thead>
<tr>
<th>High</th>
<th>Medium</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>C₁</td>
<td>C₂⁺</td>
</tr>
<tr>
<td>H₂O</td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2 Relative permeability of typical components (Miller and Stoecker, 1989)

A simplified membrane separation process is shown in Figure 6.7 (Winston and Sirkar, 1992).

![Figure 6.7 A simplified membrane separation process (Winston and Sirkar, 1992)](image)

The product stream containing hydrogen and components with higher permeability is termed as permeate (Winston and Sirkar, 1992). The permeate enriches in the low pressure side of the membrane. The pressure difference between permeate and residue streams provides the driving force in membrane separation process and causes the diffusion of gas across the membrane (Miller and Stoecker, 1989). Membrane separation cannot remove impurities to a very low level like pressure swing adsorption process. However, it has the advantage of lower capital cost and ease of operation (Miller and Stoecker, 1989).

Cryogenic separation and gas-liquid absorption are some of the other means of purifying hydrogen source streams; these purification processes are not
incorporated in the automated design of hydrogen networks because pressure swing adsorption and membrane separation are widely employed purification processes in petroleum refineries (Liu, 2002). Cryogenic separation exploits the difference in relative volatility of hydrogen and other components. Cryogenic separation is operated at low temperatures (Peramanu et al., 1999).

Purification units may be introduced into the superstructure for automated design of hydrogen networks. A simplified schematic diagram of a purification unit is shown in Figure 6.8.

![Figure 6.8 Schematic diagram of a purification unit for hydrogen network superstructure (Liu, 2002)](image)

The superstructure developed for automated design of hydrogen networks with purification processes is represented in Figure 6.9 (Liu, 2002).
This superstructure takes into account all the possible matches between hydrogen producing and hydrogen consuming processes as well as purification units (Liu, 2002). The design of a hydrogen network with minimum total annualised cost is obtained by reducing this superstructure using mixed integer non-linear programming optimisation (Liu, 2002).

The approach developed by Liu (2002) for automated design of hydrogen networks addresses some of the limitations of pinch analysis and design approach by taking...
into account practical constraints such as pressure differences, compression and piping costs. This approach integrates purification processes to improve the scope of reduction of hydrogen utility. However, there are two major limitations in automated design approach. The first limitation arises as the approach for automated design of hydrogen networks assumes hydrogen streams to be binary mixtures of hydrogen and methane by combining all impurities as methane. As the molecular weight of hydrogen is very low even small changes in the composition of impurities can significantly affect the molecular weight of the stream (Hallale et al. 2002). The impact of changes in impurity composition, of recycle and purge streams from hydrogen consuming processes, on process performance parameters such as hydrogen partial pressure and hydrogen-to-oil ratio cannot be captured if the hydrogen streams are treated as binary mixtures of hydrogen and methane (Singh, 2004).

The second drawback of the automated design approach, and its predecessors, is the assumption of constant operating conditions for all refinery processes constituting a hydrogen network. Because of this assumption, these hydrogen management techniques may only help reduce the hydrogen utility but do not provide a framework for analysing the optimal utilisation of the possible saving of hydrogen surplus (Hallale et al., 2002). Sun (2004) illustrated the utilisation of hydrogen, freed up using the network design methods, to improve the performance of a diesel hydrotreater. However, the impact of the changing process conditions on the performance of the hydrogen network is not addressed in the analysis of Sun (2004).

A new methodology is developed in this work to account for changing operating conditions of hydrogen consuming processes. The impact of changing process conditions on the performance of a hydrogen network is addressed in the new methodology for hydrogen management.
6.3 Multi-period hydrogen management

The hydrogen network design approaches discussed so far do not provide a framework for optimal utilisation of hydrogen to improve the economic performance of refinery processes (Hallale et al., 2002). For example, increasing hydrogen partial pressure may enhance the reactor conversion, throughput, product yields and catalyst life of hydrogen consuming processes (Hallale et al., 2002). Another feature that may influence the performance of a hydrogen network is the changing operating conditions of refinery processes, e.g. composition of feedstock, operating temperature, and pressure resulting in different conversion of reactions. Consequently, the hydrogen consumption, flow rate, and purity of recycle and purge streams of hydrogen consuming processes may also change. Hydrogen networks designed using data for one set of process conditions, i.e. a single-period data, may not be able to satisfy the requirements of hydrogen consuming processes when the operating conditions of one or more refinery processes are changed. A novel approach for multi-period design of hydrogen networks is developed in this work to account for the changing operating conditions of refinery processes.

The methodology developed for multi-period hydrogen management is an extension of the automated design approach of Liu (2002) for multiple periods of operation. The methodology developed for multi-period hydrogen management can provide retrofit and design of flexible hydrogen networks, i.e. hydrogen networks that can operate under different operating conditions, with minimum total annualised cost. This section presents the mathematical formulation developed for the multi-period design of hydrogen networks, as well as the optimisation framework. Each is addressed in turn here.

6.3.1 Process constraints

The design of hydrogen networks for multiple periods of operation requires process constraints to be satisfied for all the sources and sinks of a system for all the operating period under consideration. The process constraints include the overall material and hydrogen balance. These constraints ensure that each
hydrogen sink is supplied by a sufficient flow rate, and hydrogen purity of a hydrogen rich gas given by equations 6.5 and 6.6.

\[
\sum_v F_{v,Sk,p} = F_{Sk,p}^* \quad (6.5)
\]

\[
\sum_v F_{v,Sk,p} \cdot y_{v,p} = F_{Sk,p}^* \cdot y_{Sk,p} \quad (6.6)
\]

Similarly, the amount of gas supplied to all the sinks including the fuel system must be equal to the amount available from each hydrogen source:

\[
\sum_w F_{Sr,w,p} = F_{Sr,p}^* \quad (6.7)
\]

where \(F\) represents the flow rate of a stream, \(y\) the hydrogen purity of a stream in weight fraction, the subscripts \(p, Sk, Sr, v,\) and \(w\) represent a period of operation, sink of a hydrogen consumer, source from a hydrogen consumer, a source in a given hydrogen network, and a sink in a given hydrogen network respectively. The superscript \(^*\) represents the total flow rate of a source or sink in a given hydrogen network.

### 6.3.2 Compressors

For multi-period design of hydrogen networks, the mathematical formulation for compressors is similar to the automated design approach of Liu (2002). A compressor is incorporated in the superstructure as one sink and one source to represent the compressor inlet and outlet. The flow rate of the inlet stream of a compressor must be equal to the flow rate of the outlet stream:

\[
\sum_w F_{Comp,w,p} = \sum_v F_{v,Comp,p} \quad (6.8)
\]

where the subscripts \(Comp_v,\) and \(Comp_w\) represent a compressor source and a compressor sink respectively. Similarly, the amount of pure hydrogen entering a compressor must be equal to the amount of pure hydrogen leaving the compressor:

\[
\sum_w F_{Comp,w,p} \cdot y_{Comp,p} = \sum_v F_{v,Comp,p} \cdot y_{v,p} \quad (6.9)
\]
The above formulation may also be used to represent new compressors with inlet and outlet pressures as variables. The inlet pressure of a new compressor may be assigned the lowest pressure over all the sources that feed the compressor, while the outlet pressure may be assigned the highest pressure over all the sinks that the compressor will feed (Liu, 2002).

An additional constraint may be required for existing compressors as these machines would be designed for a maximum stream flow rate:

\[
\sum_{v} F_{v, \text{Comp}, p} \leq F_{\text{Max Comp}}
\]  

(6.10)

The compressor model used in this work is a shortcut model developed by Liu (2002). This model for compressors is developed using the power and cost equations from Peters and Timmerhaus (1991).

The power required by compressors is estimated using the following equations. It should be noted here that new compressors and purifications units are represented with sources and sinks with unknown pressure while all other components of a hydrogen network are represented as sources and sinks with known pressure (Liu, 2002):

From a source with known pressure to a sink with known pressure:

\[
\text{Power}_{\text{Comp}, p} - U_{\text{Comp}} (\frac{F_{\text{Comp}}^{\text{SrFixed, SrFixed}}}{P_{\text{SrFixed, SrFixed}}} - 1) \geq \left( c_{\text{COMP}} + d_{\text{COMP}} \frac{P_{\text{SrFixed, p}}}{P_{\text{SrFixed, p}}} \right) F_{\text{SrFixed, SrFixed}}
\]

(6.11)

\[
\text{Power}_{\text{Comp}, p} - U_{\text{Comp}} (\frac{F_{\text{Comp}}^{\text{SrFixed, SrFixed}}}{P_{\text{SrFixed, SrFixed}}} - 1) \leq \left( c_{\text{COMP}} + d_{\text{COMP}} \frac{P_{\text{SrFixed, p}}}{P_{\text{SrFixed, p}}} \right) F_{\text{SrFixed, SrFixed}}
\]
\[ Power_{COMP,p} - U_{COMP} \cdot I_{SrFixed,SFixed}^{COMP} \leq 0 \] (6.12)

From a source with known pressure to a sink with unknown pressure:

\[ Power_{COMP,p} - U_{COMP} \left( I_{SrFixed,SVaried}^{COMP} \right) \geq \left( c_{COMP} + d_{COMP} \cdot \frac{P_{SrFixed,p}}{P_{SVaried,p}} \right) F_{SrFixed,SVaried,p} \] (6.13)

\[ Power_{COMP,p} - U_{COMP} \left( I_{SrFixed,SVaried}^{COMP} \right) \leq \left( c_{COMP} + d_{COMP} \cdot \frac{P_{SrFixed,p}}{P_{SVaried,p}} \right) F_{SrFixed,SVaried,p} \] (6.14)

\[ Power_{COMP,p} - U_{COMP} \cdot I_{SrFixed,SVaried}^{COMP} \leq 0 \] (6.15)

From a source with unknown pressure to a sink with known pressure:

\[ Power_{COMP,p} - U_{COMP} \left( I_{SrVaried,SFixed}^{COMP} \right) \geq \left( c_{COMP} + d_{COMP} \cdot \frac{P_{SrFixed,p}}{P_{SVaried,p}} \right) F_{SrVaried,SFixed,p} \] (6.16)

\[ Power_{COMP,p} - U_{COMP} \left( I_{SrVaried,SFixed}^{COMP} \right) \leq \left( c_{COMP} + d_{COMP} \cdot \frac{P_{SrFixed,p}}{P_{SVaried,p}} \right) F_{SrVaried,SFixed,p} \] (6.17)

\[ Power_{COMP,p} - U_{COMP} \cdot I_{SrVaried,SFixed}^{COMP} \leq 0 \] (6.18)

From a source with unknown pressure to a sink with unknown pressure:

\[ Power_{COMP,p} - U_{COMP} \left( I_{SrVaried,SVaried}^{COMP} \right) \geq \left( c_{COMP} + d_{COMP} \cdot \frac{P_{SrFixed,p}}{P_{SVaried,p}} \right) F_{SrVaried,SVaried,p} \] (6.19)

\[ Power_{COMP,p} - U_{COMP} \cdot I_{SrVaried,SVaried}^{COMP} \leq 0 \] (6.20)
where $Power$ represents the power required by a compressor $COMP$, $U$ is the upper bound for compressor power for which the relationships hold (Liu, 2002), $If_{COMP}$ is the binary variable indicating the existence of a compressor, $P$ represents pressure at a source or a sink in hydrogen network, $c$ and $d$ represent the coefficients of the correlation for compression power (Liu, 2002), the subscripts $SkFixed$, $SkVaried$, $SrFixed$, and $SrVaried$ represent sinks of known pressure, sinks of unknown pressures, e.g. new compressors and purification units, sources of known pressure, and sources of unknown pressure in a given hydrogen network respectively.

The capital cost of a new compressor is calculated using the linear correlation:

$$I_{COMP,p}[\$US] = a_{COMP} \cdot If_{COMP} + b_{COMP} \cdot Power_{COMP,p}[kW]$$

(6.23)

where $I_{COMP}$ is the capital cost of a compressor $COMP$, $a$ and $b$ are the cost coefficients for estimation of capital cost of a compressor (Liu, 2002).

### 6.3.3 Purification units

Liu (2002) proposed heuristics for appropriate placement of purification units in a hydrogen network and illustrated that a reduction in hydrogen utility is possible if the purity of the product stream of the purification unit is higher than the hydrogen pinch purity and the purity of the residue stream of the purification unit is lower than the highest purity among the sources that are sent to the fuel system. This deduction leads to the assumption that the product stream of the purification unit will not be sent to the fuel system and the residue stream will not feed any process sinks (Liu and Zhang, 2004). Following this assumption, the mass and hydrogen balance for a hydrogen network with a purification process are:
\[
\sum_{v} F_{v, p}^* - \sum_{v} F_{v, \text{fuel}, p}^* + \sum_{w} F_{H, U, w, p}^* + \sum_{w} F_{\text{product}, w, p}^* + \sum_{w} F_{\text{residue}, w, p}^* = \sum_{w} F_{w, p}^* + \sum_{v} F_{v, \text{feed}, p}^*
\]  
(6.24)

\[
\sum_{v} F_{v, p}^* \cdot Y_{v, p}^* - \sum_{v} F_{v, \text{fuel}, p}^* \cdot Y_{v, \text{fuel}, p}^* + \sum_{w} F_{H, U, w, p}^* \cdot Y_{H, U, p}^* + \sum_{w} F_{\text{product}, w, p}^* \cdot Y_{\text{product}, p}^* + \sum_{w} F_{\text{residue}, w, p}^* \cdot Y_{\text{residue}, p}^* = \sum_{w} F_{w, p}^* \cdot Y_{w, p}^* + \sum_{v} F_{v, \text{feed}, p}^* \cdot Y_{v, \text{feed}, p}^*
\]  
(6.25)

where the subscripts \textit{fuel}, \textit{H}_2\text{U}, \textit{product}, and \textit{residue} represent the fuel system of the refinery, hydrogen utility, i.e. the hydrogen plant, product stream of a purification process, and residue stream of a purification process respectively. As discussed in Section 6.2.3.2, in this work only pressure swing adsorption and membrane purification processes are considered for integration with hydrogen networks. The mass and hydrogen balances of equations 6.5 to 6.7 may be alternatively expressed as:

\[
\sum_{w} F_{w, p}^* = F_{w, p}^*
\]  
(6.26)

\[
\sum_{v} F_{v, p}^* = F_{v, p}^*
\]  
(6.27)

\[
\sum_{w} F_{w, p}^* \cdot Y_{w, p}^* + F_{\text{PSAf}, p} \cdot Y_{\text{PSAf}} + F_{\text{PSAp}, p} \cdot Y_{\text{PSAp}} + F_{\text{PSAr}, p} \cdot Y_{\text{PSAr}} + F_{\text{MemAf}, p} \cdot Y_{\text{MemAf}} + F_{\text{MemAp}, p} \cdot Y_{\text{MemAp}} = F_{\text{Skp}, p} \cdot Y_{\text{Skp}}
\]  
(6.28)

### 6.3.3.1 Pressure swing adsorption unit

The model for pressure swing adsorption process is an extension of the shortcut model developed by Liu (2002) for multiple periods of operation. The overall mass balance for pressure swing adsorption unit can be given by:

\[
\sum_{v} F_{v, \text{PSAf}, p} = \sum_{w} F_{\text{PSAp}, w, p} + \sum_{w} F_{\text{PSAr}, w, p}
\]  
(6.29)

where the subscripts \textit{PSAf}, \textit{PSAp}, and \textit{PSAr} represent the feed, product and residue stream of a pressure swing adsorption unit respectively. The hydrogen recovery of a pressure swing adsorption unit is dependant on process parameters such as feed purity, product purity, feed pressure and product pressure.
where $R_{PSA}$ is the hydrogen recovery of a pressure swing adsorption unit. The purity of product stream is a fixed parameter set at a constant value.

$$P_{PSAr,p} = P_{PSAp,p} \cdot y_{PSAf,p} \cdot \left(1 - \frac{R_{PSA,p}}{1 - \theta}\right)$$  \hspace{1cm} (6.31)

where $\theta$ is the adsorbent selectivity. The hydrogen balance for a given period of operation is given by:

$$\sum_v F_{v,PSAf,p} \cdot y_{PSAf,p} = \sum_w F_{PSAp,w,p} \cdot y_{PSAp,p} + \sum_w F_{PSAr,w,p} \cdot y_{PSAr,p}$$  \hspace{1cm} (6.32)

$$\sum_v F_{v,PSAf,p} \cdot Y_{PSAf} = \sum_{S_{Fixed}} F_{S_{Fixed},PSAf,p} \cdot Y^{*}_{S_{Fixed},p} + \sum_{S_{Varied}} F_{S_{Varied},PSAf,p} \cdot Y_{S_{Varied},p}$$  \hspace{1cm} (6.33)

As there is a very low pressure drop in pressure swing adsorption process (Hallale et al., 2002) the pressure of the product stream is assumed to be the same as the pressure of feed stream (Liu, 2002):

$$P_{PSAp,p} = P_{PSAf,p}$$  \hspace{1cm} (6.34)

$$P_{PSAp,p} \leq P_{PSAp,p}^{\text{up}}$$  \hspace{1cm} (6.35)

The existence of a pressure swing adsorption unit for purification of a hydrogen source stream is indicated by the binary variable $I_f^{PSA}$ through the following inequality constraints:

$$\sum_v F_{v,PSA,p} - I_f^{PSA} \cdot \sum_v U_{f_{flow}} \leq 0$$  \hspace{1cm} (6.36)

$$\sum_v F_{v,PSA,p} - I_f^{PSA} \cdot \sum_v u_{f_{flow}} \geq 0$$  \hspace{1cm} (6.37)
where $U_{flow}$ and $u_{flow}$ are the maximum and minimum flow rates of the streams fed to the pressure swing adsorption unit. The capital cost of a pressure swing adsorption unit is estimated using the following relationship (Liu, 2002):

$$I_{PSA,p} [k\$/US] = 503.8 + 347.4 \cdot F_{PSA,p} [Mscfd]$$

(6.38)

where $I_{PSA}$ represents the capital cost of a pressure swing adsorption unit.

### 6.3.3.2 Membrane purification unit

The shortcut model for membrane purification process employed in this work is for single-stage membrane separation process (Liu, 2002). The shortcut model developed by Liu (2002) for membrane purification units considers permeability of only two components, i.e. hydrogen and methane, as hydrogen gas streams are assumed to be binary mixtures of hydrogen and methane. The mass balance for membrane purification unit is given by:

$$\sum F_{v,MEMf,p} = \sum F_{MEMp,w,p} + \sum F_{MEMr,w,p}$$

(6.39)

where the subscripts $MEMf$, $MEMp$, and $MEMr$ represent the feed, product, and residue stream of a membrane purification unit. The hydrogen balance may be given by:

$$\sum F_{v,MEMf,p} \cdot y_{MEMf,p} = \sum F_{MEMp,w,p} \cdot y_{MEMp,p} + \sum F_{MEMr,w,p} \cdot y_{MEMr,p}$$

(6.40)

$$\sum F_{v,MEMf,p} \cdot y_{MEMf,p} = \sum F_{SrFixed, MEMf,p} \cdot y_{SrFixed,p}^* + \sum F_{SrVaried, MEMf,p} \cdot y_{SrVaried,p}$$

(6.41)

The hydrogen recovered in the product stream of the membrane purification unit is calculated using the permeability of hydrogen and methane through the membrane given by:

$$\sum F_{MEMp,w,p} \cdot y_{MEMp,p} = L_8 H_2 A_{MEM,p} \left( P_{MEMf,p} \cdot y_{MEMf,p} - P_{MEMp} \cdot y_{MEMp,p} \right)$$

(6.42)
where $L_{gH_2}$ is the permeability of hydrogen through the membrane, $L_{gCH_4}$ is the permeability of methane, and $A_{MEM}$ is the area of a membrane purification unit. The residue stream pressure is set equal to the feed stream pressure because of a very little pressure drop between the two streams.

$$P_{MEMr,p} = P_{MEMf,p}$$  \hspace{5cm} (6.44)

The ratio of the residue stream pressure and product stream pressure needs to be maintained within a tolerance based on the maximum strength of the membrane while the hydrogen partial pressure of residue streams needs to remain higher than the hydrogen partial pressure of product stream to maintain the gradient for permeability. These constraints are given as (Liu, 2002):

$$P_{MEMr} \leq L_{mMEM} \cdot P_{MEMp}$$  \hspace{5cm} (6.45)

where $L_{mMEM}$ is the maximum pressure ratio across the membrane.

$$P_{MEMr} \cdot y_{MEMr} \geq P_{MEMp} \cdot y_{MEMp}$$  \hspace{5cm} (6.46)

The existence of a membrane purification unit is indicated by a binary variable $\text{If}^{MEM}$. Some additional constraints may be specified for the flow rate and area of a membrane purification unit to ensure practicable designs.

$$\sum_v F_{v,MEMf,p} - \text{If}^{MEM} \cdot \sum_v U_{\text{flow}} \leq 0$$  \hspace{5cm} (6.47)

$$\sum_v F_{v,MEMf,p} - \text{If}^{MEM} \cdot \sum_v U_{\text{flow}} \geq 0$$  \hspace{5cm} (6.48)

$$A_{MEM,p} - \text{If}^{MEM} \cdot U_{\text{Area,MEM}} \leq 0$$  \hspace{5cm} (6.49)

$$A_{MEM,p} - \text{If}^{MEM} \cdot U_{\text{Area,MEM}} \geq 0$$  \hspace{5cm} (6.50)

The capital cost of the membrane purification unit is estimated by:
\[ I_{MEM,p} = a_{MEM} \cdot I_f^{MEM} + b_{MEM} \cdot A_{MEM,p} \]  

(6.51)

where \( I_{MEM} \) is the capital cost, \( a \) and \( b \) are the cost coefficients for estimation of capital cost of the membrane purification unit (Liu, 2002).

### 6.3.4 Piping system

The sources and sinks of a hydrogen network are connected to each other through the piping system. The existence of a piping connection depends on the flow of gas from a source to a sink and is indicated by the binary variable \( I_f^{PIPE} \). The following inequality constraints describe the piping connections between sources and sinks of a hydrogen network:

\[ F_{v,w} - I_f^{PIPE} \cdot U_{flow} \leq 0 \]  

(6.52)

\[ F_{v,w} - I_f^{PIPE} \cdot u_{flow} \geq 0 \]  

(6.53)

The capital cost of the piping system for hydrogen network with purification processes is given by:

\[ I_{PIPE}^{Fixed,w,p} [\text{US}] = \left( a_{Fixed,w} \cdot I_f^{PIPE} + b_{Fixed,w} \cdot \frac{0.02352 F_{Fixed,w,p} [\text{MMscf/d}]}{P_{Fixed,p} [\text{MPa}]} \right) \cdot L_{Fixed,w} [\text{m}] \]  

(6.54)

\[ I_{PIPE}^{Varied,w,p} [\text{US}] = \left( a_{Varied,w} \cdot I_f^{PIPE} + b_{Varied,w} \cdot \frac{0.02352 F_{Varied,w,p} [\text{MMscf/d}]}{P_{Varied,p} [\text{MPa}]} \right) \cdot L_{Varied,w} [\text{m}] \]  

(6.55)

where \( I_{PIPE} \) is the capital cost of a piping connection, and \( L_{PIPE} \) is the length a the piping connection between a source and a sink in hydrogen network. The length of piping connections may be specified for an existing hydrogen network or for a new design using the information about the plant layout (Liu, 2002).

### 6.3.5 Pressure constraints

One of the major drawbacks of the hydrogen pinch analysis and design approach of Alves (1999) is that pressure differences between sources and sinks are not taken
into account. Thus, to achieve the estimated reduction in hydrogen utility extra compression may be required resulting in higher capital investment (Hallale and Liu, 2001).

Pressure constraints have been incorporated in the automated design approach for hydrogen networks by Liu (2002) to account for the capital and operating costs of compressors required to meet the pressure differences between sources and sinks of a hydrogen network. Pressure constraints dictate the choice of installation of new compressors in the design of hydrogen networks. The need to install a new compressor depends on the conditions; that there is a flow of gas between a source and a sink, and that the pressure of sink is higher than the source, i.e. the pressure difference is less than zero:

\[
\text{If}_{v,w}^{\text{PIPE}} = 1 \text{ And } \text{If}_{v,w}^{\text{dp}} = 1 \rightarrow \text{If}_{v,w}^{\text{COMP}} = 1
\]  

(6.56)

where \(\text{If}_{v,w}^{\text{dp}}\) represents the binary variable to indicate the requirement to install a compressor because of pressure difference between a source and sink in hydrogen network. This condition is expressed as:

\[
P_{v,p} - P_{v,p} - \text{If}_{v,w}^{\text{dp}} \cdot U_{dp} \leq 0
\]  

(6.57)

\[
P_{v,p} - P_{v,p} + (1 - \text{If}_{v,w}^{\text{dp}}) \cdot U_{dp} \geq u_{dp}
\]  

(6.58)

The logical constraints for installation of a new compressor may be expressed as (Liu, 2002):

\[
\text{If}_{v,w}^{\text{COMP}} - \text{If}_{v,w}^{\text{dp}} \leq 0
\]  

(6.59)

\[
\text{If}_{v,w}^{\text{COMP}} - \text{If}_{v,w}^{\text{PIPE}} \leq 0
\]  

(6.60)

\[
\text{If}_{v,w}^{\text{dp}} + \text{If}_{v,w}^{\text{PIPE}} - \text{If}_{v,w}^{\text{COMP}} \leq 1
\]  

(6.61)
6.3.6 Objective function

The objective function for design and optimisation of hydrogen networks for multiple periods of operation is chosen to be the total annualised cost. The choice of total annualised cost as the objective function gives the advantage of expressing both the capital and operating costs of the hydrogen network on a common basis (Liu and Zhang, 2004). The total annualised cost (TAC) is given by (Liu and Zhang, 2004):

\[
TAC = \text{Cost}_{H_2} - \text{Cost}_{\text{Fuel}} + \text{Cost}_{\text{Power}} + Af \cdot \left( \sum_{\text{COMP}} I_{\text{COMP}} + I_{\text{PSA}} + I_{\text{MEM}} + \sum_{\text{PIPE}} I_{\text{PIPE}} \right)
\]  

(6.62)

where \(Af\) is the annualisation factor may be given by (Smith, 2005):

\[
Af = \frac{i \cdot (1+i)^n}{(1+i)^n - 1}
\]

(6.63)

where \(i\) is the fractional interest rate per year, and \(n\) is the number of years.

For a multi-period design the capital and operating costs may vary for different operating periods as the operating conditions of refinery processes may have to be modified in order to satisfy the product demands. For example, in the operation of hydrocracking and hydrotreating processes, operating conditions, such as reactor inlet temperature, is varied to compensate catalyst deactivation. Changing market demands may also influence the operation of individual refinery processes. The objective function, i.e. the total annualised cost therefore needs to be the sum of the capital and operating costs taking into account the maximum loads, and capacities on individual units from all the operating periods under consideration.
The cost of hydrogen utility, i.e. the cost of producing hydrogen in the hydrogen plant for a given hydrogen network, or the cost of hydrogen imported to a hydrogen network is given by (Liu, 2002):

\[
\text{Cost}_{H_2} \geq \text{Cost}_{H_2,p} = o_y \cdot \sum_w F_{H_2,w,p} \cdot P_{I H_2}
\]  

(6.64)

where \( P_{I H_2} \) represents the price per unit of hydrogen, and \( o_y \) represents the annual number of hours of operation. The credit for gas sent to the fuel system is calculated using the heating value of the components of the gas stream, i.e. hydrogen and methane (Liu, 2002):

\[
\text{Cost}_{Fuel} \geq \text{Cost}_{Fuel,p} = o_y \left( F_{H_2,Fuel,p} \cdot HV_{H_2} + F_{CH_4,Fuel,p} \cdot HV_{CH_4} \right) \cdot P_{I HV}
\]  

(6.65)

where \( HV \) represents the heating value of a component. The operating cost of compressors consisting of the power consumed is given as (Liu, 2002):

\[
\text{Cost}_{Power} \geq \text{Cost}_{Power,p} = o_y \cdot \sum_{COMP} P_{\text{Power},COMP,p} \cdot P_{I Power}
\]  

(6.66)

The capital cost of compressors, purification units and piping system is also handled in a similar fashion. The constraints presented here take into account the capital and operating costs corresponding to the maximum capacities and loads on individual units over all the operating periods under consideration.

6.3.7 Optimisation framework for multi-period design of hydrogen networks

The modelling equations described in Sections 6.3.2, 6.3.3, and 6.3.4 consist of some of the equation with non-linear terms in them. The non-linear terms appear in some of the equations for the mass balance of hydrogen consumers, i.e. equations 6.25, and 6.28, in the model for compressors, i.e. equations 6.14, 6.15, 6.17, 6.18, 6.20, and 6.21, in the model for purification units, i.e. equations 6.30 to 6.33 and equations 6.40 to 6.43, and equation 6.46, and in the model for piping system, i.e. equation 6.55. The presence of discrete variables along with non-linear terms makes the design and optimisation of multi-period hydrogen networks a mixed
integer non-linear programming problem. This section presents the optimisation framework adopted in this work for multi-period design of hydrogen networks.

6.3.7.1 Linear relaxation of non-linear terms

For mixed integer non-linear programming optimisation problems a global optimum may not be guaranteed if the problem is non-convex (Biegler et al., 1997). However, a suitable initialisation may lead the program to a good local optimum (Liu, 2002). All the non-linear terms in the hydrogen network model are either in bilinear form or can be converted to a bilinear form (Liu, 2002). Quesada and Grossmann (1995) proposed a methodology for optimisation of problems with networks consisting of splitters, mixers etc. involving multi-component streams, using linear relaxation of bilinear terms in order to improve the robustness of optimisation and help locate good local optimum. According to this approach, a bilinear term may be transformed into four linear inequalities using the upper and lower bounds for the two variables constituting the bilinear term (Quesada and Grossmann, 1995).

The Non-linear terms consisting of three variables, such as in equation 6.30, may be transformed to linear form in two stages (Liu, 2002). First a new variable may be declared as the product of any two of the three variables. The bilinear term formed due to this new variable is transformed into linear form using linear relaxation method. In the second step the new variable which had been declared as a product of two variables is linearly relaxed. Liu (2002) illustrated successful application of this strategy for automated design of hydrogen networks. Therefore, this approach is employed in this work for design and optimisation of hydrogen networks for multiple periods of operation.

The application of linear relaxation of bilinear terms is illustrated for equation 6.30, as an example. The equation 6.30 describes the amount of hydrogen recovered in the product stream of a pressure swing adsorption unit. The non-linear
term in this equation consists of a product of three variables so the linear relaxation should be carried out in two steps.

In the first step a new variable $F_y$ is declared as the product of the flow rate and purity of the streams fed to the pressure swing adsorption unit. Equation 6.30 may be expressed in terms of this variable as:

$$F_y_{PSA,p} \cdot R_{PSA,p} = \sum_w F_{PSA,w,p} \cdot y_{PSA,p}$$  \hspace{1cm} (6.67)

The new variable forms a bilinear term with the recovery of the pressure swing adsorption unit, represented as $R_{PSA}$. This bilinear term may be relaxed into four linear inequalities as follows:

$$F_y_{PSA,p} \cdot R_{PSA,p} \geq F_y_{PSA,p} \cdot R_{PSA,p} + F_y_{PSA,p} \cdot R_{PSA,p} - F_y_{PSA,p} \cdot R_{PSA,p}$$ \hspace{1cm} (6.68)

$$F_y_{PSA,p} \cdot R_{PSA,p} \geq F_y_{PSA,p} \cdot R_{PSA,p} + F_y_{PSA,p} \cdot R_{PSA,p} - F_y_{PSA,p} \cdot R_{PSA,p}$$ \hspace{1cm} (6.69)

$$F_y_{PSA,p} \cdot R_{PSA,p} \leq F_y_{PSA,p} \cdot R_{PSA,p} + F_y_{PSA,p} \cdot R_{PSA,p} - F_y_{PSA,p} \cdot R_{PSA,p}$$ \hspace{1cm} (6.70)

$$F_y_{PSA,p} \cdot R_{PSA,p} \leq F_y_{PSA,p} \cdot R_{PSA,p} + F_y_{PSA,p} \cdot R_{PSA,p} - F_y_{PSA,p} \cdot R_{PSA,p}$$ \hspace{1cm} (6.71)

In the second step, the new variable which is itself a product of two variables is relaxed into four linear inequalities as follows:

$$F_y_{PSA,p} \geq F_y_{PSA,p} \cdot y_{PSA,p} + F_y_{PSA,p} \cdot y_{PSA,p} - F_y_{PSA,p} \cdot y_{PSA,p}$$ \hspace{1cm} (6.72)

$$F_y_{PSA,p} \geq F_y_{PSA,p} \cdot y_{PSA,p} + F_y_{PSA,p} \cdot y_{PSA,p} - F_y_{PSA,p} \cdot y_{PSA,p}$$ \hspace{1cm} (6.73)

$$F_y_{PSA,p} \leq F_y_{PSA,p} \cdot y_{PSA,p} + F_y_{PSA,p} \cdot y_{PSA,p} - F_y_{PSA,p} \cdot y_{PSA,p}$$ \hspace{1cm} (6.74)

$$F_y_{PSA,p} \leq F_y_{PSA,p} \cdot y_{PSA,p} + F_y_{PSA,p} \cdot y_{PSA,p} - F_y_{PSA,p} \cdot y_{PSA,p}$$ \hspace{1cm} (6.75)

The flow rate of the net feed of the pressure swing adsorption unit in a given operating period is the sum of all the sources to be purified:

$$F_{PSA,p} = \sum_v F_{v,PSA,p}$$ \hspace{1cm} (6.76)
All the non-linear terms of the multi-period hydrogen network model are linearised using this method and the original mixed integer non-linear programming problem is transformed into a mixed integer linear programming problem. The upper and lower bounds for variables may be specified easily using physical insight of a given system.

6.3.7.2 Design and optimisation algorithm

The linear relaxation methodology explained in Section 6.3.7.1 transforms the optimisation problem, for design of hydrogen networks, into a mixed integer linear programming (MILP) problem for which a global optimum may be obtained (Liu, 2002). The solution of the mixed integer linear programming formulation is employed as an initialisation of the original mixed integer non-linear programming formulation. In this way the convergence to a feasible solution may be achieved and the probability of obtaining a good local optimum solution is improved (Liu, 2002).

This design and optimisation strategy for multi-period hydrogen network management is shown in Figure 6.10. As the approach developed in this work for design of hydrogen networks, for multiple periods of operation, is an extension of automated design approach of Liu (2002). This approach also assumes that there is a compressor between every source and sink because of the unknown pressures initially. This assumption leads to a higher number of compressors with some of them providing only small compression duties (Liu, 2002). In order to avoid a higher number of new compressors, the design obtained by the optimisation procedure may be evolved by merging new compressors, and piping connections to achieve practicable and simplified network designs (Liu, 2002).
6.4 Case study

In this section a case study is presented to illustrate the application and benefits of the methodology developed for multi-period hydrogen management. This case study also elucidates the importance and impact of changing operating conditions of refinery processes on the design of hydrogen networks. The objective of this case study is to design a hydrogen network with a lower total annualised cost, compared to conventional design approaches, i.e. single period hydrogen network design and optimisation. The multi-period hydrogen network designed using the methodology developed in this work would also satisfy the demands of hydrogen consuming processes, for all the periods of operation under consideration, with minimum total annualised cost unlike the design obtained using previous approach of Liu (2002).
The refinery configuration for which a hydrogen network needs to be designed is taken from Sun (2004). A simplified representation of the refinery configuration under consideration is shown in Figure 6.11.

![Figure 6.11 A simplified refinery configuration for design of hydrogen network (Sun, 2004)](image)

It should be noted here that some refinery processes with minor hydrogen consumptions have been represented as a combined process sink “CPROC”. The process data for refinery processes is classified as source and sink data and is shown in Table 6.3 and Table 6.4 (Sun, 2004).
<table>
<thead>
<tr>
<th>Unit</th>
<th>Flow rate (t/h)</th>
<th>Purity (mass fraction)</th>
<th>Pure H₂ Flow (t/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHT</td>
<td>3.108</td>
<td>0.262</td>
<td>0.815</td>
</tr>
<tr>
<td>RHT</td>
<td>5.081</td>
<td>0.2624</td>
<td>1.333</td>
</tr>
<tr>
<td>HC</td>
<td>3.251</td>
<td>0.2624</td>
<td>0.853</td>
</tr>
<tr>
<td>DHT</td>
<td>25.798</td>
<td>0.2015</td>
<td>5.198</td>
</tr>
<tr>
<td>ISOM</td>
<td>5.913</td>
<td>0.2596</td>
<td>1.535</td>
</tr>
<tr>
<td>CPROC</td>
<td>2.53494</td>
<td>0.2624</td>
<td>0.665</td>
</tr>
<tr>
<td>CCR fuel</td>
<td>0.446</td>
<td>0.2624</td>
<td>0.117</td>
</tr>
</tbody>
</table>

Table 6.3 Net hydrogen sink data of the hydrogen network under consideration

<table>
<thead>
<tr>
<th>Unit</th>
<th>Flow rate (t/h)</th>
<th>Purity (mass fraction)</th>
<th>Pure H₂ Flow (t/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCR</td>
<td>16.73</td>
<td>0.2624</td>
<td>4.39</td>
</tr>
<tr>
<td>NHT</td>
<td>2.24</td>
<td>0.2857</td>
<td>0.64</td>
</tr>
<tr>
<td>RHT</td>
<td>4.95</td>
<td>0.2436</td>
<td>1.21</td>
</tr>
<tr>
<td>HC</td>
<td>3.16</td>
<td>0.2436</td>
<td>0.77</td>
</tr>
<tr>
<td>DHT</td>
<td>18.79</td>
<td>0.1802</td>
<td>3.38</td>
</tr>
<tr>
<td>ISOM</td>
<td>4.58</td>
<td>0.2588</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 6.4 Net hydrogen source data of the hydrogen network under consideration

Hydrogen pinch analysis provides a graphical overview of the system is used to estimate the minimum amount of hydrogen required from the hydrogen producer, i.e. the catalytic reformer in this case, to satisfy the demands of hydrogen.
consuming processes. Figure 6.12 shows the balanced hydrogen surplus diagram for the given hydrogen network.

![Hydrogen surplus diagram](image)

**Figure 6.12 Hydrogen surplus diagram of the hydrogen network under consideration**

Hydrogen pinch analysis indicates a reduction of 3.42 t/h of hydrogen gas stream flow rate is possible in the hydrogen producer, i.e. the catalytic reformer, for the system under consideration. It may be observed from the hydrogen surplus diagram that the hydrogen pinch occurs at a hydrogen mass fraction of 0.201. This purity corresponds to the requirements of the diesel hydrotreating unit, as can be seen in Table 6.3. The purity level, at which hydrogen pinch occurs, indicates that the diesel hydrotreating unit may cause a bottleneck for any expansion that may require additional hydrogen consumption.

The hydrogen surplus available in the system may be beneficial for reducing the hydrogen utility of this hydrogen network, or for utilisation in a refinery process to increase the profit of the refinery. As this hydrogen surplus is available from the catalytic reformer unit, with a specified production, and not from a hydrogen production plant. Utilising this hydrogen surplus to improve the performance of refinery processes would be the logical choice (Sun, 2004).
Sun (2004) illustrated two different ways to improve the economic performance of the diesel hydrotreating unit through utilising the surplus hydrogen available in the hydrogen network under consideration:

1. Increase the throughput of the diesel hydrotreater.

2. Blend light cycle oil into the diesel hydrotreater feed.

The option of blending light cycle oil to diesel hydrotreater feed enables the upgrading of cheaper feedstock. However, the higher sulphur and aromatic content of light cycle oil would require higher hydrogen consumption and may shorten the catalyst life for the process (Sun, 2004). Sun (2004) illustrated that the available surplus hydrogen may be utilised for blending 5 volume % of light cycle oil with the diesel hydrotreater feed. Blending 5 volume % of light cycle oil with the diesel hydrotreater feed increases the net sink requirement of the diesel hydrotreating process to 27.8 t/h and consumes the surplus hydrogen that was originally available in the given refinery hydrogen network.

In this case study first a hydrogen network is designed for the new scenario with increased hydrogen consumption of diesel hydrotreating process using the automated design approach of Liu (2002). The automated design approach of Liu (2002) can only handle single period operating conditions. In this case study the changing operating conditions of diesel hydrotreating process resulting in change in hydrogen consumption of diesel hydrotreater are taken into account. A multi-period hydrogen network is designed for the same refinery configuration using the methodology developed in this work. The hydrogen network designed using the new methodology is compared with the network generated using the automated design approach of Liu (2002) to elucidate the advantages of the approach for design of hydrogen networks for multiple periods of operation. The comparison also demonstrates the ability of the approach developed in this work to account for changing operating conditions of refinery processes.
The economic data for this case study, i.e. the capital and operating cost data for compressors, purification units, and piping system is taken from Liu (2002) and are shown in Table 6.5. The capital costs are annualised over 5 years, with 5% interest rate.
### Operating cost

- **Hydrogen cost**: $2000/MMscfd
- **Electricity cost**: $0.03/kWh

### Capital costs

#### Compressors

\[
\text{Cost}[kSUS] = 764.86 \cdot I_f^{COMP} + 1.7596 \cdot \text{Power}_{COMP}[kW]
\]

#### Membrane

\[
\text{Cost}[kSUS] = 50 \cdot I_f^{MEM} + 0.4 \cdot A_{MEM}[m^2]
\]

#### Piping system

\[
\begin{align*}
\text{Cost}_{\text{ PIPE }_{\text{St} \text{Fixed},w} \text{ SUS}} &= \left(420.74 \cdot I_f^{\text{ PIPE }_{\text{St} \text{Fixed},w} \text{ SUS}} + 1484.76 \cdot \frac{0.02352 F_{\text{St} \text{Fixed},w} \text{ [MMscfd]}}{P_{\text{St} \text{Fixed},w} \text{ [MPa]}}\right) \cdot L^{\text{ PIPE }_{\text{St} \text{Fixed},w} \text{ [m]}} \\
\text{Cost}_{\text{ PIPE }_{\text{St} \text{Varied},w} \text{ SUS}} &= \left(420.74 \cdot I_f^{\text{ PIPE }_{\text{St} \text{Varied},w} \text{ SUS}} + 1484.76 \cdot \frac{0.02352 F_{\text{St} \text{Varied},w} \text{ [MMscfd]}}{P_{\text{St} \text{Varied},w} \text{ [MPa]}}\right) \cdot L^{\text{ PIPE }_{\text{St} \text{Varied},w} \text{ [m]}}
\end{align*}
\]

Table 6.5 Economic data for case study on design of hydrogen networks (Liu, 2002)
A simplified block diagram of the hydrogen network designed using automated design approach of Liu (2002) is shown in Figure 6.13. The flow rates of all the gas streams between the sources and sinks of the hydrogen network shown in Figure 6.13 are presented in a tabular form in Appendix C.

Figure 6.13 Hydrogen network design using single-period automated design approach

The hydrogen purity of streams is given in terms of mass percentage in Figure 6.13. The cost breakdown for the hydrogen network designed using automated design approach of Liu (2002) is shown in Table 6.6.
<table>
<thead>
<tr>
<th>Operating cost (MM $US/yr)</th>
<th>133.508</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen cost</td>
<td>130.309</td>
</tr>
<tr>
<td>Electricity cost</td>
<td>3.198</td>
</tr>
<tr>
<td><strong>Capital cost (MM $US)</strong></td>
<td>49.901</td>
</tr>
<tr>
<td>Compressors</td>
<td>43.535</td>
</tr>
<tr>
<td>Piping system</td>
<td>6.365</td>
</tr>
<tr>
<td><strong>Total annualised cost (MM $US/yr)</strong></td>
<td>147.305</td>
</tr>
</tbody>
</table>

**Table 6.6 Cost breakdown for single-period design obtained using automated design approach of Liu (2002)**

The total annualised cost of the hydrogen network designed using automated design approach of Liu (2002) is 147.3 MM $US/yr. The capital cost consists of the investment for installation of compressors and the piping system. The operating cost of the hydrogen network consists of the power tariff, and cost of hydrogen, equivalent to the economic value of hydrogen, from the catalytic reforming unit.

The automated design approach of Liu (2002), as well as hydrogen pinch analysis and design approach of Alves (1999), assume constant operating conditions of refinery processes and do not provide a framework for analysis of influence of changing operating conditions on the performance of a hydrogen network. For example, the operating conditions e.g. reactor temperature of diesel hydrotreating process, which is the largest hydrogen consumer in the given hydrogen network, will change periodically in order to compensate for the catalyst deactivation due to coke formation. The changing operating conditions of the diesel hydrotreating process result in a change in the hydrogen requirements and therefore, in the net source flow rate from the diesel hydrotreating unit.

The impact of catalyst deactivation on the process conditions and net source flow rate of the diesel hydrotreating unit is predicted using the molecular model of
diesel hydrotreater presented in Section 4.2. Table 6.7 shows the process data for the diesel hydrotreating unit obtained using the molecular model of diesel hydrotreater.

<table>
<thead>
<tr>
<th>Operating period</th>
<th>Catalyst activity (%)</th>
<th>Reactor temperature (K)</th>
<th>Hydrogen consumption (t/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84</td>
<td>618.68</td>
<td>0.681</td>
</tr>
<tr>
<td>2</td>
<td>57</td>
<td>625.36</td>
<td>0.601</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>634.9</td>
<td>0.494</td>
</tr>
</tbody>
</table>

Table 6.7 Process data for diesel hydrotreating unit using molecular diesel hydrotreating reaction model

The operating conditions of the diesel hydrotreating unit are varied in order to satisfy the product specifications. The operating conditions of diesel hydrotreating unit have been classified into three operating periods, using the catalyst life, in this work. The percentage catalyst activity, reactor temperature and hydrogen consumption of the unit as shown in Table 6.7 are the average values for each operating period. These values are calculated using the results obtained from simulation of molecular model of diesel hydrotreater for run-length calculation (See Section 4.2.6 for details). The changing hydrogen consumption of the diesel hydrotreating unit results in different net sources flows, i.e. the recycle and purge flows available from the diesel hydrotreating unit, for each operating period. Table 6.8 shows the net source data of the diesel hydrotreating unit for the three operating periods under consideration.
<table>
<thead>
<tr>
<th>Operating period</th>
<th>Flow rate (t/h)</th>
<th>Purity (Mass fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.795</td>
<td>0.1802</td>
</tr>
<tr>
<td>2</td>
<td>19.239</td>
<td>0.1802</td>
</tr>
<tr>
<td>3</td>
<td>19.833</td>
<td>0.1802</td>
</tr>
</tbody>
</table>

Table 6.8 Net source data of diesel hydrotreating unit for the three operating periods under consideration

It can be seen in Table 6.8 that the net source flow rate available from the diesel hydrotreating process increases in the second and third operating periods. This change results in additional hydrogen flow of up to 0.187 t/h. The additional hydrogen available from the diesel hydrotreating unit may be utilised to improve allocation of hydrogen in later operating periods. The single-period approaches (e.g. Alves, 1999; Liu, 2002) for design of hydrogen networks do not account for such considerations. The hydrogen networks designed using single-period approaches may usually send excess hydrogen to the fuel system or to be flared eventually.

The proposed methodology takes into consideration the information available from all the operating periods of refinery processes, e.g. the diesel hydrotreating unit in this case. Figure 6.14 shows a simplified block diagram of the hydrogen network designed using the proposed methodology. The flow rates of gas streams shown in Figure 6.14 represent the maximum flow rates overall the three periods of operation under consideration. The flow rates of all the gas streams between the sources and sinks of the hydrogen network shown in Figure 6.14 are presented in a tabular form in Appendix C for each operating period.
Figure 6.14 Hydrogen network designed using the proposed methodology for multi-period hydrogen management

The design obtained using the proposed methodology is similar to the single-period design obtained using the automated design approach of Liu (2002) in terms of structural features. However, additional compression and piping connections of the multi-period design provide flexibility for better utilisation and saving of hydrogen in all the three operating periods. A comparison of the cost breakdown for the multi-period design of hydrogen network with the single-period design obtained using the automated design approach of Liu (2002) is shown in Table 6.9.
Table 6.9 A comparison of cost breakdown between the hydrogen network designs

<table>
<thead>
<tr>
<th></th>
<th>Single-period hydrogen network design</th>
<th>Multi-period hydrogen network design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating cost (MM $US/yr)</td>
<td>133.508</td>
<td>123.304</td>
</tr>
<tr>
<td>Hydrogen cost</td>
<td>130.309</td>
<td>118.551</td>
</tr>
<tr>
<td>Electricity</td>
<td>3.198</td>
<td>4.753</td>
</tr>
<tr>
<td>Capital cost (MM $US)</td>
<td>49.901</td>
<td>56.908</td>
</tr>
<tr>
<td>Compressors</td>
<td>43.535</td>
<td>47.897</td>
</tr>
<tr>
<td>Piping</td>
<td>6.365</td>
<td>9.010</td>
</tr>
<tr>
<td>TAC (MM $US/yr)</td>
<td>147.305</td>
<td>136.450</td>
</tr>
</tbody>
</table>

A characteristic feature of multi-period designs may be observed from Table 6.9 that multi-period designs may require higher capital costs compared to single-period designs. The reason for higher capital costs of multi-period design is the consideration of different operating conditions that may require different capacities of equipment e.g. compressor loads, purification capacities. In multi-period design the capital costs are calculated using the maximum load and capacity of all the equipment for a given system. This feature is evident in Table 6.9 which shows that the capital cost of compressors and piping system is higher for the multi-period design compared to the single-period design. However, the hydrogen network designed using the proposed methodology provides improved hydrogen allocation resulting in lower operating cost i.e. the hydrogen cost.
The hydrogen network designed using the multi-period formulation has a total annualised cost of 136.45 MM $US/yr and results in a saving of 10.86 MM $US/yr corresponding to a reduction of 7.4% in the total annualised cost compared to the hydrogen network designed using the automated design approach of Liu (2002).

The integration of purification processes in multi-period design of hydrogen networks may provide scope for further improvement of the design. The membrane purification process is chosen over pressure swing adsorption process because of its cost efficiency for small scale purification capacities (Miller and Stoecker, 1989). A simplified block diagram of the hydrogen network with membrane purification designed using the proposed methodology for multi-period hydrogen management is shown in Figure 6.15. The flow rates of gas streams shown in Figure 6.15 represent the maximum flow rates overall the three periods of operation under consideration. The flow rates of all the gas streams between the sources and sinks of the hydrogen network shown in Figure 6.15 are presented in a tabular form in Appendix C for each operating period.
The hydrogen network with a membrane purification unit designed using the proposed approach for multi-period design is different from both the hydrogen networks shown in Figure 6.13 and Figure 6.14. The hydrogen network, with membrane purification, designed for multi-period operation has a considerably higher capital costs for piping system and new compressors. However, savings in operating costs due to improved hydrogen utilisation, and recovery of hydrogen through purification results in a lower total annualised cost compared to the single-period hydrogen network and the multi-period hydrogen network without purification unit. A comparison of the cost breakdown for the hydrogen network design, including membrane purification unit, with the single-period design obtained using the automated design approach of Liu (2002) is shown in Table 6.10.
### Table 6.10 A comparison of cost breakdown for multi-period hydrogen network, including membrane purification, with single-period hydrogen network

<table>
<thead>
<tr>
<th></th>
<th>Single-period hydrogen network</th>
<th>Multi-period hydrogen network with purification</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating cost (MM $US/yr)</strong></td>
<td>133.508</td>
<td>115.117</td>
</tr>
<tr>
<td><strong>Hydrogen cost</strong></td>
<td>130.309</td>
<td>110.320</td>
</tr>
<tr>
<td><strong>Electricity</strong></td>
<td>3.198</td>
<td>4.797</td>
</tr>
<tr>
<td><strong>Capital cost (MM $US)</strong></td>
<td>49.901</td>
<td>66.788</td>
</tr>
<tr>
<td><strong>Compressors</strong></td>
<td>43.535</td>
<td>55.979</td>
</tr>
<tr>
<td><strong>Piping</strong></td>
<td>6.365</td>
<td>10.759</td>
</tr>
<tr>
<td><strong>Membrane</strong></td>
<td></td>
<td>0.0501</td>
</tr>
<tr>
<td><strong>TAC (MM $US/yr)</strong></td>
<td>147.305</td>
<td>130.545</td>
</tr>
</tbody>
</table>

The hydrogen network with membrane purification unit has a total annualised cost of 130.45 MM $US/yr and results in a saving of 16.76 MM $US/yr corresponding to a reduction of 11.4% in the total annualised cost compared to the hydrogen network designed using the automated design approach of Liu (2002).

### 6.5 Conclusions

Hydrogen management is essential for efficient and economic operation of a refinery. Hydrogen pinch analysis developed by Alves (1999) estimates the minimum hydrogen utility required to satisfy the demands of hydrogen consuming processes for a given hydrogen network. Hydrogen pinch analysis represents refinery processes in a framework of sources and sinks. A source is defined as a stream that supplies hydrogen to the system, while a sink is a stream that consumes
hydrogen (Alves, 1999). One of the major drawbacks of hydrogen pinch analysis is that the operating conditions of refinery processes are assumed to remain constant. Another limitation of hydrogen pinch analysis is that the pressure differences between sources and sinks of a given hydrogen network are neglected. The estimated minimum amount of hydrogen utility required to satisfy the demands of a hydrogen network using this assumption may only be achieved at the expense of extra compression costs (Hallale and Liu, 2001).

Liu (2002) developed automated design approach for design of hydrogen networks addressing some of the limitations of the hydrogen pinch analysis. The automated design approach of Liu (2002) accounts for the pressure differences between sources and sinks of a given hydrogen network. Liu (2002) also developed short-cut models for compressors, and purification units. However, the automated design approach of Liu (2002) also assumes constant operating conditions of refinery processes.

A multi-period approach for design of hydrogen networks is developed in this work to address the limitation in previous approaches, for design of hydrogen networks, due to the simplifying assumption of constant operating conditions of refinery processes. The proposed methodology accounts for the changing operating conditions of refinery processes. The hydrogen networks designed using the proposed methodology for multi-period hydrogen management can operate under multiple periods of operation with lower total annualised cost compared to the hydrogen networks designed using single-period design approaches.
Chapter 7 Conclusions and Future work

A hydrotreating process consists of three subsystems, i.e. a reactor, a separation system, and an associated heat recovery system. Hydrotreating processes mainly produce transportation fuels such as gasoline, diesel in petroleum refineries. Increasing demand of cleaner and more environmentally benign transportation fuels has motivated petroleum refineries to operate existing hydrotreating units at more severe operating conditions, and to increase the capacities of hydrotreating processes. In order to improve the performance of refinery processes, e.g. hydrotreating processes, modelling of refinery processes in this era of cleaner transportation fuels requires methods and techniques to account for detailed reaction chemistry, and molecular level analysis of composition of petroleum fractions.

A molecular model of diesel hydrotreater developed by Sun (2004) addresses the requirement for detailed modelling of hydrotreating reactions for improved prediction of composition and properties of products of a diesel hydrotreater. The molecular model of diesel hydrotreater employs molecular type and homologous series (MTHS) matrix representation of petroleum fractions. The molecular type and homologous series matrix representation of petroleum fractions is a detailed characterisation approach developed by Peng (1999) to represent the composition of petroleum fractions in a matrix form using the compound class and carbon number, i.e. molecular size, information of components of a mixture. Peng (1999) also developed an approach for generating pseudo-components from the MTHS matrix representation of a petroleum fraction. The pseudo-component approach
developed by Peng (1999) allows the use of commercial simulation software for modelling of separation processes, such as distillation, for refinery processes.

Previous research efforts (e.g. Peng, 1999; Zhang, 1999; Sun, 2004) on molecular modelling of refinery processes using detailed characterisation approaches, e.g. MTHS matrix representation, have only focused on individual subsystems of refinery processes. For example Sun (2004) developed a molecular model of diesel hydrotreater. The methodologies developed by these researchers do not provide a framework, to analyse the interaction of subsystems of a refinery process, to account for the changing operating conditions of an individual subsystem, e.g. a reactor, on the overall performance of a process. In order to address these limitations, the objective of this research work has been to develop a framework for integrated and multi-period design of hydrotreating processes.

7.1 Conclusions

Petroleum refineries have been motivated to increase the capacities of hydrotreating processes in order to meet the increasing demand of transportation fuels. The recent trends in processing of heavier crudes with higher sulphur contents and more stringent product specifications for cleaner transportations fuels, such as ultra-low sulphur diesel, require more severe operating conditions and higher hydrogen consumption in existing and newly built hydrotreating units.

In this era of cleaner fuels revamp projects and design activities may require detailed molecular modelling of refinery processes. A framework for integrated design and optimisation of diesel hydrotreating process is presented in this work using the molecular type and homologous series matrix representation of petroleum fractions. The application of the molecular type and homologous series matrix characterisation approach is extended beyond the molecular model of diesel hydrotreater to modelling of the separation system of the diesel hydrotreating process consisting of flash separation and a distillation column. A delumping methodology is developed in this work to facilitate the application of pseudo-
component based approach with short-cut distillation model. The delumping methodology developed in this work helps retain the molecular information needed for improved design and optimisation of hydrotreating processes. Group contribution methods have been applied with in the molecular type and homologous series matrix representation to estimate individual component properties as well as bulk physical and thermal properties of mixtures, thereby providing a consistent modelling framework for the reaction, separation and heat recovery system of the diesel hydrotreating process.

Multi-period operation refers to the periodic change in operating conditions of a process in order to maintain satisfactory performance, and to meet the product specifications and market demands. The main reason behind multi-period operation of diesel hydrotreating process is catalyst de-activation. Multi-period operation of diesel hydrotreating process has been incorporated in the design of multi-period heat exchanger networks and refinery hydrogen networks. The multi-period design approach developed in this work provides a framework for analysis of affect of changing operating conditions of a diesel hydrotreater on the design of heat exchanger networks, and the refinery hydrogen network. The multi-period design approach provides designs that can remain operable under different operating conditions, i.e. multiple periods of operation, with lower total annualised costs compared to the previous design methodologies. The approach developed for integrated and multi-period design has been demonstrated for diesel hydrotreating process design and optimisation. These methods may also be applicable to other hydrotreating processes, such as naphtha, vacuum gas oil and residue hydrotreating processes.

7.1.1 Characterisation and estimation of properties of petroleum fractions

The molecular type and homologous series matrix representation of petroleum fractions developed by Peng (1999) is a matrix representation of composition of petroleum fractions using carbon number and homologous series to identify the individual components existing in a given petroleum mixture. A modified matrix generation procedure is proposed to obtain molecular composition information, using the bulk properties and carbon number distribution of a petroleum fraction,
in the absence of detailed composition analysis of petroleum fractions. The molecular structure-property correlations developed by Zhang (1999) do not encompass the broad range of compound classes existing in heavier petroleum fractions. Therefore, a methodology using group contribution method of Joback (1987) has been developed for estimation of individual component properties of not only hydrocarbon compounds but also hydrocarbons with hetero-atoms, e.g. sulphur containing compounds. These properties of individual components are employed in estimation of bulk physical properties of petroleum streams using mixing rules and correlations available in the literature. The methodology developed for estimation of physical properties of petroleum fractions is applicable to middle distillate and heavy petroleum fractions, as the physical properties of components of a broader range of compound classes is possible using group contribution methods.

7.1.2 Molecular modelling of separation and heat recovery system

The application of molecular type and homologous series matrix representation was previously limited to modelling of reaction systems only. The methodology developed for prediction of detailed production distribution for distillation processes is a novel delumping procedure using short-cut distillation model. This methodology may help retain detailed molecular information of composition of diesel hydrotreating process streams. The delumping methodology developed for predicting detailed product distribution for distillation processes extends the premise of molecular modelling to separation processes such as single stage flash separation and distillation.

The methodology developed for estimation of individual component properties using group contribution methods is employed in estimation of not only the bulk physical properties but also thermal properties of process streams, such as the heat capacities. The gap between molecular level composition information in terms of individual molecular structures and bulk thermal properties of process streams is addressed to facilitate targeting techniques, i.e. preliminary estimation of capital
and operating cost of heat recovery system, as well as heat exchanger network design.

7.1.3 Integrated diesel hydrotreating process design

A novel approach for integrated design is developed for diesel hydrotreating process using molecular type and homologous series matrix representation of middle distillate fractions. The framework developed for design of diesel hydrotreating process employs simulated annealing algorithm for optimisation. This framework is the first integrated design approach using detailed characterisation and molecular modelling of refinery hydrotreating processes. The design approach is optimisation based using simulated annealing algorithm for minimising the total annualised cost of the overall process, comprising the diesel hydrotreater, distillation column and heat recovery system. The energy and capital cost of the heat recovery system is estimated using targeting techniques. This integrated framework can not only provide overall process designs with lower total annualised cost compared to design obtained using sequential approach to process design, but can also help analyse the effect of changing operating conditions of individual units, such as the diesel hydrotreater, and the distillation column, on the overall process performance.

7.1.4 Multi-period heat exchanger network design

Simulated annealing algorithm has been implemented for the first time for the design of heat exchanger networks for multiple periods of operation. The heat exchanger networks designed using the approach developed in this work satisfy the heating and cooling requirements of a given system with minimum total annualised cost. The existing simultaneous design approaches (Aaltola, 2002; Verheyen and Zhang, 2006) employ deterministic optimisation methods using simplified superstructure, i.e. neglect some topological options. The new methodology developed for the design of multi-period heat exchanger networks addresses the limitation of existing simultaneous design approaches. The proposed methodology is independent of any explicit superstructures and provides better results in terms of total annualised cost.
7.1.5 Multi-period hydrogen management

The increasing hydrogen consumption with additional hydrotreating capacities of refineries requires careful management of hydrogen demand and supply in refinery hydrogen networks. The existing techniques for hydrogen management (Alves, 1999; Liu, 2002) assume constant operating conditions of refinery processes and treat gas streams as binary mixtures of hydrogen and methane. The multi-period operation, i.e. changing operating conditions, of diesel hydrotreating process and other hydrogen consumers may result in sub-optimal performance of a hydrogen network designed using the existing techniques for hydrogen management. A novel approach for design of hydrogen networks for multi-period operation is presented in this work. The hydrogen networks designed using the new methodology can remain operable under multiple periods of operation having minimum total annualised cost.

The methods developed in this work enable the design of hydrotreating processes with lower overall costs compared to conventional approach to process design, as illustrated by the case study on integrated design of diesel hydrotreating process. The approach developed for design of heat exchanger networks and hydrogen networks for multi-period operation accounts for the changing operating conditions of refinery processes. This research work may be refined and applied to achieve the objective of refinery design and optimisation for multi-period operation. A summary of the methods developed in this work for integrated and multi-period design of diesel hydrotreating process along with the contribution of previous researchers is shown in Table 7.1.
<table>
<thead>
<tr>
<th>Previous research work</th>
<th>Contribution of this research work</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Characterisation and estimation of properties of petroleum fractions</strong></td>
<td></td>
</tr>
<tr>
<td>• Peng (1999) developed molecular type and homologous series matrix representation of petroleum fractions</td>
<td>• Estimation of physical properties of individual components, for a broader range of compounds including hydrocarbons with heteroatoms, using group contribution method of Joback (1987)</td>
</tr>
<tr>
<td>• Zhang (1999) developed molecular structure-property correlations for estimation of normal boiling temperature and density of hydrocarbon compounds</td>
<td></td>
</tr>
<tr>
<td>• Zhang (1999) developed an interpolation based method for generation of MTHS matrices</td>
<td>• Modified matrix generation approach using measured bulk physical properties and carbon number distribution of petroleum fractions</td>
</tr>
<tr>
<td>• Saine Aye (2003) developed a matrix generation approach using measured bulk physical properties of petroleum fractions</td>
<td></td>
</tr>
<tr>
<td><strong>Modelling of separation and heat recovery system using molecular type and homologous series matrix representation of petroleum fractions</strong></td>
<td></td>
</tr>
<tr>
<td>• Peng (1999) developed a pseudo-component generation method, using mixing rules, to lump matrix entries and allow use of commercial simulation software for modelling distillation</td>
<td>• Pseudo-component generation method developed, using cut-points and physical property correlations available in literature, to lump matrix entries</td>
</tr>
<tr>
<td>• Peng (1999) developed a delumping approach assuming constant distribution of components of a lump</td>
<td>• Flash calculation model developed using the method proposed by Sandler (1989)</td>
</tr>
</tbody>
</table>
| Overall design of diesel hydrotreating processes | • Peng (1999) developed a short-cut approach for predicting products of a distillation column of fixed configuration assuming constant recovery ratios of components | • Fenske-Underwood-Gilliland method employed for short-cut modelling of distillation  
• Delumping procedure of Leibovici et al., (1996) for single-stage flash separation  
• Delumping methodology developed for prediction of detailed product distribution for distillation  
• Estimation of bulk thermal properties of process streams, using mixing rules with group contribution method of Joback (1987) |
|---|---|---|
| Sun (2004) developed a molecular model of diesel hydrotreater | | • Modifications proposed for improved prediction of conversion of reaction from molecular model of diesel hydrotreater  
• Integrated approach developed for design of diesel hydrotreating process |
| Design of heat exchanger networks | • Single-period design of heat exchanger networks (See Section 5.2)  
• Multi-period design of heat exchanger networks (See Section 5.3) using deterministic optimisation methods | • Multi-period design of heat exchanger networks using simulated annealing algorithm for optimisation |
<table>
<thead>
<tr>
<th>Hydrogen management</th>
<th>Hydrogen pinch analysis developed by Alves (1999) to estimate minimum hydrogen utility, assuming constant operating conditions and ignoring pressure differences between sources and sinks, of a given hydrogen network</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Automated design approach developed by Liu (2002) for design of hydrogen networks assuming constant operating conditions of refinery processes</td>
</tr>
<tr>
<td></td>
<td>Multi-period approach developed for design of hydrogen networks to account for changing operating conditions of refinery processes</td>
</tr>
</tbody>
</table>

Table 7.1 Summary of research work in the area of Integrated and multi-period design of diesel hydrotreating processes
7.2 Future work

This research work has addressed some limitations and key issues in the area of molecular modelling of hydrotreating processes using molecular type and homologous series matrix representation of petroleum fractions. A novel framework for integrated and multi-period design of hydrotreating processes is presented in this work. It is recommended that future work is carried out to increase the accuracy and applicability of the approaches developed.

1. The molecular type and homologous series matrix representation of petroleum fractions employed in this work neglects the contribution of different isomers, for a given molecular size, on the bulk properties of mixtures. This lumping at isomer level is a result of the limitation of current analytical techniques. However, methods to account for distribution of isomers and their effect on the bulk properties of petroleum fractions could improve the accuracy of estimation of stream properties.

2. The molecular model of the diesel hydrotreater may be improved by incorporating quantitative structure-reactivity correlations for reaction rate parameters of sulphur compounds, as illustrated in section 4.3. The key assumptions of pseudo-homogeneous reactor model are complete wetting of catalyst particles, ignoring the resistance to gas-liquid mass transfer, and assuming no radial variation of concentrations and temperature. Modelling techniques to address for these simplifications may improve the accuracy of predictions.

3. The approach developed in this work for design of heat exchanger networks for multi-period operation assumes constant thermal properties similar to the conventional heat exchanger network design approaches. The dependence of thermal properties of process streams has been taken into account for the single-period design of heat exchanger networks by Chen (2008). Similarly the multi-period approach for design of heat exchanger...
networks could be improved by accounting for the temperature dependence of thermal properties of process streams.

4. The design of hydrogen networks for multi-period operation is a mixed integer non-linear programming problem solved using deterministic optimisation methods in this work. Stochastic optimisation methods such as the simulated annealing algorithm could be implemented for multi-period hydrogen management with a higher probability of finding a solution close to the global optimum. The impact of impurities on multi-period hydrogen network design could be analysed. An integrated framework to analyse the trade-offs between hydroprocessing units and hydrogen network could be developed to facilitate improving the economic performance of hydrocracking and hydrotreating processes.
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APPENDIX A

DIESEL HYDROTREATER DATA

This appendix provides the information regarding the reaction system of diesel hydrotreating process employed in the case study on integrated diesel hydrotreating process design in Chapter 4 and the case study on multi-period hydrogen management in Chapter 6. Both the case studies are an extension of the same base case refinery configuration. This appendix is reproduced from the work of Sun (2004), i.e. the source of base case of diesel hydrotreater and refinery hydrogen network configuration.

<table>
<thead>
<tr>
<th>Reaction Family</th>
<th>Ea (kJ/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ↔ N</td>
<td>54.0</td>
</tr>
<tr>
<td>AA ↔ AN</td>
<td>105.0</td>
</tr>
<tr>
<td>AN ↔ NN</td>
<td>106.0</td>
</tr>
<tr>
<td>AAA ↔ AAN</td>
<td>115.0</td>
</tr>
<tr>
<td>AAN ↔ ANN</td>
<td>115.0</td>
</tr>
<tr>
<td>ANN ↔ NNN</td>
<td>115.0</td>
</tr>
</tbody>
</table>

Table A.2 Values for kinetics parameters of aromatics hydrogenation (Equation 4.9, Stanislaus and Cooper, 1994)
### Table A.3 Values for kinetics parameters of aromatics hydrogenation (Equation 4.9, Korre et al. 1994, 1995)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate parameters (mol kg\text{cat}^{-1} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (C_8, A) \leftrightarrow (C_8, N) )</td>
<td>0.00947</td>
</tr>
<tr>
<td>( (C_9, A) \leftrightarrow (C_9, N) )</td>
<td>0.10474</td>
</tr>
<tr>
<td>( (C_{10}, A) \leftrightarrow (C_{10}, N) )</td>
<td>0.011484</td>
</tr>
<tr>
<td>( (C_{11}, A) \leftrightarrow (C_{11}, N) )</td>
<td>0.012646</td>
</tr>
<tr>
<td>( (C_{12}, A) \leftrightarrow (C_{12}, N) )</td>
<td>0.013926</td>
</tr>
<tr>
<td>( (C_{13}, A) \leftrightarrow (C_{13}, N) )</td>
<td>0.015335</td>
</tr>
<tr>
<td>( (C_{14}, A) \leftrightarrow (C_{14}, N) )</td>
<td>0.016887</td>
</tr>
<tr>
<td>( (C_{10}, AA) \leftrightarrow (C_{10}, AN) )</td>
<td>0.394</td>
</tr>
<tr>
<td>( (C_{10}, AN) \leftrightarrow (C_{10}, NN) )</td>
<td>0.0269</td>
</tr>
<tr>
<td>( (C_{14}, AAA) \leftrightarrow (C_{14}, AAN) )</td>
<td>0.155</td>
</tr>
<tr>
<td>( (C_{14}, AAN) \leftrightarrow (C_{14}, ANN) )</td>
<td>0.345</td>
</tr>
<tr>
<td>( (C_{14}, ANN) \leftrightarrow (C_{14}, NNN) )</td>
<td>0.00875</td>
</tr>
</tbody>
</table>

### Table A.4 Adsorption constants of some representative elements of molecular type and homologous series matrix (Equation 4.9, Korre et al. 1994, 1995)

<table>
<thead>
<tr>
<th>Matrix Elements</th>
<th>Adsorption constant (Lmol^{-1})</th>
<th>Matrix Elements</th>
<th>Adsorption constant (Lmol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (C_{14}, P) )</td>
<td>10.9</td>
<td>( (C_{11}, N) )</td>
<td>8.2</td>
</tr>
<tr>
<td>( (C_8, A) )</td>
<td>6.6</td>
<td>( (C_{12}, N) )</td>
<td>9.0</td>
</tr>
<tr>
<td>( (C_8, A) )</td>
<td>7.3</td>
<td>( (C_{13}, N) )</td>
<td>9.9</td>
</tr>
<tr>
<td>( (C_{10}, A) )</td>
<td>8.0</td>
<td>( (C_{14}, N) )</td>
<td>10.9</td>
</tr>
<tr>
<td>( (C_{11}, A) )</td>
<td>8.8</td>
<td>( (C_{10}, AA) )</td>
<td>10.5</td>
</tr>
<tr>
<td>( (C_{12}, A) )</td>
<td>9.7</td>
<td>( (C_{10}, AN) )</td>
<td>8.0</td>
</tr>
<tr>
<td>( (C_{13}, A) )</td>
<td>10.7</td>
<td>( (C_{10}, NN) )</td>
<td>7.4</td>
</tr>
<tr>
<td>( (C_{14}, A) )</td>
<td>11.8</td>
<td>( (C_{14}, AAA) )</td>
<td>20.1</td>
</tr>
<tr>
<td>( (C_8, N) )</td>
<td>6.1</td>
<td>( (C_{14}, AAN) )</td>
<td>15.4</td>
</tr>
<tr>
<td>( (C_8, N) )</td>
<td>6.7</td>
<td>( (C_{14}, ANN) )</td>
<td>11.8</td>
</tr>
<tr>
<td>( (C_{10}, N) )</td>
<td>7.4</td>
<td>( (C_{14}, NNN) )</td>
<td>10.9</td>
</tr>
</tbody>
</table>

### Table A.5 Values for kinetics parameters of hydrodenitrogenation reactions (Equation 4.28, Satterfield and Yang, 1984; Yoshiki Sato, 1997)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \text{Ea (kJ/gmol)} )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (C_6, NIII) \leftrightarrow (C_6, A) + (C_0, NI) )</td>
<td>60.99</td>
<td>3.74</td>
</tr>
<tr>
<td>( (C_9, NI) \leftrightarrow (C_9, A) + (C_0, NI) )</td>
<td>125.87</td>
<td>0.687</td>
</tr>
<tr>
<td>( (C_8, NI) \leftrightarrow (C_8, NIII) )</td>
<td>153.34</td>
<td>0.0</td>
</tr>
<tr>
<td>( (C_8, NI) \leftrightarrow (C_8, A) + (C_0, NI) )</td>
<td>153.55</td>
<td>1.47</td>
</tr>
<tr>
<td>( (C_9, NI) \leftrightarrow (C_9, NI) )</td>
<td>106.72</td>
<td>0.0</td>
</tr>
<tr>
<td>( (C_{12}, NII) \leftrightarrow (C_{12}, A) + (C_0, NI) )</td>
<td>153.5</td>
<td>3.39</td>
</tr>
<tr>
<td>Nitrogen Element</td>
<td>$n_i$</td>
<td>Adsorption constant $K_{n_i}$</td>
</tr>
<tr>
<td>------------------</td>
<td>------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>(C₉, NI)</td>
<td>0.25</td>
<td>661.2</td>
</tr>
<tr>
<td>(C₈, NII)</td>
<td>0.5</td>
<td>1834.9</td>
</tr>
<tr>
<td>(C₁₂, NII)</td>
<td>0.5</td>
<td>328.3</td>
</tr>
</tbody>
</table>

Table A.6 Adsorption constants for the nitrogen compounds (Equation 4.28, Georgina et al. 2001)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c$ (kJ/mol)</td>
<td>210</td>
</tr>
<tr>
<td>$E_t$ (kJ/mol)</td>
<td>15</td>
</tr>
<tr>
<td>$K_{ad}$ (m$^3$/mol)</td>
<td>20000</td>
</tr>
<tr>
<td>$k_t$ (kg/(kmol s))</td>
<td>0.05</td>
</tr>
<tr>
<td>$k_c$ (kg/(kg s))</td>
<td>$3*10^{-7}$</td>
</tr>
</tbody>
</table>


Table A.7 Model parameters of deactivation model (Equation 4.32 - 4.37, De Jong, 1994a, b)
<table>
<thead>
<tr>
<th>Feed</th>
<th>AGO</th>
<th>LCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>830</td>
<td>934</td>
</tr>
<tr>
<td>Distillation (D86)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial boiling point</td>
<td>155</td>
<td>210</td>
</tr>
<tr>
<td>0.1</td>
<td>230</td>
<td>260</td>
</tr>
<tr>
<td>0.3</td>
<td>260</td>
<td>285</td>
</tr>
<tr>
<td>0.5</td>
<td>275</td>
<td>300</td>
</tr>
<tr>
<td>0.7</td>
<td>300</td>
<td>315</td>
</tr>
<tr>
<td>0.9</td>
<td>325</td>
<td>330</td>
</tr>
<tr>
<td>Final boiling point</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Total Sulphur (wt %)</td>
<td>0.3</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Table A.8 Properties of atmospheric gas oil (AGO) and light cycle oil (LCO) for diesel hydrotreating process employed in the case studies (Sun, 2004)

<table>
<thead>
<tr>
<th>Catalyst volume (m³)</th>
<th>374</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst weight (kg)</td>
<td>330000</td>
</tr>
<tr>
<td>Reactor inlet Press. (Bar)</td>
<td>34</td>
</tr>
<tr>
<td>Purge Rate (Nm³/hr)</td>
<td>6400</td>
</tr>
<tr>
<td>H₂ Composition (volume %):</td>
<td>81.6</td>
</tr>
<tr>
<td>C1</td>
<td>3.5</td>
</tr>
<tr>
<td>C2</td>
<td>3.1</td>
</tr>
<tr>
<td>C3</td>
<td>4.1</td>
</tr>
<tr>
<td>C4</td>
<td>4.0</td>
</tr>
<tr>
<td>C5</td>
<td>2.8</td>
</tr>
<tr>
<td>&gt;C5</td>
<td>0.74</td>
</tr>
<tr>
<td>H2S</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table A.9 Operating conditions of diesel hydrotreater (Sun, 2004)

<table>
<thead>
<tr>
<th>Atmospheric gas oil</th>
<th>131 $/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light cycle oil</td>
<td>121 $/m³</td>
</tr>
<tr>
<td>Diesel</td>
<td>141.03 $/m³</td>
</tr>
<tr>
<td>H2 price</td>
<td>0.002 $/scf</td>
</tr>
<tr>
<td>Catalyst cost</td>
<td>9679 $/day</td>
</tr>
<tr>
<td>Cost of catalyst replacement</td>
<td>1,500,000 $</td>
</tr>
</tbody>
</table>

Table A.10 Economic data of diesel hydrotreater used in the integrated diesel hydrotreating process design case study (Sun, 2004)
<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>N</th>
<th>NN</th>
<th>NNN</th>
<th>A</th>
<th>AN</th>
<th>ANN</th>
<th>AA</th>
<th>ANA</th>
<th>AAA</th>
<th>NI</th>
<th>NII</th>
<th>SI</th>
<th>SII</th>
<th>SIII</th>
<th>SIV</th>
<th>SV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 8</td>
<td>3.246</td>
<td>0.017</td>
<td>0</td>
<td>0</td>
<td>0.100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.001</td>
<td>0</td>
<td>0.022</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 9</td>
<td>6.906</td>
<td>0.045</td>
<td>0</td>
<td>0</td>
<td>0.237</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.007</td>
<td>0</td>
<td>0.037</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 10</td>
<td>7.700</td>
<td>0.059</td>
<td>0.108</td>
<td>0</td>
<td>0.847</td>
<td>0.034</td>
<td>0</td>
<td>0.301</td>
<td>0</td>
<td>0</td>
<td>0.019</td>
<td>0</td>
<td>0.062</td>
<td>0.066</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 11</td>
<td>5.956</td>
<td>0.232</td>
<td>0.109</td>
<td>0</td>
<td>1.889</td>
<td>0.034</td>
<td>0</td>
<td>2.598</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.004</td>
<td>0.037</td>
<td>0.126</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>C 12</td>
<td>3.316</td>
<td>0.595</td>
<td>1.086</td>
<td>0</td>
<td>2.602</td>
<td>0.341</td>
<td>0</td>
<td>3.744</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.015</td>
<td>0.073</td>
<td>0.178</td>
<td>0.060</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 13</td>
<td>1.665</td>
<td>1.566</td>
<td>1.41</td>
<td>0</td>
<td>2.430</td>
<td>0.854</td>
<td>0</td>
<td>2.392</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.018</td>
<td>0.069</td>
<td>0.099</td>
<td>0.146</td>
<td>0.001</td>
<td>0</td>
</tr>
<tr>
<td>C 14</td>
<td>0.632</td>
<td>3.307</td>
<td>7.168</td>
<td>0</td>
<td>1.662</td>
<td>1.231</td>
<td>0.369</td>
<td>0.073</td>
<td>0.621</td>
<td>0.760</td>
<td>0</td>
<td>0.023</td>
<td>0.052</td>
<td>0.108</td>
<td>0.228</td>
<td>0.002</td>
<td>0.041</td>
</tr>
<tr>
<td>C 15</td>
<td>0.264</td>
<td>7.987</td>
<td>2.063</td>
<td>0.152</td>
<td>1.831</td>
<td>0.351</td>
<td>1.107</td>
<td>0</td>
<td>1.242</td>
<td>0</td>
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<td>0</td>
<td>0.051</td>
<td>0.048</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 16</td>
<td>0.068</td>
<td>1.810</td>
<td>0.977</td>
<td>6.725</td>
<td>1.065</td>
<td>0.103</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0.058</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 17</td>
<td>0.881</td>
<td>1.115</td>
<td>0.326</td>
<td>0.327</td>
<td>0.861</td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.056</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C 18</td>
<td>0.100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A.11 MTHS matrix of atmospheric gas oil stream of diesel hydrotreater feedstock (wt %) Sun (2004)
<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>N</th>
<th>NN</th>
<th>NNN</th>
<th>A</th>
<th>AN</th>
<th>ANN</th>
<th>AA</th>
<th>ANA</th>
<th>AAA</th>
<th>NI</th>
<th>NII</th>
<th>SI</th>
<th>SII</th>
<th>SIII</th>
<th>SIV</th>
<th>SV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>11</td>
<td>2.068</td>
<td>0.364</td>
<td>0.041</td>
<td>0</td>
<td>0.139</td>
<td>0.031</td>
<td>0</td>
<td>0.599</td>
<td>0</td>
<td>0</td>
<td>0.001</td>
<td>0.009</td>
<td>0.184</td>
<td>1.630</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>12</td>
<td>3.727</td>
<td>1.323</td>
<td>0.042</td>
<td>0</td>
<td>0.063</td>
<td>0.032</td>
<td>0</td>
<td>2.512</td>
<td>0</td>
<td>0</td>
<td>0.003</td>
<td>0.030</td>
<td>0.364</td>
<td>2.492</td>
<td>0.203</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>13</td>
<td>4.054</td>
<td>1.640</td>
<td>0.091</td>
<td>0</td>
<td>0.269</td>
<td>0.095</td>
<td>0</td>
<td>1.991</td>
<td>0</td>
<td>0</td>
<td>0.013</td>
<td>0.037</td>
<td>0.341</td>
<td>1.487</td>
<td>0.423</td>
<td>0.282</td>
</tr>
<tr>
<td>C</td>
<td>14</td>
<td>2.629</td>
<td>1.624</td>
<td>0.417</td>
<td>0</td>
<td>0.206</td>
<td>0.322</td>
<td>0.056</td>
<td>2.708</td>
<td>1.680</td>
<td>0.102</td>
<td>0.038</td>
<td>0.046</td>
<td>0.254</td>
<td>1.735</td>
<td>0.570</td>
<td>0.380</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>1.261</td>
<td>1.219</td>
<td>0.559</td>
<td>0.107</td>
<td>0.091</td>
<td>0.780</td>
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<td>0.561</td>
<td>4.586</td>
<td>0</td>
<td>4.914</td>
<td>0</td>
<td>0</td>
<td>0.185</td>
<td>0</td>
<td>0.362</td>
<td>0.241</td>
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<tr>
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<td>0.244</td>
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<td>0.445</td>
<td>1.361</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

Table A.12 MTHS matrix of light cycle oil stream of diesel hydrotreater feedstock (wt %) Sun (2004)
APPENDIX B

CAPITAL AND OPERATING COST DATA FOR DISTILLATION COLUMN AND HEAT EXCHANGERS

This appendix provides the cost correlations and economic data used for estimation of capital and energy cost of distillation column for integrated diesel hydrotreating process design and multi-period heat exchanger network design.

B.1 Column capital cost

The capital cost of the distillation column is calculated based on the cost of the column shell and the cost of column trays. The cost correlations have been taken from Douglas (1988).

The cost of column shell is calculated using the following equation:

\[
Column_{shell} \text{Cost (US$)} = \left( \frac{M \& S. Index}{280} \right) \times \left( 101.9 (D_{Column})^{0.066} (H_{Column})^{0.802} (2.18 + F_c) \right)
\]

(B.1)

\[F_c = F_m \cdot F_p\]

(B.2)

Where \(M&\&S. Index\) represents the Marshall and Swift cost index,

\(D_{Column}\) is the diameter of the column in ft,

\(H_{Column}\) is the height of the column in ft,

\(F_c\) is the cost correction factor,

\(F_m\) is the correction factor for material,

\(F_p\) is the correction factor for pressure.

The cost of column trays is estimated using the following correlation:
Column\textsubscript{tray} Cost (US$) = \left( \frac{M & S. Index}{280} \right)^{1.55} H_{\text{trays}} F_c \quad (B.3)

\[ F_c = F_s + F_t + F_m \quad (B.4) \]

Where $H_{\text{trays}}$ is the height from top to the bottom tray in ft,

$F_s$ is the correction factor for tray spacing,

$F_t$ is the correction factor for tray type.

**B.1.1 Calculation of column height**

The height of the distillation column is calculated based on the number of trays and the tray spacing:

\[ H_{\text{column}} = (N_{\text{real}} - 1) \cdot h_{\text{ray}} + h_{\text{top}} + h_{\text{bottom}} \quad (B.5) \]

Where $N_{\text{real}}$ is the number of real trays.

The tray spacing, top and bottom spacing used are:

$h_{\text{ray}} = 0.46$ m

$h_{\text{top}} = h_{\text{bottom}} = 2.0$ m.

The number of real stages is calculated based on the theoretical number of trays and tray efficiency:

\[ N_{\text{real}} = \frac{N_{\text{theoretical}}}{\text{efficiency}_{\text{tray}}} \quad (B.6) \]

The tray efficiency is calculated using the following correlation (Douglas, 1988):

\[ \text{efficiency}_{\text{tray}} = 10^{1.6975 - 0.252 \log(\mu \alpha)} \quad (B.7) \]

Where $\mu$ is the viscosity of feed in cp, and $\alpha$ is the average relative volatility between the top and bottom section.

**B.1.2 Calculation of column diameter**
The diameter of the distillation column is calculated based on the vapour flow and the vapour velocity in the column:

\[
D_{\text{column}} = \frac{4 * V}{\pi \cdot v_v \cdot (1 - KXS)}
\]  

(B.8)

Where \( V \) is the vapour flow, \( v_v \) is the vapour velocity, and \( KXS \) is the area of down comer as a fraction of the cross sectional area of the column (usually 12 %).

The vapour velocity is calculated from the maximum allowable vapour velocity calculated using the following correlation (Sounder and Brown, 1934):

\[
v_{v,\text{Max}} = K_v \cdot \sqrt{\frac{\rho_L - \rho_v}{\rho_v}}
\]  

(B.9)

Where \( K_v \) is the empirical constant.

\( K_v = 0.243 \) for the tray spacing chosen. The vapour velocity is assumed to be 70 % of the maximum vapour velocity (Triantafyllou, 1991). The diameter of the column is calculated for the top and bottom section and the maximum value is used in cost estimation.

**B.2 Heat exchanger cost data**

The capital cost of heat exchangers are calculated using the following equation (Verheyen and Zhang, 2006):

\[
Hx.\text{Cost} = C_{\text{fixed}} + C_{\text{Area}} \cdot \text{Area}^B
\]  

(B.10)

Where \( C_{\text{fixed}} \) is the fixed cost of a heat exchanger = 8333.3 €. 

\( C_{\text{Area}} \) is the area cost coefficient for a heat exchanger = 641.7 €/m².

\( B \) is the area exponent = 1.
Economic data for energy costs are also taken from Verheyen and Zhang (2006) and are as follows:

$C_{cu}$ is the cost of cold utility = 1.3 €/kWy.

$C_{hu}$ is the cost of hot utility = 115.2 €/kWy.
APPENDIX C
TABULAR INFORMATION ON DESIGNS OBTAINED IN CASE STUDY ON MULTI-PERIOD HYDROGEN MANAGEMENT

This appendix presents information about the flow rates of gas streams between all the sources and sinks of the hydrogen networks designed in the case study on multi-period hydrogen management.

C.1 Hydrogen network designed using automated design approach of Liu (2002)

The flow rates (t/h) of gas streams between all the sources and sinks of hydrogen network designed using the automated design approach of Liu (2002) for the case study presented in Section 6.4 are shown in Table C.1.

<table>
<thead>
<tr>
<th>Sources</th>
<th>NHT</th>
<th>RHT</th>
<th>HC</th>
<th>DHT</th>
<th>ISOM</th>
<th>CPROC</th>
<th>CCR fuel</th>
<th>OFFGAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCR</td>
<td>3.108</td>
<td>5.081</td>
<td>2.825</td>
<td>1.131</td>
<td>1.333</td>
<td>2.535</td>
<td>0.446</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
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</tr>
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<td></td>
<td></td>
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</tr>
<tr>
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<td></td>
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<td></td>
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<td></td>
<td>4.579</td>
</tr>
</tbody>
</table>

Table C.1 Flow rates (t/h) of gas streams of hydrogen network designed using automated design approach of Liu (2002)
C.2 Hydrogen network designed using the methodology developed in this work for multi-period hydrogen management

The flow rates (t/h) of gas streams between all the sources and sinks of hydrogen network designed using the methodology, developed in this work, for multi-period hydrogen management are presented for each operating period.

C.2.1 Multi-period design of hydrogen network

This section presents the flow rates (t/h) of gas streams between all the sources and sinks of the hydrogen network designed using the proposed methodology without any hydrogen recovered using purification processes.

<table>
<thead>
<tr>
<th>Sources</th>
<th>NHT</th>
<th>RHT</th>
<th>HC</th>
<th>DHT</th>
<th>ISOM</th>
<th>CPROC</th>
<th>CCR fuel</th>
<th>OFFGAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCR</td>
<td>3.042</td>
<td>5.026</td>
<td>3.251</td>
<td>1.018</td>
<td>1.682</td>
<td>2.535</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NHT</td>
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<td>4.91</td>
<td>3.097</td>
<td>0.012</td>
<td>18.763</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
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<td>0.01</td>
<td>4.186</td>
<td>0.383</td>
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<tr>
<td>ISOM</td>
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<td>4.186</td>
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Table C.2 Flow rates (t/h) of gas streams of hydrogen network, designed using the proposed methodology, in first operating period
<table>
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<tr>
<th>Sources</th>
<th>Sinks</th>
<th>NHT</th>
<th>RHT</th>
<th>HC</th>
<th>DHT</th>
<th>ISOM</th>
<th>CPROC</th>
<th>CCR fuel</th>
<th>OFFGAS</th>
</tr>
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<td>CCR</td>
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<td>1.682</td>
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</tr>
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<td></td>
<td>0.063</td>
<td>0.571</td>
</tr>
<tr>
<td>RHT</td>
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<td>4.91</td>
<td>0.035</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC</td>
<td>0.066</td>
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<td>3.097</td>
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<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISOM</td>
<td></td>
<td>0.01</td>
<td>4.186</td>
<td></td>
<td></td>
<td></td>
<td>0.383</td>
<td></td>
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</tr>
</tbody>
</table>

Table C.3 Flow rates (t/h) of gas streams of hydrogen network, designed using the proposed methodology, in second operating period

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<th>Sinks</th>
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<th>RHT</th>
<th>HC</th>
<th>DHT</th>
<th>ISOM</th>
<th>CPROC</th>
<th>CCR fuel</th>
<th>OFFGAS</th>
</tr>
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<tbody>
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<td>2.535</td>
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<td>0.01</td>
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<tr>
<td>RHT</td>
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<td></td>
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Table C.4 Flow rates (t/h) of gas streams of hydrogen network, designed using the proposed methodology, in third operating period

**C.2.1 Multi-period design of hydrogen network with purification**

This section presents the flow rates (t/h) of gas streams between all the sources and sinks of the hydrogen network designed using the proposed methodology with hydrogen recovered using a membrane purification unit.
Table C.5 Flow rates (t/h) of gas streams of hydrogen network, with membrane purification, in first operating period

<table>
<thead>
<tr>
<th>Sources</th>
<th>NHT</th>
<th>RHT</th>
<th>HC</th>
<th>DHT</th>
<th>ISOM</th>
<th>CPROC</th>
<th>CCR fuel</th>
<th>OFFGAS</th>
<th>MemF</th>
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<tbody>
<tr>
<td>CCR</td>
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<td>4.385</td>
<td>0.085</td>
<td>0.338</td>
<td>5.654</td>
<td>0.474</td>
<td>0.446</td>
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<tr>
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</tr>
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<td>ISOM</td>
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<td>0.01</td>
<td>2.05</td>
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<td></td>
<td></td>
<td></td>
<td>0.777</td>
</tr>
<tr>
<td>MemP</td>
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<td>0.022</td>
<td>0.01</td>
<td>0.064</td>
<td>0.011</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Table C.5 Flow rates (t/h) of gas streams of hydrogen network, with membrane purification, in first operating period*
<table>
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<tr>
<th>Sources</th>
<th>NHT</th>
<th>RHT</th>
<th>HC</th>
<th>DHT</th>
<th>ISOM</th>
<th>CPROC</th>
<th>CCR fuel</th>
<th>OFFGAS</th>
<th>MemF</th>
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<tbody>
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<td>5.654</td>
<td>0.474</td>
<td>0.446</td>
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<td>NHT</td>
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</tr>
<tr>
<td>HC</td>
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<td></td>
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<tr>
<td>DHT</td>
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</tr>
<tr>
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<td>0.777</td>
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</tr>
<tr>
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<td>0.027</td>
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</tbody>
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Table C.6 Flow rates (t/h) of gas streams of hydrogen network, with membrane purification, in second operating period
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<th>RHT</th>
<th>HC</th>
<th>DHT</th>
<th>ISOM</th>
<th>CPROC</th>
<th>CCR fuel</th>
<th>OFFGAS</th>
<th>MemF</th>
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<td>0.085</td>
<td>0.338</td>
<td>5.035</td>
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<td>0.446</td>
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</tr>
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<tr>
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<td>1.29</td>
<td>2.571</td>
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<tr>
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Table C.7 Flow rates (t/h) of gas streams of hydrogen network, with membrane purification, in third operating period