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FACULTY OF ENGINEERING AND INFORMATION TECHNOLOGIES
ADVANCED OPERATION AND OPTIMISATION

OF AN

INDUSTRIAL ETHYLENE OXIDE PLANT

By
Shahla Aryana

A dissertation submitted for the degree of

DOCTOR OF PHILOSOPHY

(Chemical Engineering)

At the

University of Sydney

2008
To my love

Mehdi (Babak)

And

My parents
DECLARATIONS

I declare that the entire contents of this thesis are, to the best of my knowledge and belief, original, unless otherwise acknowledged in the text. I have not submitted this material, in whole or part, for another degree at this or any other institution.

Shahla Aryana

March 2008
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SHAHLA ARYANA

The University of Sydney
March 2008
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ADVANCED OPERATION AND OPTIMISATION

OF AN

INDUSTRIAL ETHYLENE OXIDE PLANT

ABSTRACT

Ethylene oxide (EO) is produced by vapour-phase oxidation of ethylene with oxygen, utilizing supported silver catalyst. It is used mainly for the production of ethylene glycol, with major end uses in polyester and antifreeze. EO is one of the major chemicals manufactured in the United States with a production of 5.56 billion pounds in 1992. Based on the world tonnage of ethylene used in its manufacture, EO is the second most important (after polyethylene) ethylene-derived chemical.

The production of EO is a critical process. The EO production process is highly exothermic and an upset in the process could cause thermal runaway. The system, at start of runaway, is unstable leading to catalyst damage or even explosion. Therefore the safety issues for an EO reactor are dominant as industry tries to operate them in an economically advantageous manner.

The work undertaken in this study focuses on advanced modeling and optimisation of an industrial ethylene oxide plant. The final aim of this work is to develop a validated dynamic model of EO plant to allow the optimal operation of the EO plant while maintaining systems integrity, operability and safety.

In this thesis, a one-dimensional heterogeneous dynamic model of the EO reactor has been developed. The partial and total ethylene oxidation as well as the EO oxidation has been considered with emphasis on the inhibiting effect of dichloroethane as an inhibitor. Also a detail heat transfer model has been developed and integrated with the process model. The set of nonlinear kinetic expressions has been coupled with heat and mass conservation equations and variable physical properties along the reactor
length. The catalyst deactivation has been analysed and modelled as a function of time and oil inlet temperature.

The catalyst vendor data has been used to estimate the kinetics constants and the catalyst deactivation parameters. The plant data from Huntsman EO reactor have been used to validate the model. The results have shown satisfactory agreement between the model prediction and the plant data with no fitting data. Thus the model has been validated.

HYSYS software platform has been used to simulate the other units in the EO plant (the EO scrubber, gas-gas heat exchanger and hot oil cooler). The dynamic model predictions for the EO scrubber have been benchmarked against the plant data. The model prediction results have shown the satisfactory agreement with the plant data, thus the model has been considered validated and can be used to represent the real plant.

The EO reactor model has been linked to the EO plant model in HYSYS using CAPE-OPEN environment to create a dynamic hybrid model for simulating the process under variable operating conditions and schedules. The outcome results between the HYSYS and EO reactor model have been compared.

The validated models of the EO reactor and the EO scrubber have been used to conduct a sensitivity analysis to determine the control variables. The EDC level, oil inlet temperature, ethylene and oxygen concentration in feed have been determined as suitable control variables since they had significant effect on the reactor performance.

The sensitivity analysis of the EO plant model has shown that the EO scrubber had a strong effect on the reactor performance. By increasing EO concentration in the recycle gas, the selectivity decreased significantly resulting in loss of desired product and efficiency.

The point optimisations have been carried out for two different scenarios: low product (110 Ton/day EO) and high product (130 Ton EO/day). The results from point optimisation study have shown that the ethylene concentration and the EDC level
acted as active bounds. In high production rate, the oxygen concentration acted as lower active bound in response to a flammability point.

The outcome of point optimisation has been used as initial condition for the dynamic optimisation. In dynamic optimisation study, firstly, the oil inlet temperature has been used as control variable to compensate the catalyst activity losses during 3 years operating time to obtain desire work-rate (127 T/day) according to maximise selectivity. The results has been compared to the vendor data where concluded nevertheless the selectivity could be improved by more than 2%. Furthermore, optimal transition profiles for the oil inlet temperature and the oxygen concentration have been obtained to shift the work-rate from 110 (Ton/day) to 127 (Ton/day) according to maximise the selectivity.

The work presented in this dissertation could be extended further and amalgamated with complementary research topics. The EO plant model could be used to develop a model-based control strategy for optimal operation of the EO plant. In summary, a solid platform for further research has been presented.
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GLOSSARY OF SYMBOLS

a_i
A
a
C_f
C_i
C_P
D_{ax}
D_t
D_O
D_s
d_p
EDC
E_a
e
f_i
F_i
f_l
G
H_i
h
J_h
J
K_i
K_w
L
m
n
N_T
Nu
P_i
Pe
Pr
Q
R_i
R
Re
S_m
S and S_V
R_i
\tau
T
U
void
V

Catalyst deactivation term
area [m^2]
surface area of catalyst sphere per unit volume of bed
gas specific heat
correlation factor
heat capacity [kJ/kmol °C]
axial diffusion [m^2/s]
tube inside diameter [m]
tube outside diameter [m]
reactor shell diameter [m]
particle diameter [m]
1, 2-dichloroethene
Activation Energy [kJ/mol]
catalyst bed voidage
reaction rate [mol O_2/g cat s]
mole flow [kmol/hr]
tube fouling term [m2 °C/kW]
mass gas flow per cross area [kg/m^2]
heat of reaction [kJ/kmol]
heat transfer coefficient
Chilton Colburn j-factor
heat transfer correlation factor
Kinetic Constant [mol/(gcat h bar)].
coductivity of the tube wall [kW/m K]
length [m]
mass [kg]
mole [kmol]
number of tubes
Nusselt’s number
partial pressure of component i [Bar unless noted]
Peclet’s number
Prandtl’s number
mass flow rate per unit cross-sectional area of empty tubes [kmol/m^2 s]
reaction rate [kmol/s]
gas constant [kPa m^3/kmol K]
Reynold’s number
oil flow area near centerline [m^2]
specific surface area [m^2/m^3]
Overall reaction rate [kmol O_2/m^3 s]
time [s]
temperature [°C unless noted]
heat transfer (overall unless stated) [kW/m2 °C]
void fraction
volume [m^3]
\( V_{\text{gas}} \) velocity [m/s]
\( x \) mole fraction
\( Z \) length in tube direction

**Greek letters**

\( \alpha \) heat transfer coefficient [kW/m² °C]
\( \lambda \) thermal conductivity [kW/m °C]
\( \nu \) stoichiometric coefficient
\( \eta \) viscosity [Ns/m²]
\( \rho \) density [kg/m³]
\( \pi \) Pi Number
\( \varepsilon \) error

**Subscripts**

0 inlet condition
1 reaction 1 (\( \text{C}_2\text{H}_4 + 1/2\text{O}_2 \Rightarrow \text{C}_2\text{H}_4\text{O} \))
2 reaction 2 (\( \text{C}_2\text{H}_4 + 3\text{O}_2 \Rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \))
3 reaction 3 (\( \text{C}_2\text{H}_4\text{O} + 5/2\text{O}_2 \Rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \))
amb ambient
Ar argon
oil cooling oil
c cross (e.g. area)
Eth ethylene
EO ethylene oxide
Oxy oxygen
EDC 1, 2-dichloroethene
f fluid
H2O water
I inside tube
N2 Nitrogen
O outside tube
oil cooling oil
R reactor
S shell
T tube or total
wall tube wall
Chapter 1

Introduction

This chapter provides some background information on Ethylene Oxide, its properties and application. The thesis objectives, structure, scopes and contributions are also presented.
1.1 Ethylene Oxide

Ethylene oxide (Oxirane) is the simplest cyclic ether. It is a colorless gas or liquid and has a sweet, etheric odor. Boiling point is 10.5°C and it forms an explosive mixture with air. The structure of an ethylene oxide (EO) molecule is shown in Figure 1-1. The C-C bond is short and the bond angles strained [1].

Figure 1-1- The EO Molecule (the atomic distances are given in angstroms)

EO is very reactive, because its highly strained ring can be opened easily, and it is one of the most versatile chemical intermediates species used in chemical manufacturing and processing. The main reason for this is the EO is both polar, and an organic substance, meaning that products made using EO can dissolve organic materials, such as fats and grease in water.

Occupational Safety and Health Administration (OHSA) classified EO as an occupational carcinogen and as a “de minimis” carcinogen, meaning that minimum amount of the chemical set by OHSA is considered to be carcinogenic. It is listed on EPA’s Toxic Release Inventory (TRI) as a “de minimis” carcinogen, as well. It is also defined as a substance “which may reasonably be anticipated to be a carcinogen” by the U.S. department of health and Human services, National Toxicology Program’s Fifth Annual Report on Carcinogens [2].

Demand for EO and hence its production continues to increase over the years. It was estimated that worldwide demand for EO was about 27 billion pounds (equivalent to over 12 million metric tons) in 1999, with well over one third of that consumed in
North America. The forecast for the year 2001 is 3% growth rate due to tight supply and strong growth in its derivatives, particularly ethylene glycol [3].

EO gas kills bacteria, mold, and fungi, and can therefore be used to sterilize substances that would be damaged by sterilizing techniques such as pasteurization that rely on heat. EO sterilization for the preservation of spices was patented in 1938 by the American chemist Lloyd Hall, and it is still used in that role. Additionally, EO is widely used to sterilize medical supplies such as bandages, sutures, and surgical implements [4].

Most ethylene oxide, however, is further reacted to produce other chemicals. Its most important derivative is ethylene glycol, which is used for the manufacture of polyester and in automotive antifreeze. Other EO derivatives include surfactants, solvents, amines, and poly (ethylene) glycols.

Furthermore, Products derived from EO have many different uses [5]. They include:

- **Mono-ethylene Glycol**: Antifreeze for engines, production of polyethylene terephthalate (polyester fibers, film, and bottles), and heat transfer liquids.
- **Diethylene Glycol**: Polyurethanes, polyesters, softeners (cork, glue, casein, and paper), plasticizers, gas drying, solvents, and de-icing of aircraft and runways.
- **Tri-ethylene Glycol**: Lacquers, solvents, plasticizers, gas drying, and humectants (moisture-retaining agents).
- **Poly (ethylene) Glycols**: Cosmetics, ointments, pharmaceutical preparations, lubricants (finishing of textiles, ceramics), solvents (paints and drugs), and plasticizers (adhesives and printing inks).
- **Ethylene Glycol Ethers**: Brake fluids, detergents, solvents (paints and lacquers), and extractants for SO₂, H₂S, CO₂, and mercaptans from natural gas and refinery gas.
- **Ethanolamine**: Chemicals for textile finishing, cosmetics, soaps, detergents, and natural gas purification.
- Ethoxylation products of fatty alcohols, fatty amines, alkyl phenols, cellulose, and poly(propylene glycol): Detergents and surfactants (non-ionic), biodegradable detergents, emulsifiers, and dispersants.

Figure 1-2 shows the percentage of EO used in each of the main derivative areas for further EO processing. This distribution was for 1978, but is still typical of current market trends.

![Percentage of EO use for derivative production](image)

**Figure 1-2- Percentage of EO use for derivative production [6]**

The largest EO producers worldwide are Union Carbide (which became wholly owned subsidiary of The Dow Chemical Company, 2001), with the annual capacity of 1.9 million metric tons (MMt) and Shell with 1.2 MMt. These are followed by Mitsubishi, Dow, BASF, SABIC, Huntsman, Formosa, Equistar, and Honam Petrochemical. Most EO producers are well integrated into downstream derivative manufacture and hence consume the majority of their EO captively to produce EG and other EO derivatives. Few other companies including BASF, Shell and Equistar sell significant amounts of their EO to other consumer companies such as Bayer, Rhodia etc. Although this merchant market for EO is small and expected to shrink as the producers improve their ability in product integration [4].

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1.2 RESEARCH AIM

The overall work undertaken in this study focuses on advanced modeling and optimisation of an industrial ethylene oxide plant. The main components of this thesis are:

- A comprehensive dynamic model of the EO plant containing the reactor unit, scrubber unit, gas-gas heat-exchanger and hot oil cooler unit that is capable to accurately predict the performance of the EO plant over a wide range of operating conditions. This model is to be computationally efficient to be later used to optimise the EO plant operation. The model is to incorporate both the exothermal control through cooling oil recirculation and reaction rate moderation and selectivity enhancement through chloride addition.

- Dynamic model is to include catalyst deactivation model. The model requires to be benchmarked against an industrial plant data during the catalyst life time.

- Once the rigorous dynamic model of the plant is available it is to be used in multiple fronts:

  ➢ To carry out parametric sensitivity analysis of the reactor and the scrubber to understand and subsequently to prevent run-away conditions.

  ➢ To perform rigorous steady-state optimisation to identify optimal set points for desired production rate with respect to safety and all physical and operating constraints.

  ➢ To carry out dynamic optimisation to identify optimal trajectories of control variables, operating policies and transition planning strategies to achieve optimality while maintaining reactor operability and safety.
1.3 Thesis Organization

The layout of this thesis is as follows.

A review of published works in the area of kinetics, catalyst deactivation, modelling and simulation of EO reactor are detailed in Chapter 2. Also the different process technology of EO production in the world and Australia are discussed followed by a brief introduction on Huntsman Corporation Australia (HCA), who initiated/supported this project, and who are involved with the EO process and production issues. The research direction of this thesis based on the literature review is also detailed.

Chapter 3 details the EO reactor and development of the simulation model that will be used in this work. A detailed treatment of the mathematical modelling of the EO reactor is made with emphasis on the importance of dichloroethane (EDC) addition. The set of nonlinear kinetic rates of the partial and total oxidation of ethylene as well as oxidation of EO were coupled with heat and mass transfer and physical properties along the bed. The mathematical models, comprising coupled sets of non-linear differential and algebraic equations are solved using the gPROMS software package. The verification of the models is also detailed. gPROMS and HYSYS are introduced as softwares that will be used to model the whole plant.

In chapter 4, first the reaction rate parameters and the catalyst deactivation parameters are evaluated using forecast data from the catalyst vendor. Catalyst deactivation is modelled as a nonlinear function of the operating time and the oil inlet temperature. Afterward, the model predictions are benchmarked against the data from HCA’s EO reactor. Finally, a thorough discussion of the validation results is presented.

In chapter 5, the EO scrubber, hot oil cooler and gas-gas heat exchanger are described in details. Theses units are modelled using HYSYS simulation package and the simulation results are benchmarked against the plant data. Also, the development of an ‘open’ simulation environment for simulation and analysis of complex process is presented following a review on world developments in standardising software communications and work to date. This is followed by the detail of dynamic

Shahla Aryana
modelling of the EO reactor in gPROMS and the dynamic simulation of the other three units -including the EO scrubber, hot oil cooler and gas-gas heat exchanger- in HYSYS which could communicate together through CAPE-OPEN environment. Therefore, a complete simulation of the EO plant would then be possible as this environment would take into account the particular nature of the process within the entire facility.

In Chapter 6, a series of sensitivity analyses is performed on selected variables and parameters of the EO reactor model and the EO scrubber model. Also the effect of the scrubber performance on the reactor performance and vice versa, are presented. The variables having significant impact on work-rate and selectivity are investigated and used as control variables in optimisation section. Point optimisation and off-line dynamic optimisation are described in the context of the EO plant. The objective of the optimisation is to maximize the reaction rate up to the "flammability" limit - the fundamental limit of the reactor after which the ethylene burns and the reaction can run away. Using the model, an optimised oil inlet temperature for three years operating time is calculated using the gOPT facility in gPROMS. Also, the optimal profile for transition management of the EO plant is obtained to maximise the reactor selectivity.

Finally, in Chapter 7, the conclusions of this work and recommendations for further research are presented.

1.4 Thesis Contribution

The main contributions in this work are illustrated as follows:

- The mathematical development, without data fitting, of a reactor model, that is suitable for real-time simulations. The kinetic rates include total and partial oxidation of ethylene and oxidation of EO as well as the effect of dichloroethane as an inhibitor on the all reactions.
- The investigation of catalyst deactivation as a nonlinear function of time and oil inlet temperature which was benchmarked against the plant data.

- Investigation of the influence of the operation parameters on the reactor performance. The effects of the EDC level, the reactant concentrations, the pressure of reactor, the coolant temperature and the feed temperature on the reactor performance were studied.

- The dynamic simulation of the EO scrubber, hot oil cooler and gas-gas heat exchanger that were benchmarked against the plant data.

- The development of an ‘open’ simulation environment for simulation and analysis of complex process. A complete dynamic simulation of the EO reactor model and EO scrubber would then be possible as this environment would take into account the particulate nature of the process within the entire facility.

- Investigation of the influence of the EO reactor operation on the EO scrubber operation and vice versa.

- The use of the dynamic model for generating the optimal set point and optimal profiles to achieve the efficient production of ethylene oxide, consistent with process safety.
1.5 Author Publication


* Papers written in maiden name of Ghaffari.
1.6 Bibliography


The relevant literature of ethylene epoxidation kinetics and its mechanism are reviewed and also the review of the inhibiting effect of dichloroethane on the kinetic rates is covered. Thereafter, the effect of catalyst deactivation on the reaction rates and modelling aspects are discussed followed by a review of process technology of EO production, a brief introduction on Huntsman Corporation Australia (HCA), who motivated this project on the EO process and production issues. The gaps in knowledge are identified and future research is defined.
2.1 INTRODUCTION

EO was first prepared in 1859 by Wurtz [1] using potassium hydroxide solution to eliminate hydrochloric acid from ethylene chlorhydrin. The chlorhydrin process developed from Wurtz's discovery and industrial production began in 1914. The importance and commercial production of EO have steadily grown since then.

During World War I, the process based on ethylene chlorhydrin was commercialised by Badische Anilin-und Soda-Fabrik (BASF) in Germany. In 1930's and 40's, today's industrial method started to be investigated. This method consists in the oxidation of ethylene by elementary oxygen to EO [2]. In 1931, S. Lehner [3] investigated the noncatalytic reaction between ethylene and oxygen. He produced EO and Formaldehyde as primary products. However he noted a strong influence of the nature and extent of the surface of the reaction vessel on reaction rates and the amount of different products. So the test was not that noncatalytic after all.

In 1931, Lefort [5] was the first to disclose and patent silver as the catalyst for the reaction published in a patent which still is the leading industrial catalyst. The specific activity of silver as a catalyst in that reaction was first reported by Francon [4], in 1933. Since that time many studies of the reaction have been made, and important industrial process have been developed. Much private research has not been published and many patents have been issued. Nevertheless, the main facts are clear. The catalyst is metallic silver and its surface should be moderated with a very small amount of a halogen or similar electronegative material for optimum selectivity. The support or carrier plays a small role; it should be inert and of rather low surface area.

The selective oxidation, or epoxidation, to produce EO takes place between adsorbed ethylene and adsorbed oxygen. Neglecting the form of adsorbed oxygen (molecular or atomic), the basic reaction stoichiometry can be described as:

\[ C_2H_4 + \frac{1}{2} O_2 \rightarrow C_2H_4O \]  

Equation 2-1
Since EO is such a reactive species, due to its highly strained 3-member ring structure, care must be taken to stop the oxidation after the EO is formed and not to further oxidize the product to carbon dioxide and water. In fact, care must also be taken to prevent the total oxidation, or combustion, of ethylene to carbon dioxide and water.

\[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \] \hspace{2cm} \text{Equation 2-2}

\[ C_2H_4O + \frac{5}{2}O_2 \rightarrow 2CO_2 + 2H_2O \] \hspace{2cm} \text{Equation 2-3}

Suppression of the parasitic reaction, i.e., increased selectivity for ethylene oxide, is achieved either by adding compounds or electronegative elements such as Cl, S, Se, Te and P to the catalyst upon its preparation or by introducing trace amounts of chlorinated organic compounds into the feed gas stream or both [6,7]. The industrial gas-phase promoter employed is usually 1,2-dichloroethane (ethylene dichloride), concentration is normally 1-2 ppm.

The purpose of the Chloride is to partly cover the catalyst and inhibit the undesired ethylene combustion without affecting the desired selective oxidation. Without any chloride present, the selectivity will be as low as 40% but with the optimum coverage, the selectivity reaches up to 80% [8]. The optimum chloride coverage is often said to be 25% of the silver catalytic sites [9]. However at higher coverage both reaction rates will strongly decrease and the yield of EO is also decreased.

### 2.2 Kinetics and Mechanism

In 1946, G. H. Twigg [10] made the first investigation of the mechanism of the silver catalysed oxidation. He concluded that the first step in the reaction was adsorption of oxygen in the forms of atomsEthylene was not at all or very weakly adsorbed and reacted either with atomic oxygen to form EO or with molecular oxygen which leads to combustion.
In 1985, L. Petrov, A. Eliyas and D. Shopov [11] did a review of their own and others work up to that time. They concluded that there were three working hypotheses for ethylene epoxidation which have been put forward up to that time:

$$ZO_2 \rightarrow C_2H_4O$$  
$$ZO \rightarrow CO_2 + H_2O$$  
$$ZO \rightarrow CO_2 + H_2O$$  

Scheme I  
Scheme II  
Scheme III

Which most investigators favour reaction scheme I, according to which adsorbed molecular oxygen produces ethylene oxide, whereas the atomic oxygen is responsible for the complete oxidation reaction [12,13,14,15,16,17]. Other authors argue in favour of scheme II. They consider adsorbed atomic oxygen as a common precursor for both $C_2H_4O$ and for $CO_2 + H_2O$ [18,19,20,21,22,23]. A number of studies suggest a scheme in which the molecular oxygen species reacts with ethylene to give both epoxide and carbon dioxide - scheme III [10,24,25,26,27,28].

A Rideal-Eley mechanism is proposed by the majority of the authors. They conclude that gaseous or weakly adsorbed ethylene interacts with chemisorbed oxygen [10,13,15,16,17,19,21,24,26,27,28,29]. Other authors, contemplating the data on the dependence of reaction rate on $C_2H_4$ partial pressure, which is not linear over the entire range, propose a Langmuir-Hinshelwood type of mechanism, according to which both ethylene and oxygen are chemisorbed and interact in the adsorbed state on the Ag surface [14,18,30,31,32]. There is also spectroscopic evidence suggesting an adsorbed ethylene intermediate [18,23].

The prevailing numbers of studies support a single site mechanism. In the case of a Langmuir-Hinshelwood mechanism, a competitive adsorption of oxygen and ethylene on the same type of active sites is assumed. The nature of the active site is Ag$_2$O, according to [13,24,27,28] or a single silver surface atom [33]. A dual site mechanism is proposed in [9,31,34,35]. According to their concept, oxygen adsorbs on
completely reduced silver atoms, while ethylene adsorption requires a positively charged silver atom.

Twigg concluded in early work [10] that oxygen adsorption is the slowest and therefore the rate-controlling step. However, in more recent studies, an agreement exists between the investigators that the rate-determining step is a surface reaction. This is, in fact, the only point in the mechanism that has found general acceptance.

A parallel-consecutive scheme dominates over the parallel scheme of the reaction, which means that further oxidation of $C_2H_4O$ is considered highly probable by most of the authors.

Kilty’s and Sachtler [67] did their own IR spectroscopic studies and they conclude that the way oxygen is adsorbed decides what product it will form with ethylene. The molecular oxygen will give the desired EO while on the other hand dissociative adsorbed (atomic) oxygen will lead to carbon dioxide and water (note that this is in contrast to Twiggs’s conclusion [10]).

L. Petrov, A. Eliyas and D. Shopov [11] did some experiments to study the kinetics of ethylene oxidation over a supported silver catalyst and to propose a reaction scheme and a kinetic model of the process. The experiments were conducted under steady state conditions in the temperature interval 210 °C -292 °C and atmospheric pressure. They considered only two linearly independent reactions, the partial and total oxidation of ethylene. They carried out the kinetic study by the circulation flow method and proposed the unique mechanism for ethylene oxidation which is represented by the reaction scheme (II).

In this mechanism they concluded that the Steps 2) and 4) are irreversible and Step 4) obviously combines several fast consecutive steps. The mechanism assumed both non-dissociative and dissociative adsorption of oxygen on the silver surface, resulting in adsorbed molecular as well as atomic oxygen.
1. \( Z + O_2 \rightleftharpoons ZO_2 \) \\
2. \( ZO_2 + C_2H_4 \rightarrow ZO + C_2H_4O \) \\
3. \( 2ZO \rightleftharpoons 2Z + O_2 \) \\
4. \( C_2H_4 + 6ZO \rightarrow 2CO_2 + 2H_2O + 6Z \)

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<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
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<tr>
<td>1</td>
<td>-3</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

I) \( C_2H_4 + 3O_2 \rightarrow C_2H_4O \) \\
II) \( C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \)

Equation 2-4

It is impossible to make an assumption about the nature of the active site \( Z \) only on the basis of their kinetic study but Temkin assumed that \( Z \) is a molecule of the surface compound \( AgO_2 \) \([6,36]\). The \( ZO \) and \( ZO_2 \) are also surface oxides, respectively \( Ag_2O_2 \) and \( Ag_2O_3 \). On the basis of Temkin assumption, the equations corresponded to a single site Rideal-Eley type of mechanism with the ethylene molecule participating from the gas phase. Adsorbed molecular oxygen interacts with ethylene to produce ethylene oxide, while the atomic oxygen is the precursor of carbon dioxide and water.

Finally, they concluded that selectivity decreases with temperature increase and with decrease of the oxygen content in the feedstock.

In 1988, Petrov et al \([37]\) did another series of experiments and studied the kinetics of the complete oxidation of EO over a supported silver catalyst using same method. They applied a sequential experimental design for the determination of the parameters and the simultaneous discrimination of rival kinetic models. A kinetic model was proposed that describes the rate of uninhibited EO oxidation in the temperature range 250 °C -300 °C. The model corresponded to a mechanism in which EO and oxygen adsorptions (dissociative and non-dissociative) are fast steps at equilibrium. They conclude that the rate limiting steps were EO oxidation to formaldehyde and further to carbon dioxide and water with the participation of both atomic and molecular adsorbed oxygen which were irreversible. The calculated kinetic constants offer the possibility of evaluating tentatively the rate constants of the irreversible steps and the equilibrium constants of the fast reversible steps.
In the late 80's and early 90’s, the general opinion started to shift more toward the two different forms of atomically adsorbed oxygen which are present instead of molecular oxygen [38]. The explanations of the mechanism also started to get more complicated. Van Santen et al. [39] were proposed the essential involvement of subsurface sites. In 1992, Rigas, Svoboda and Gleaves [40] made an extensive research by transient response techniques. In their non steady state experiments they noted that the carbon dioxide production initially follows the ethylene input. In contrast, the EO production resembles the delayed oxygen chemisorption. From these findings they proposed a mechanism related to Van Santen et al.'s [41] ideas where oxygen is adsorbed atomically on two different sites; surface and subsurface sites. Surface adsorption leads to carbon dioxide production while subsurface adsorption is necessary for the selective oxidation to ethylene oxide.

### 2.3 Inhibiting Effect of Dichloroethane

Force and Bell [7] reported that the presence of 1,2-dichloroethane (EDC) causes a reduction in the oxidation rate and an increase in the selectivity. In their opinion, this is due to a reduction in the adsorption of ethylene. Kamensky et al. [42] proposed kinetic equations involving parameters which are functions of the content of selectivity promoter. The same authors conclude [24] that the activity and selectivity of an industrial silver catalyst increase when its surface is covered by 1-7% chloride. Ayame et al. [43] claimed that by the addition of sodium chloride to a silver catalyst the selectivity is increased to 85-87%. Ionov et al. [36] described the kinetics of ethylene epoxidation over chlorine-promoted silver by a model which is a special case of a more general model. Kamensky and Petrov [25] proposed a generalized kinetic model for both promoted and unpromoted silver catalysts that could be used in the modelling of industrial reactors. Park et al. [17,44] reported a selectivity of 94% for a chlorine-promoted silver catalyst. Talaeva et al. [45] proposed a method to account for the influence of the EDC concentration in the gas phase on the rates of epoxidation and combustion. Kharson et al. [26] proposed a kinetic model of ethylene oxidation over a silver catalyst promoted with calcium chloride.
In 1986, Petrov et al. [46] studied quantitatively the inhibiting effect of EDC on the epoxidation and combustion of ethylene and oxidation of EO over a silver catalyst as well as its promotion of the selectivity. They examined all other factors that could possibly influence the selectivity, in order to propose a kinetic model of the process in the presence of EDC.

They concluded that the kinetic model for the unpromoted catalyst may be modified by the introduction of additional terms in the numerator, describing the inhibiting effect of the selectivity promoter when present. Also, for promoter concentrations of the order of ppm the reaction order with respect to EDC was found to be less than 0.5.

They observed that EDC was both an inhibitor of the oxidation of ethylene and promoter of the selectivity for EO and the promoting effect of EDC on the selectivity increases with increasing temperature. The role of EDC was to inhibit the dissociative adsorption of oxygen, thus inhibiting the complete oxidation of ethylene.

They had derived from the previous mechanism [41] two new mechanisms – one including reversible adsorption of EDC and the other irreversible, all the other steps remaining the same.

\[ \text{Equation 2-5} \]
\[ C_2H_4Cl_2 + 2Z \leftrightarrow 2ZCl + C_2H_4 \]

The role of EDC is to occupy a portion of the active centres on the silver surface, thus inhibiting the dissociative adsorption of oxygen:

\[ \text{Equation 2-6} \]
\[ O_2 + 2Z \leftrightarrow 2ZO \]

which was proposed by Kilty et al. [47]. It is the only logical explanation for this mechanism, according to which adsorbed molecular oxygen produces EO and adsorbed atomic oxygen produces CO2:

\[ \text{Equation 2-7} \]
\[ ZO_2 + C_2H_4 \leftrightarrow C_2H_4O + ZO \]

\[ \text{Equation 2-8} \]
\[ 6ZO + C_2H_4 \leftrightarrow 2CO_2 + 2H_2O + 6Z \]
The new kinetic model was based on a previous one [41], modified by the addition of a new term describing the decrease in oxidation rate in the presence of the inhibitor.

Later in 1988, Petrov et al [37] did another series of experiments studying the inhibiting effect of EDC on the oxidation of EO. They experienced that EDC had a strong inhibiting effect on the oxidation of EO as well, although the inhibiting effect was reversible. After discontinuing the EDC dosage the initial high catalytic activity had been restored completely. The inhibiting effect decreased with the increase in temperature.

They proposed a kinetic model that includes the inhibitor partial pressure in its functional form. It describes adequately the dependence of the conversion on the contact time, feed composition, temperature and inhibitor concentration and also the dependence of the oxidation rate on the outlet partial pressures of oxygen and ethylene oxide. They observed Catalytic decomposition of EO at high temperatures and with oxygen shortage.

To prevent overchlorination, a so called scavenger is used to desorb the adsorbed Chloride. Ethane is the strongest known scavenger, but ethylene oxide, Water and Methane also act as scavengers. The dechlorination rate with Ethane is however at least an order of magnitude higher than the other compounds mentioned [12]. Ethane naturally exists in ppm values in the ethylene feed stock. However, if ethane in ethylene feed is high, more chloride has to be added to compensate.

Table 2-1 shows a brief survey of reported kinetic expressions for the reaction rates. As there is no agreement on the reaction mechanism, kinetic relations presented by different authors vary in forms and in parameter values. Reaction rates as a function of ethylene partial pressures go through a maximum depending on the oxygen partial pressure [44]. Reaction rates as a function of oxygen partial pressures also go through a maximum, which depends on ethylene partial pressures [48]. Reported reaction orders vary between -0.3 and 2 for oxygen and -0.2 and 1 for ethylene. Wide range of effects of inhibitors such as CO₂ on reaction rates has been proposed [49]. Most of
the reaction rates are independent of EDC and some of them do not include the third reaction.

Table 2-1 - Survey of different rate expressions for the oxidation of ethylene

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reaction Rate Expressions</th>
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</table>
| Klugherz and Harriot (1971) [32] | \[
\begin{align*}
  r_1 &= \frac{K_{i}P_{E}P_{O}^{2}}{(1 + K_{E,1}P_{E} + K_{O,1}P_{O} + K_{P,1}P_{P})^2(1 + \sqrt{K_{S,2}P_{O}})^2} \\
  r_2 &= \frac{K_{i}P_{E}P_{O}^{2}}{(1 + K_{E,2}P_{E} + \sqrt{K_{O,2}P_{O} + K_{P,2}P_{P}})^2(1 + \sqrt{K_{S,2}P_{O}})^2}
\end{align*}
\] |
| Metcalf and Harriot (1972) [48]  | \[
\begin{align*}
  r_2 &= \frac{K_{i}P_{E}P_{O}^{2}}{(1 + K_{i}P_{O}^{0.2} + K_{P}P_{E} + K_{P}P_{P} + K_{P}P_{O}^{0.2} + K_{P}P_{O}^{0.2} + K_{P}P_{O}^{0.2})^2}
\end{align*}
\] |
\begin{align*}
  r_1 &= \frac{K_{i}K_{E,1}P_{E}P_{O}}{(1 + K_{E,1}P_{E} + K_{O,P}P_{O} + K_{E,P}P_{E})^2} \\
  r_2 &= \frac{K_{i}K_{E,1}P_{E}P_{O}}{(1 + K_{E,1}P_{E} + K_{O,P}P_{O} + K_{E,P}P_{E})^2}
\end{align*}
\] |
| Stoukides and Pavlou (1986) [52] | \[
\begin{align*}
  r_1 &= \frac{k_{i}K_{E,1}P_{E} - k_{3}K_{E,1}P_{E}^{0.2}}{1 + K_{E}P_{E} + K_{E}\rho_{EO}^{2}} \\
  r_2 &= \frac{k_{i}K_{E,1}P_{E} + k_{3}K_{E,1}P_{E}^{2}}{1 + K_{E}P_{E} + K_{E}\rho_{EO}^{2}}
\end{align*}
\] |
\begin{align*}
  r_1 &= \frac{K_{i}P_{E}P_{O} - K_{i}P_{E}P_{O}\rho_{DCE}}{1 + K_{i}P_{E} + K_{i}P_{E}} \\
  r_2 &= \frac{K_{i}P_{E}P_{O} - K_{i}P_{E}P_{O}\rho_{DCE}}{1 + K_{i}P_{E} + K_{i}P_{E}} \\
  r_3 &= \frac{K_{i}P_{E}P_{O} - K_{i}P_{E}P_{O}\rho_{DCE}}{1 + K_{i}P_{E} + K_{i}P_{E}}
\end{align*}
\] |
| Al-Saleh et al. (1987) [54] | \[
\begin{align*}
  r_1 &= \frac{k_{i}P_{E}P_{O}^{0.2}}{1 + K_{C,1}P_{C}} \\
  r_2 &= \frac{k_{i}P_{E}P_{O}^{0.2}}{1 + K_{C,1}P_{C}}
\end{align*}
\] |

As was stated before, the epoxidation of ethylene to produce EO is a catalytic process and silver is the main ingredient of all the active and selective catalysts. A major factor in determining the cost effectiveness of many catalytic industrial process is the loss of catalyst efficiency with time on stream. Very few catalytic systems do not show such decay and the associated time constant varies from days to years for different process.
2.4 Catalyst Deactivation

The mechanisms of catalyst deactivation are many; nevertheless, they can be grouped into six intrinsic mechanisms of catalyst decay: (i) poisoning, (ii) fouling, (iii) thermal degradation, (iv) 1,2-dichloroethane vapor compound formation accompanied by transport, (v) vapor–solid and/or solid–solid reactions, and (vi) attrition/crushing. As (i), (iv), and (v) are chemical in nature while (ii) and (v) are mechanical, the causes of deactivation are basically three-fold: chemical, mechanical and thermal. Each of the six basic mechanisms is defined briefly in Table 2-2 and treated in some detail in the subsections which follow with an emphasis on the first three. Mechanisms (iv) and (v) are treated together, since (iv) is a subset of (v) [55].

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Type</th>
<th>Brief definition/description</th>
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<tbody>
<tr>
<td>Poisoning</td>
<td>Chemical</td>
<td>Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction</td>
</tr>
<tr>
<td>Fouling</td>
<td>Mechanical</td>
<td>Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores</td>
</tr>
<tr>
<td>Thermal degradation</td>
<td>Thermal</td>
<td>Thermally induced loss of catalytic surface area, support area, and active phase–support reactions</td>
</tr>
<tr>
<td>Vapor formation</td>
<td>Chemical</td>
<td>Reaction of gas with catalyst phase to produce volatile compound</td>
</tr>
</tbody>
</table>
| Vapor-solid and solid-solid reactions | Chemical | Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase  
| Attrition/crushing         | Mechanical | Loss of catalytic material due to abrasion. Loss of internal surface area due to mechanical-induced crushing of the catalyst particle |

Thermally induced deactivation of catalysts results from:

(i) Loss of catalytic surface area due to crystallite growth of the catalytic phase,

(ii) Loss of support area due to support collapse and loss of catalytic surface area due to pore collapse on crystallites of the active phase, and/or

(iii) Chemical transformations of catalytic phases to non-catalytic phases.
The first two process are typically referred to as "sintering" [55]. Sintering process generally take place at high reaction temperatures and are generally accelerated by the presence of water vapor. Most of the previous sintering and redispersion work has focused on supported metals. Experimental and theoretical studies of sintering and redispersion of supported metals published before 1997 have been reviewed fairly extensively [56–66]. Three principal mechanisms of metal crystallite growth have been advanced: (1) crystallite migration, (2) atomic migration, and (3) (at very high temperatures) vapor transport.

The only effective catalyst for the partial oxidation of ethylene is silver [67] and its development has been the subject of research for many years [68]. Over the years the selectivity of these catalysts improved from about 70% to more than 80% as reported in the patent literature [67]. Nevertheless, stability is still an important issue since these catalysts deactivate under industrial operating conditions.

There are several possible causes for Ag-catalysts deactivation, such as catalyst poisoning either by impurities [69,70] or by an excess of chlorine-based promoters in the feed [71], accumulation of carbon deposits on the catalyst surface [17,72–75], and increase of both silver particles size [8,70,76–79] as well. Among several possible mechanisms for deactivation of Ag-based catalyst, sintering of the active metal is broadly accepted as, if not the single, but in any case, the most important one [78–80].

To compensate for the loss in catalyst activity under industrial conditional, reaction temperature is usually increased [68]. To prolong the period of high catalyst activity a kinetic model of deactivation predicting the optimal operation mode would be helpful.

Montrasi and et al (1983) [8], investigated the deactivation of a silver catalyst for ethylene epoxidation after six years of industrial use. They unloaded some tubes of the reactor and divided the catalyst into five parts: sample $U_i$ at the gas inlet (top of the reactor) to sample $U_3$ at the gas outlet were compared with fresh catalyst (F). This permitted the determination of a deactivation profile along the reactor. The performances of the fresh and discharged catalysts were examined in an internal recycle reactor in the range 503 - 543 K. They observed that the rate of ethylene
oxidation (at a constant feed composition and reaction temperature) and the selectivity to EO (at a constant ethylene conversion) varied in response to a sequence \( F >> U_5 \approx U_4 \approx U_3 > U_2 > U_1 \). Thus, at the same temperature, \( U_1 \) and \( U_2 \) were not only the least active, but also the least selective catalysts.

In early 2004, Zhou and Yuan [81], considered sintering caused silver particle growth to be the result of random migration and coalescence, on the basis of which a random walk model was proposed. Simulation results showed that the particle size evolution could be well fitted by generalized power law expression, indicating that the random walk model was valid for sintering process with different sintering rates and time scales. With the assumption of identical grain sizes, changes in the specific surface intergrain boundary length during particle sintering were predicted by the random walk model and the epoxidation rate was related to the specific surface intergrain boundary length in terms of a selectivity factor. They showed that the results elucidated quite well the phenomenon of nonmonotonic change of the selectivity during silver catalyst sintering.

In 2004, Boskovic and et al [82] developed an accelerated deactivation procedure for a commercial Ag-based prospective commercial by a change of parameters without changing the deactivation mechanism defined as true deactivation. They did series of experiments using a Berty-type gradientless recycle reactor. They concluded that acceleration of the deactivation of a commercial \( Ag/Ag_2O_3 \) catalyst can be achieved by increasing reaction temperature and oxygen concentration within the applied range of reaction conditions. They observed the catalyst declined fastest at the highest reaction temperature and oxygen concentration applied, indicating a cooperative effect in the deactivation process.

Later the same year, Boskovic and et al [83] used the same procedure and investigated deactivation kinetics for a commercial \( Ag/Ag_2O_3 \) catalyst to find an equation that describes the catalyst activity decline as a function of time. Change of catalyst activity with time on stream was described by an equation originally derived by Levenspiel
[84], but later modified by introducing the term of steady-state activity, $a_s$, reached at infinite time [85]:

$$-\frac{da}{dt} = K_\alpha P_\alpha^\alpha (a - a_s)^a$$  \hspace{1cm} \text{Equation 2-9}$$

They described the deactivation by using the general power-law equation with an order of 1 with respect to driving force ($a - a_s$). In the applied range of conditions,

$$a = a_s + (1 - a_s) \exp\left(-K_\alpha^0 \left(-\frac{E_\alpha}{RT}\right) P_\alpha^\alpha t\right)$$  \hspace{1cm} \text{Equation 2-10}$$

where the overall kinetics could be described by:

$$R_i = f_i(T, p) a_i(t, T, p)$$  \hspace{1cm} \text{Equation 2-11}$$

### 2.5 PROCESS TECHNOLOGY

An overview of the beginnings of commercial EO production can be found in [86]. The production of EO can be undertaken via two process, air based system and oxygen based system. Production technologies for EO plants based on the direct oxidation process are licensed by Shell, Scientific Design (SD), UCC, Japan Catalytic, Snam Progetti, and Hüls. Due to improved catalysts and production technology, large plants with capacities of up to 400 000 t/a can now be built.

The technologies are very similar, but differences exist, depending on whether air or pure oxygen is used for oxidation [87]. Shell plants use only pure oxygen, while Scientific Design and UCC have developed air-based oxidation plants in the past as well.

Figure 2-1 and Figure 2-2 show simplified schemes for the air-based and oxygen-based processes, respectively. In both systems, oxygen is used as the oxidising material, and the major difference being the large build up of inerts associated with the air based system. The reactor effluent from the air based system undergoes a series of adsorption and desorption process to reach an EO quality of 99% [88]. After the
stream has passed through the scrubbers the majority of the stream is recycled back to the reactor, with the remainder of the stream being purged to prevent the build up of the inert gases, such as Nitrogen and argon.

Figure 2-1- Flow scheme for EO production by the oxygen-based oxidation of ethylene

The oxygen based process uses a reactor feed comprising compressed oxygen and ethylene along with the system cycle gas. The cycle gas is a mixture of un-reacted oxygen and ethylene, carbon dioxide and water which are produced in the reactor, and a significant proportion of nitrogen. The nitrogen is a critical component of the cycle gas as it is used as a ballast to minimise the risk of the ethylene and oxygen, or the EO and oxygen reaching concentrations that could cause an explosive vapor mix to form [88].
The EO recovery and refining systems incorporated are identical for both process [89]. The reactor effluent passes through a water scrubber where close to all the EO is transferred from the vapor to the liquid phase along with the majority of the water that is produced in the reactor. The gas phase product from the absorbers is compressed and returned to the cycle gas system for re-use in the reactor. Before the compression, a percentage of the stream is purged off to prevent inert build-up. The EO rich water exiting the scrubbers is sent to the EO strippers to strip off the EO and soluble inerts [89]. The clean water separated via this process is recycled back to the scrubbers. The stripper vapor outlet stream is sent to the light ends rejection system where EO is separated from the inert and non-condensable gases which are vented or compressed and recycled. The EO is recovered from this stream is purified to the specification required.
2.6 EO PLANT IN AUSTRALIA

While historically the oxychlorination process was primarily an achievement of Australian research and development, and polythene in essence was the result of technology transfer, whereas EO and its derivatives were a mixture of the two. In the UK, ICI and in Australia, Timbrol had long made ethylene-glycol, an important chemical intermediate best known to the wider public for only one of its uses, as a car radiator fluid. The ICI process based on epichlorohydrin did not suit ICI Australia in the 60's; chlorine prices were rising and the process appeared obsolete. Research and development teams, therefore, evaluated alternative process and, eventually, secured an early licence from an emergent American company, R. Landau's Scientific Design. This was a matter of prudent buying, as the process was still at an early development stage, when entry terms were favourable but entailed an element of risk, and hence confidence in one's own evaluation.

The process itself, however, was only half the issue. To create adequate markets a major effort of process and end-use development for the derivatives was needed: Polyethylene glycol (polyol) plants, new surface active agents and a multiplicity of new uses for their variants in many industries [90]. The polyols were one of the two principal constituents of polyurethane plastics.

The process of market penetration had begun before the plant was built and continued for some years. Finally, ICI Australia's chemists had the satisfaction that not only did their UK colleagues follow them in process selection but they even purchased know-how on EO derivatives and plants from the subsidiary. By 1963 the EO plant was completed, on line and performing well. The third step to the Botany ethylene cracker was in place (Figure 2-3).

It was a new phase for Australia's chemical technology; the entry into fully integrated petrochemical, plastics and plastics processing industry some key elements of which rested on competitive advantages derived from Australian industrial research.
In 1998 Orica Australia, previously ICI Australia sold the surfactants business at Botany, NSW to Huntsman. This is the only EO plant in Australia. This plant has a capacity of up to 45,000 tons of EO per annum.

2.7 Huntsman Profile

Huntsman is one of the world's largest privately held chemical company. Its operating companies manufacture a range of chemical products for a variety of global industries including chemicals, plastics, automotive, footwear, construction, paints and coatings, healthcare, detergent, personal care and packaging. Today Huntsman-held companies have revenues of over $12 billion USD, more than 15,000 employees and facilities in more than 40 countries. Through strategic acquisitions of plants from leading surfactant companies such as Texaco Chemical Company, Baker Performance Chemicals and Albright and Wilson's, Huntsman entered the surfactants business [92].

As stated before the surfactants operation of Orica Ltd., Australia was sold to Huntsman in 1998 and since then it has been known as Huntsman Corporation Australia (HCA). The plant is located at Botany Bay, New South Wales and produces around 40 kt EO annually for its surfactant production (Figure 2-4).
In 2001, after a major overhaul of its EO plant, where a new batch of catalyst was put in place, the company is looking into increasing its EO production to around 40 kte annually [92].

Commercial catalysts generally report selectivity values starting around 80% [93] and the Huntsman reactor at Botany runs in the same range, with the selectivity decreasing as the catalyst ages. There is a theoretical limit of 85.7% for the overall selectivity in the plant based on reaction stoichiometry; however there have been numerous laboratory studies that have shown selectivity above this maximum [88,92], although these experiments have not been commercialised.

HCA’s EO plant is unique in two aspects:

- At 40 ktpa, it is amongst the smallest in the world with newer plants coming on-stream in the Asia Pacific region having up to ten times the capacity;
- Over 70% of the EO produced is used in the downstream manufacture of non-ionic surfactants, whereas the bulk of the EO output of competitors is used in making commodity chemicals (e.g. glycols and glycol ethers).
These characteristics have important consequences:

- Firstly, the small size of its EO plant means for HCA a serious diseconomy of scale relative to its overseas competitors. It therefore imposes a critical demand to be world’s best in terms of manufacturing efficiency in all other aspects associated with this plant. Optimising control (involving on-line data analysis, modelling and optimisation, together with advanced process control) is seen as the key to achieving a higher manufacturing efficiency, and thus a vital competitive advantage.

- Secondly, the chemical industry is a sector of major economic and strategic importance to Australia, with annual exports of about six billion dollars. However, Australia’s current trade balance in chemicals runs a deficit of some five billion dollars, especially in the “value-added” end of the market. The bulk of HCA’s EO output is used in making non-ionic surfactants for different markets (eg agrochemical, manufacturing and mining/mineral processing sectors). They therefore account for a key part of Australia’s specialty chemicals industry. HCA’s failure in the face of overseas competition would spell the demise of a very significant section of the value-added end of the Australian chemical industry.

2.8 EO PRODUCTION IN INDUSTRY

Figure 2-5 shows a simplified typical process flow sheet in industry (as in Huntsman EO production plant). The typical EO plant makes use of the oxygen based technology.

The raw feed including 99.99% pure ethylene and 99.7% pure oxygen mixed with the cycle gas stream from the scrubbers. The resulting gas passes through a heat exchanger to be heated by cooling down the reactor outlet steam and feed to the PBR reactor. The cooled reactor outlet is then sent to the EO scrubbing system to recover the EO product by absorbing it with the lean recycle water.
Figure 2-5- Huntsman EO production process

The gas exiting the top of the main scrubber is recycled back to the reactor which some percentage (around 20%) of that sending to CO₂ Removal unit. The gas coming out at the top of the CO₂ removal unit, goes through a series of operations to remove CO₂ then is discharged to prevent accumulation of CO₂ and other inert species such as argon and back to the cycle gas stream. Rich cycle water (Scrubber bottoms) is heated and flashed to a low pressure before entering the Stripping Column. The flashing feed releases most of the EO and other gases. Steam is used to drive off the remaining EO.

In the oil circuit, the coolant oil, MobilTherm, is used to cool the reacting gas in EO reactor. A portion of the heated coolant is passed through a kettle-like heat exchanger to produce steam, and the coolant stream is recycled back to the shell side of the process. Simple proportional-integral-derivative (PID) controllers manipulate the inlet oxygen and ethylene flow rates and the inlet oil cooler temperature.
2.9 Ethylene Oxide Production Practice

It has been recognised that there is a discrepancy in EO production data from laboratories and from actual plants. Generally, reactor selectivity is reported to be higher in laboratories than what has been achieved in practice. Commercially available catalysts have been reported to operate with selectivity starting 80% [93]. Patent examples for silver catalysts and academic studies have consistently claimed experimental selectivity close to 90% [88,93], however it declines quickly and CO₂ level has to be very low (< 2%).

There are a number of important factors, which could be used to explain the gap between actual practice and laboratory study. The first factor is believed to lie in heat transfer control. It is well known that EO production involves highly exothermic reactions. In addition, higher operating temperature favours complete combustion and hence results in lower selectivity. These conditions have made multitubular fixed bed reactor almost used exclusively in EO production industry, due to its definite advantage of higher heat transfer area [88]. However, higher surface area only provides a potential to achieve but does not guarantee adequate heat transfer. "Hot spots", where low heat transfer results in higher temperature, are likely to occur unless proper operating and control practice are employed, which has in turn called for modelling and subsequently devising proper control of heat transport phenomena in EO production process.

The second factor, which is believed to contribute to the discrepancy in academic studies and industrial practice in EO production, involves selection of catalyst promoters, moderators and their operating procedures. Improvement in selectivity could be achieved through selection and use of alkaline promoters (e.g. K, Cs), organohalides as feed additives, which is more commonly used. It is believed that such organohalides as 1,2-dichloroethane (EDC) would act as catalyst poisoning agent to suppress complete combustion of ethylene and hence improve the selectivity [71,88]. However, excessive amount of EDC (in order of a few ppm) would cause catalyst deactivation and so reduce the production by chlorinating the silver catalyst.
surface. To overcome this issue, a small amount (in order of ppm) of moderators such as ethane is frequently added to the reactor to promote the removal of surface chlorine and in doing so, the catalyst activity would be controlled [94, 95]. Consequently, the catalyst activity and hence the production is significantly influenced by two control parameters including the level of EDC promoter and ethane moderator. As these two parameters are to be in the order of a few ppm, adequate control strategy must be implemented.

On the other hand, the remaining EO in cycle gas stream that is an inlet to the reactor has a major effect on the reactor selectivity and overall product quality. Result shows that on increasing the EO inlet mole fraction about 1.5%, the loss on selectivity and work-rate are 9% and 15 (Ton/day) respectively which is significant loss [96].

EO reactor optimisation study shows that for 1.5% EO (Mole based) in feed, the maximum work-rate can be achieved is 120 Ton/day, and the optimum selectivity will be 71%. While for 0.01% EO (mole based) in feed with same condition, the work-rate and selectivity would be 130 Ton/day and 81% respectively [96].

As a consequence, the proper model of the reactor is required to understand the reactor performance and using for further optimisation and control of EO reactor in order to achieve adequate heat transfer as well as maintain proper catalyst activity and selectivity.

2.10 MODELLING

Modelling is an important step toward a genuine understanding of the operation status of a given process. It allows for performance studies which otherwise would be impossible due to limitations in the possible operational changes in the real plant. This is of certain importance when dealing with a process like the EO reactor which operates close to both runaway and explosive conditions.

In 1995, Lam [97] developed a simplified steady state model for EO reactor. He assumed only ethylene and oxygen are reacted and ignored the EO oxidation.
Following Lam's work, in 1996, Lindewald [98] developed a steady state and dynamic model of EO reactor using SPEEDUP. He assumed that all three reactions (total and partial ethylene epoxidation along with EO oxidation) occurred inside the reactor. However, the effect of EDC on the reaction rates was neglected. Some of parameters were fitted using plant data; also the model prediction was not validated against the plant data. Some point optimisation was done though the results which were not reliable. Nevertheless, the model approach is adequate and needs to be improved.

In 2001, Tien [99] developed a 1-D pseudo-homogeneous dynamic model for the tube side using gPROMS as well as a simplified model of the shell-side using the computational fluid dynamic package CFX (Version 5.4.1) to evaluate heat transfer characteristics.

The major assumptions made for his model included- homogeneous temperature and concentration in both the gas and solid catalyst phase; negligible axial and radial mixing and plug flow. Also, only partial and total oxidation of ethylene were considered neglecting the EO oxidation. Using the CFX model, he investigated three scenarios - (i) a reactor shell with no baffle, (ii) with one baffle and (iii) with two baffles. He concluded that baffles significantly alter the velocity distribution by inducing fluid cross-flow in the shell and hence enhancing heat transfer and the baffled scenarios show velocity distributions with larger region of high velocity. Specifically, at the tube wall, the "dead spot" region- where the fluid velocity is very low and hence the heat transfer is poor- was much smaller once baffles had been introduced.

In 2004, in the PSE group, a steady state model of the EO scrubber was developed using HYSYS software package. The effect of the reactor and the scrubber performance on each other was investigated. However this was steady state and offline investigation [96].
2.11 CONCLUSION AND RESEARCH DIRECTION

As discussed above, preliminary dynamic modelling work on the EO reactor, was begun earlier by researcher, however the model was substantially incomplete and no benchmarking and validating against plant data were carried out. Also, the effect of EDC on the reaction rate was ignored.

Previously, conventional kinetic models have been used with component balance equations to develop a mathematical model for the EO reactor. However, the experimental results have shown that the EDC has a strong effect on the overall reaction rate on the work-rate and the selectivity.

In this research project, we focused on expanding the capabilities of the existing model to include such phenomena, to allow the model to predict the reactor performance over the period of operation.

In addition, the previous models thus far have been restricted, for simplicity to mainly the reactor unit operation. This restriction limits the capabilities of the model to offline dynamic simulation applications. To overcome this, and at the same time to be able to adequately model the complete process with various unit operations, a novel hybrid modelling environment has been constructed. Thus we propose to develop effective tool for studying process as well as control strategy design and their industrial implementation.

The overall aim of this work is to develop an integrated model-based decision support framework to allow the optimal operation of the EO plant while maintaining systems integrity, operability and safety.
2.12 BIBLIOGRAPHY


72- S.A. Tan, R.B. Grant, R.M. Lambert (1987), "Pressure Dependence of Ethylene Oxidation Kinetics and the Effects of Added CO2 and Cs: A Study on Ag(111) and Ag/a-Al2O3 Catalysts", Applied Catalysis, 31: 159.


Chapter 3

EO Reactor Mathematical Modelling

In this chapter the EO reactor unit is first extensively described, followed by an enumeration of all used model equations with explanations. Finally all the physical properties used in the EO reactor modelling are presented, including a description of how suitable software packages to model were chosen.
3.1 INTRODUCTION

In the current world market, competitiveness is translated into higher productivity goals and tighter quality specifications. However, enhanced process performance cannot be sustained or continuously improved unless it results from increased in-house knowledge. On the one hand, process monitoring is often incapable of meeting these objectives.

Indeed, tools for process analysis and improvement and advanced process control are needed to reach those goals. On the other hand, abundant plant data, which is vital for monitoring and regulatory control of modern processing plants, offers an inconsistent and incomplete picture of the system's status. For instance, process measurements rarely satisfy implicit and explicit redundancy due to improper sensor calibration and random measuring errors, the former being much more relevant from an operational and economic viewpoint than the latter. The incomplete nature of plant data arises form the fact that only a minor subset of the system variables are actually measured, and therefore available to the user. This set of measurements is located to facilitate the daily operation of the process equipment, not to ease process analysis or indicate the direction for process improvement, unless additional knowledge is combined with existing plant data.

Although rules-of-thumb or previous experience could seed this knowledge, only in-depth understanding of the physical and chemical transformations occurring in the system and their interactions would ultimately lead to increased in-house qualitative and quantitative knowledge. Process models derived from fundamental principles are the most promising tools to achieve this extended understanding. For example, if available plant data is combined with model-based process simulation, mechanisms driving natural phenomena could be quantified, and the resolution of spatially- and topologically-poor plant data could be increased simultaneously. Offline and on-line process simulation could be used for a widespread of support activities such as soft-sensing and personnel training, or analysis studies such as process troubleshooting and performance evaluation. Undeniably, the scope for integration of plant data and
model-based applications is extensive. For example, dynamic parameter estimation could be used to obtain the magnitude of key operating parameters such as fouling resistances, catalyst deactivation or temporal variations of unmeasured properties of raw materials.

However, the spectrum of application of model-based activities is not restricted to the availability of plant data. The improvement of operating conditions is a complementary task to detailed process analysis. Model-based process optimisation at nominal production levels is a convenient tool to explore operating scenarios that would ensure more stringent quality specifications or more profitable productivity margins. Finding novel operating procedures to manage transient process operation due to scheduled production changes or unplanned disturbances and unexpected constraints could also be attained by means of model-based process optimisation.

Finally, embedding a fundamental process model into an on-line application for advanced model-based control is an initiative that could lead to an enormous quality control and profitability boost.

In light of the facts presented above, it should be noted that process analysis and improvement is better attained with the assistance of advanced simulation and optimisation, as well as advanced process control. Mechanistic process models seem to be vital for the success of these model-based activities. Qualitative and quantitative knowledge gained from these advanced tools will ultimately lead to a continuous improvement of competitiveness, meeting higher productivity goals and tighter quality specifications.

The Process Industries very often develop or acquire customized technology to address their needs for monitoring, process analysis and supervision. However, these diverse software components offer a fragmented description of the process system, failing to provide results at higher levels of plant hierarchy. Among their intrinsic limitations, the incapacity to account for operative constraints imposed by upstream and downstream process equipment is probably the most important downfall.
Additionally, budget restrictions and/or an incomplete understanding of the underlying chemical and physical transformations result in the introduction of excessive simplifications into some in-house developed components, which further reduces their chances to provide consistent results with other applications.

The incomplete and fragmented nature of most customised technologies provided by internal or external sources is a major impediment for the consistent integration of these tools. Synergistic interactions between process simulation, optimisation and estimation studies and, eventually, advanced process control are likely to be hindered due to inconsistency of results among activities. Additionally, since the environments of these software components probably have distinct conventions, methods and protocols, the reusability of case-studies among components is restricted, and end-users are prone to losing interest or making mistakes due to application-specific procedures for problem formulation, execution and analysis.

The development of state-of-the-art technology associated to EO production has always focused on increasing production capacities, enhancing process flexibility and improving selectivity. However, process understanding gained from exposure to previous technologies cannot always be accommodated to match the requirements of modern process. For example, guidelines, operating manuals and existing rules-of-thumb are generally available for design conditions only and are rarely site-specific. Therefore, it is imperative to provide advanced tools for process analysis and improvement studies that will result in a better understanding and tighter control of these formidable units.

As discussed in chapter 2, HCA’s EO plant is the smallest in the world and it is one of major economic and strategic importance to Australia. Therefore, the need for proper modelling and control of EO plant is critical in order to achieve the efficient production of ethylene oxide, consistent with process safety.

Figure 3-1 shows a schematic of the EO plant. The EO reactor is the most important unit in the EO process. It is well known that chemical reactors especially EO reactor, sometimes may go out of control after a minor upset in critical operating parameters.
Subsequently, run-away conditions may occur and cause damage to the expensive catalyst. Consequently, detailed dynamic modelling of the EO reactor is vital toward an accurate understanding of the operation.

To model the reactor unit accurately, it is necessary to understand the fundamentals of catalytic oxidation phenomena and the dynamic behaviour of the catalytic reactor. The reactor model is not available from predefined model libraries. Hence, it is necessary to use equation-based software to solve the governing equations.

![Figure 3-1- Schematic of EO Plant](image)

However, as will be discussed later, predefined models (model-defined software) are available to model the other three units involved in the EO plant, namely, the gas-gas heat exchanger, the EO scrubber and the hot oil cooler.

In this chapter the detailed dynamic model of the reactor is presented. The software packages used for solving equations and simulating the units are discussed.
3.2 The Ethylene Oxide Reactor

The ethylene oxide reactor at the HCA plant at Botany is a multi-tubular reactor (Figure 3-2), which has 7750 tubes packed with silver catalyst supported on $\alpha - Al_2O_3$. MobilTherm "607" flows in the 3.3 m diameter reactor shell to remove the heat generated by oxidation. The operating temperature of the reactor is about 230 °C to 260 °C while the pressure varies from 20 atm to 25 atm. The oil feed temperature is around 245 °C and heats the incoming gas in the first part of the reactor before acting as a cooling medium. The process is oxygen-based and operates in the oxygen lean zone to prevent explosion.

![Diagram of Ethylene Oxide Reactor](image)

**Figure 3-2- Schematic drawing of the EO reactor (not to scale)**

The product gas from the outlet of the reactor preheats the inlet gas in a separate heat exchanger. EO is then stripped off from the product gas mixture in 2 scrubbers. The stripped gas is thereafter partly de-carbonated before being recycled back to the reactor. The outlet cooling oil is cooled in a kettle boiler to produce saturated steam.

The recycle gas is topped up with more raw feed materials including pure oxygen and ethylene before being heated and fed to the reactor. In general, the reactor feed gas consists of 7 main components including: ethylene, oxygen, ethylene oxide (usually less than 0.01%), carbon dioxide, water (reaction's by-products), argon (built up in the system by adding oxygen) and nitrogen (used as ballast). Also, a small concentration of 1,2-dichloroethane (EDC) is intentionally added to the feed to
improve reactor selectivity and to moderate the oxidation rate. A typical reactor feed and product composition is shown in Table 3-1.

Table 3-2 shows the reactor’s typical operating condition. It is noted that there exists a difference in oil inlet temperature between start of run (SOR) and end of run (EOR) due to catalyst deactivation.

The reactor is manually controlled. The two main control variables are the oil inlet temperature and the Chloride additive.

<table>
<thead>
<tr>
<th>Table 3-1- Typical reactor feed and product composition (mol %)</th>
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<tbody>
<tr>
<td><strong>Composition (mol %)</strong></td>
</tr>
<tr>
<td>ethylene</td>
</tr>
<tr>
<td>oxygen</td>
</tr>
<tr>
<td>Ethylene oxide</td>
</tr>
<tr>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td>argon</td>
</tr>
<tr>
<td>EDC</td>
</tr>
<tr>
<td>Ethane</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3-2- Reactor operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SOR</strong></td>
</tr>
<tr>
<td>Gas feed flow rate (kg/hr)</td>
</tr>
<tr>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>Gas inlet temperature (°C)</td>
</tr>
<tr>
<td>Oil flow (kg/s)</td>
</tr>
<tr>
<td>Oil inlet temperature (°C)</td>
</tr>
</tbody>
</table>
There are three main reactions in our process.

\[
\begin{align*}
H_2C &= CH_2 + \frac{1}{2} O_2 \rightarrow C_2H_4O & \Delta H_1 &= -1.23 \times 10^5 \text{ kJ mol}^{-1} \\
H_2C &= CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O & \Delta H_2 &= -1.30 \times 10^6 \text{ kJ mol}^{-1} \\
C_2H_4O + \frac{5}{2} O_2 & \rightarrow 2CO_2 + 2H_2O & \Delta H_3 &= -1.17 \times 10^6 \text{ kJ mol}^{-1}
\end{align*}
\]

All three reactions are strongly exothermic. Reaction (1) is desired and occurs in parallel with side reactions (2) while reaction (3) appears to be a consecutive reaction of (1). A typical catalyst employed in the catalytic oxidation of ethylene is silver supported on $\alpha-Al_2O_3$ of $\sim 1 \text{ m}^2 \text{ g}^{-1}$ specific surface area.

The kinetic relations for reaction rates are vital in our reactor modelling and simulations. Although there has been extensive research on the chemistry associated with the reactions, there is no general agreement either about the reaction mechanism on the surface of the catalyst, or about the reaction kinetics.

### 3.3 Reaction Kinetics

As discussed earlier, the rate equations could be separated into two terms: a term describing the steady-state kinetics of the catalytic reaction at time zero, (hence it is independent of time), and an activity term, which by definition is the time-dependent function. Thus, the overall kinetics is described by:

\[ r_i = f_i(T, p) \times a_i(t, T, p_k) \times \rho_{\text{Cat}} \times C(t) \]  

**Equation 3-1**

The function $f_i$ represents the kinetic term of the catalytic reaction, $a_i$ is deactivation term and $C_i$ is correction factor; species i, j and k are ethylene, ethylene oxide, oxygen, and carbon dioxide [1].

The kinetics of the inhibited oxidation used in the reactor model, were developed by Eliyas et al [2] and Petrov et al [3,4]. The reaction rates are given as functions of partial pressures of oxygen, ethylene, ethylene and EDC:
\[ f_1 = \frac{K_5 P_{EO} P_{Oxy} - K_1 P_{EO} P_{Oxy} P_{EDC}^{K_1}}{1 + K_3 P_{Oxy} + K_6 P_{EO}} \]  

Equation 3-2

\[ f_2 = \frac{K_4 P_{EO} P_{Oxy} - K_2 P_{EO} P_{Oxy} P_{EDC}^{K_2}}{1 + K_3 P_{Oxy} + K_6 P_{EO}} \]  

Equation 3-3

\[ f_3 = \frac{K_9 P_{Oxy} P_{EO} - K_{10} P_{EO} P_{EDC}^{K_{10}}}{(1 + K_9 P_{Oxy} + K_{10} P_{Oxy}^{0.5} + K_{11} P_{EO} + K_{12} P_{EO} P_{Oxy}^{-0.5})^2} \]  

Equation 3-4

where:

\[ K_{i=1-4,7-8} = K_{0,i} \exp \left( -\frac{E_{a,i}}{RT} \right) \]  

Equation 3-5

\[ K_{i=5,6,9-12} = K_{0,i} \exp \left( \frac{E_{a,i}}{RT} \right) \]  

Equation 3-6

The rate units are mol/g_cat h.

The pre-exponential factors and activation energies for kinetic rates are summarised in Table 3-3 [2-4].

The catalyst deactivation is modelled using Boskovic model [1] which is a nonlinear function of operating time and catalyst temperature:

\[ a_i = a_{i,0} + (1 - a_{i,0}) \exp(-K_{d,i}(-\frac{E_{a,i}}{RT})\times t) \]  

Equation 3-7

Furthermore, it was assumed that catalyst deactivation affects the first and second reactions and not the third reaction.
Table 3-3- Values of pre-exponential factors and activation energies for kinetic rates

<table>
<thead>
<tr>
<th>Kinetic Constants $K_i$ (mol / g-cat h)</th>
<th>pre-exponential factor $K^0$ (mol / g-cat h)</th>
<th>Activation energy $E_o$ (kJ / mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>7.26 E+0</td>
<td>9.325 E+3</td>
</tr>
<tr>
<td>$K_2$</td>
<td>9.40 E+1</td>
<td>1.041 E+4</td>
</tr>
<tr>
<td>$K_3$</td>
<td>1.06 E+0</td>
<td>8.792 E-3</td>
</tr>
<tr>
<td>$K_4$</td>
<td>3.96 E+0</td>
<td>9.473 E-3</td>
</tr>
<tr>
<td>$K_5$</td>
<td>1.35 E-06</td>
<td>9.610 E+3</td>
</tr>
<tr>
<td>$K_6$</td>
<td>3.11 E-08</td>
<td>1.504 E+4</td>
</tr>
<tr>
<td>$K_7$</td>
<td>1.11 E+06</td>
<td>9.200 E+04</td>
</tr>
<tr>
<td>$K_8$</td>
<td>6.29 E+10</td>
<td>1.170 E+05</td>
</tr>
<tr>
<td>$K_9$</td>
<td>7.02 E-20</td>
<td>1.500 E+05</td>
</tr>
<tr>
<td>$K_{10}$</td>
<td>9.67 E-15</td>
<td>1.090 E+05</td>
</tr>
<tr>
<td>$K_{11}$</td>
<td>2.35 E-05</td>
<td>4.180 E+04</td>
</tr>
<tr>
<td>$K_{12}$</td>
<td>2.36 E-06</td>
<td>5.020 E+04</td>
</tr>
</tbody>
</table>

The reaction equilibrium constants are [2-4]:

$K_{13} = 0.19$, $K_{14} = 0.07$ and $K_{15} = 0.6$.

3.4 MASS BALANCE

Since the reaction occurs on the surface of the catalyst and the reactor exhibits low concentration gradients, the mass transfer is treated as a pseudo homogeneous case. In other words, it is assumed that no concentration gradient exists between the surface of the catalyst and the bulk flow of the gas.
The mass balance is given as:

$$\frac{\partial F_j}{\partial t} = V_{\text{gas}} \times (\sum_{i=1}^3 \nu_i / v_{\text{BASE}(i)} \times R_i) \times A_{c,T} \times e - V_{\text{gas}} \times \frac{\partial F_j}{\partial Z} + D_{ax} \times \frac{\partial^2 F_j}{\partial Z^2} \quad \text{Equation 3-8}$$

Where $F_j$ present the molar flow, $\nu$ is the stoichiometric coefficient, $A_{c,T}$ is the empty tube cross sectional inner area, $j$ denotes the number of the component, $i$ the number of the reaction and $\text{BASE}(i)$ is the component that the reaction $i$ is based on. For the first and second reactions, the base is oxygen and for the third reaction, the base is ethylene oxide.

The tube cross-sectional area is given by:

$$A_{c,T} = N_T \times \pi \times D_i^2 / 4 \quad \text{Equation 3-9}$$

All the components except of the inert Nitrogen and argon have their corresponding dynamic mass balance equations in the model as follows:

**Ethylene**

$$\frac{\partial F_{\text{C}_2\text{H}_4}}{\partial t} = V_{\text{gas}} \times (2 \times r_1 + 1/3 \times r_2) \times A_{c,T} \times (1-e) - V_{\text{gas}} \times \frac{\partial F_{\text{C}_2\text{H}_4}}{\partial Z} + D_{ax} \times \frac{\partial^2 F_{\text{C}_2\text{H}_4}}{\partial Z^2} \quad \text{Equation 3-10}$$

**oxygen:**

$$\frac{\partial F_{\text{O}_2}}{\partial t} = V_{\text{gas}} \times (r_1 + r_2 + 5/2 \times r_3) \times A_{c,T} \times (1-e) - V_{\text{gas}} \times \frac{\partial F_{\text{O}_2}}{\partial Z} + D_{ax} \times \frac{\partial^2 F_{\text{O}_2}}{\partial Z^2} \quad \text{Equation 3-11}$$

**Ethylene oxide:**

$$\frac{\partial F_{\text{EO}}}{\partial t} = - V_{\text{gas}} \times (2 \times r_1 - r_3) \times A_{c,T} \times (1-e) - V_{\text{gas}} \times \frac{\partial F_{\text{EO}}}{\partial Z} + D_{ax} \times \frac{\partial^2 F_{\text{EO}}}{\partial Z^2} \quad \text{Equation 3-12}$$

**Carbon dioxide:**

$$\frac{\partial F_{\text{CO}_2}}{\partial t} = - V_{\text{gas}} \times (2/3 \times r_2 + 2 \times r_3) \times A_{c,T} \times (1-e) - V_{\text{gas}} \times \frac{\partial F_{\text{CO}_2}}{\partial Z} + D_{ax} \times \frac{\partial^2 F_{\text{CO}_2}}{\partial Z^2} \quad \text{Equation 3-13}$$
Water:

\[ \frac{\partial F_{H,O}}{\partial t} = -V_{gas} \times (2/3 \times r_2 + 2 \times r_3) \times A_{c,j} \times (1 - e) - V_{gas} \times \frac{\partial F_{H,O}}{\partial Z} + D_{ax} \times \frac{\partial^2 F_{H,O}}{\partial Z^2} \]  \hspace{1cm} \text{Equation 3-14}

3.4.1 Axial dispersion

A diffusion term is introduced in the dynamic model with the primary purpose of stabilising the model when step changes in component flow are introduced. Since the Reynolds number is high and the concentration gradient during normal operation is low, the diffusion value is insignificant in the final output results of the model.

Since the diffusion term does not play an important role, its value is roughly evaluated from estimations by Fogler [6] as follows:

\[ Pe = \frac{V_{gas} \times L_R}{D_{ax}} \]  \hspace{1cm} \text{Equation 3-15}

Where \( V_{gas} \) is gas velocity, \( L_R \) is reactor length and \( D_{ax} \) is axial diffusion. Fogler estimates Peclet number (Pe) of ~1e3 in packed beds [6]. Since the reactor operates under high Peclet number conditions as stated above (high Reynolds number and low concentration gradient), Pe of 2e3 approximately is calculated which results in:

\[ D_{ax} = \frac{V_{gas} \times L_R}{2e3} \]  \hspace{1cm} \text{Equation 3-16}

3.5 Energy Balance

The reaction heat removal is an important issue to be considered when operating the oxidation reactor. Heat removal is critical for operating personnel safety and equipment integrity. In practice, the maximum temperature of the reactor is determined by the rate at which the reaction heat can be removed. The transport of heat from the core of the catalyst bed to the coolant is facilitated by increasing both contact area and the coolant transport properties. Also, the flow pattern of the coolant
through the shell side has an important effect on the heat removal capacity of the cooling system [5].

In the multi-tubular oxidation reactor the spacing of the tubes has an important effect on the temperature distribution. The temperature distribution is established by the maximum volumetric heat release rate in each of the components (packed tubes). The coolant flow pattern in the shell side of the reactor is changed by baffles. However, there is very little control of the heat of the heat removal in poor mixing zones nearby the baffles. The analysis of the coolant system of the oxidation reactor involves the following: (1) heat sources and its distributions; (2) heat transport through the catalyst bed and to the coolant; (3) heat transport along the reactor; (4) heat transfer from the primary to the secondary cooling system.

The Huntsman EO reactor is built as a shell and tube heat exchanger with one pass shell. The cross-flow is obtained by 5 segmental baffles and 6 intermediate doughnut baffles. Tubes are arranged in a triangular pitch.

3.5.1 Energy balance on catalyst pellet

The reactions occur on the catalyst surface. The catalyst temperature is assumed to be homogeneous; therefore the heat produced can just accumulate or transfer to the gas.

The general energy balance in the dynamic case is:

$$
\rho_{cat} \times C_{p_{cat}} \times \frac{\partial T_{cat}}{\partial t} = \alpha_{cat} \times S_{VP} \times (T_{gas} - T_{cat}) \\
+ \left( \sum_{i=1-4} \frac{v_j}{v_{BASE(i)}} \times r_i \times \Delta H_i \right) \times \frac{1 - \text{void}}{\text{void}}
$$

Equation 3-17

where $C_{p_{cat}}$ is the heat capacity of the solid and $\rho_{cat}$ is the density of the pellets.

The density of the pellets is calculated from catalyst pellet packing data received from plant [7]:

Bulk density = 0.88 g/cm$^3$
Packing density = 0.70 (note: this is the packing density in the delivery cylinders, not in the tubes)

\[ \rho_{\text{cat}} = \frac{0.88}{0.77} = 1.26 \quad \text{g/cm}^3 = 1260 \quad \text{Kg/m}^3 \]

### 3.5.2 Energy balance on gas side

The gas in the tubes exchanges heat with both the catalyst pellets and the inner surface of the tube wall.

\[ \rho_{\text{mol, gas}} \times C_p_{\text{gas}} \times \frac{\partial T_{\text{gas}}}{\partial t} = \rho_{\text{mol, gas}} \times C_p_{\text{gas}} \times V_{\text{gas}} \times \frac{\partial T_{\text{gas}}}{\partial Z} \]

\[ + \alpha_T \times S_{\text{yt}} \times (T_{\text{wall,l}} - T_{\text{gas}})_\text{void} + \]

\[ \alpha_c \times S_{\text{yp}} \times (T_{\text{cat}} - T_{\text{gas}})_\text{void} \]

Equation 3-18

where \( V_{\text{gas}} \) is the real gas velocity in the catalyst-filled tube (m/s), \( S_{\text{yt}} \) is the outer tube surface area per inner volume of tube and \( e \) is the void fraction of the bed.

\[ S_{\text{yt}} = D_o \times \pi \times 1/(D_o^2/4 \times \pi \times 1) \]

Equation 3-19

### 3.5.3 Energy balance on tube wall

The outer tube wall temperature is dependent on the heat transfer to the tube inner surface, which is characterised by \( \alpha_{\text{wall}} \), and the heat transfer of the shell side (\( \alpha_s \)).

\[ \rho_{\text{wall}} \times C_p_{\text{wall}} \times \frac{\partial T_{\text{wall,o}}}{\partial t} = \alpha_s \times (4 \times D_o)/(D_o^2 - D_i^2) \times (T_{\text{wall,o}} - T_{\text{wall,l}}) \]

\[ - \alpha_{\text{wall}} \times (4 \times D_o)/(D_o^2 - D_i^2) \times (T_{\text{wall,o}} - T_{\text{wall,l}}) \]

Equation 3-20

The inner side of the tube wall exchanges heat with the outer side of the tube wall as well as the gas where \( \alpha_T \) is the tube side heat transfer coefficient.
\[ \rho_{\text{wall}} \times C_{\text{p,wall}} \times \frac{\partial T_{\text{wall,j}}}{\partial t} = \alpha_{\text{wall}} \times (4 \times D_O)/(D_O^2 - D_i^2) \times (T_{\text{wall,O}} - T_{\text{wall,j}}) - \alpha_T \times (4 \times D_i)/(D_O^2 - D_i^2) \times (T_{\text{wall,j}} - T_{\text{gas}}) \]  

\textbf{Equation 3-21}

\subsection*{3.5.4 Energy balance on cooling oil}

The oil temperature is dependent on the heat transfer to the outer surface of the tube wall, which is characterised by \( \alpha_S \), and the heat loss from the shell to the surface, \( U_{\text{loss}} \).

\[ \rho_{\text{oil}} \times C_{\text{p,oil}} \times A_{e,c} \times \frac{\partial T_{\text{oil}}}{\partial t} = G_{\text{oil}} \times C_{\text{p,oil}} \times \frac{\partial T_{\text{oil}}}{\partial Z} + \alpha_s \times (\pi \times N_T \times D_O) \times (T_{\text{wall,O}} - T_{\text{oil}}) + U_{\text{loss}} \times (\pi \times D_S) \times (T_{\text{amb}} - T_{\text{oil}}) \]  

\textbf{Equation 3-22}

where \( G_{\text{oil}} \) is the mass-flow of cooling oil, \( C_{\text{p,oil}} \) is the heat capacity of the oil, \( T_{\text{oil}} \) is the temperature of the cooling oil, \( z \) the length in the tube direction (perpendicular to the cross-flow of the oil), \( A_{e,c} \) is the cross area (in the tube direction) of the reactor volume taken up by oil, \( T_{\text{wall,O}} \) the temperature of the outer surface of the tube wall and \( T_{\text{amb}} \) is the ambient temperature (typically 25°C).

\[ A_{e,c} = D_S^2 \times \pi / 4 - N_T \times D_O^2 \times \pi / 4 \]  

\textbf{Equation 3-23}

\subsection*{3.6 Pressure Drop}

The pressure drop over the reactor is based on the plant data, which is around 21 psi or 1.45 bar for normal operating conditions. The Ergun equation for pressure drop in a packed bed is [6]:

\[ \frac{dP}{dL} = -G/(\rho \times D_p) \times (1 - \phi) \times \phi^3 \times [150 \times (1 - \phi) \times \mu / D_p + 1.75G] \]
If the physical constants at normal conditions are substituted, we get:

\[ \frac{dP}{dL} \propto -G \times (0.01155 + 1.75G) \]

Since the gas flow \( G \approx 0.6 \text{ kg/m}^2 \) this relation is further simplified to:

\[ \frac{dP}{dL} \propto -G^2 \]

The reactor length is 7.35 meter, the normal operating pressure drop is 1.45 bar, thus the expression for the total pressure could be written:

\[ \frac{dP}{dZ} = -\frac{1.45}{L_R} \times \left( \frac{F_{T,i}}{F_{T,0}} \right)^2 \tag{Equation 3-24} \]

where \( L_R \) is used as the length of the reactor, \( F_T \) the total mole flow and \( F_{T,0} \) is the inlet mole flow.

### 3.7 Initial and Boundary Condition

The above hyperbolic partial differential Equation 3-10 to Equation 3-22 are subjected to the following initial and boundary equation:

At \( t = 0 \) and \( z \in [0, L_{reactor}] \),

\[ F_i = F_i^0(z), \quad T_{cut} = T_{cut}^0(z), \quad T_{gas} = T_{gas}^0(z), \quad T_{oil} = T_{oil}^0(z), \]
\[ T_{wall,i} = T_{wall,i}^0(z), \quad T_{wall,o} = T_{wall,o}^0(z) \tag{Equation 3-25} \]

At \( z = 0 \) and \( t > 0 \),

\[ F_i = F_{i,\text{in}}(t), \quad T_{gas} = T_{gas,\text{in}}(t), \quad T_{oil,\text{in}} = T_{oil}(t), \quad P = P_{\text{in}}(t) \tag{Equation 3-26} \]
The initial conditions for the system are obtained from the steady-state solution of the system.

### 3.8 Heat Transfer Coefficient

The heat transfer coefficients on the relevant energy balance equations affect by several parameters. For natural convection cases, the temperature distribution is the governing parameter, while for forced convection problems; the fluid velocity is the dominant one. For both of these conditions, the geometry of the problem plays a significant role in determining the final value.

#### 3.8.1 Heat transfer between catalyst pellet and gas

Reaction 2 and 3 are strongly exothermic and reaction 1 is moderate exothermic. The catalyst pellets in an ethylene oxide reactor have specific properties to handle and reduce the negative effects encountered with strongly exothermic reactions.

The support alumina is used due to its very good heat transfer. The catalyst is surface or subsurface (all the active silver is placed closed to the outer surface of the catalyst) to avoid temperature gradients in the pellet (which is detrimental to the selectivity). The catalyst density is far from technically maximised since the cooling oil heat exchange sets the constraint.

With surface or subsurface catalyst the intra pellet diffusion can be neglected. For the heat transfer coefficient, $\alpha_{cat}$, a correlation of the heat transfer in terms of the Chilton Colburn j-factor, $j_h$, for 1 inch alumina balls by Hougen et al. is used [8]:

$$j_h = 0.6 \times \text{Re}^{0.41}$$  \hspace{1cm} \text{Equation 3-27}

where:

$$j_h = \alpha_{cat} / (Q \times C_f) \times \text{Pr}^{2/3}$$  \hspace{1cm} \text{Equation 3-28}

and,

Shahla Aryana
Re = \frac{Q}{(\alpha \times \mu_{\text{gas}})}

Where \( C_f \) is the specific heat of the gas, \( Q \) is the mass flow rate per unit cross sectional area of empty tubes, \( \alpha \) is the surface area of sphere per unit volume of bed and \( \mu \) is the gas viscosity. The calculations of Reynolds number, Re, in the reference is based on mass flow (\( Q \)) but in the model mole flow (\( Q_{\text{mol}} \)) is used:

\[ \text{Re} = F \times M/(\alpha \times \mu) \]

To calculate \( Q_{\text{mol}} \) the empty tube cross sectional inner area \( A_{\text{c,t}} \) is used:

\[ Q_{\text{mol}} = F_T/A_{\text{c,t}} \]

\( \alpha \) is based on the specific surface area \( S_{v,p} \) for 6 mm cylinder pellets [9]:

\[ S_{v,p} = 945 \ m^2/m^3 \ \text{particle} \]

\[ a = S_{v,p} \times (1 - e) = 520 \ m^2/m^3 \ \text{bed} \]

### 3.8.2 Shell side heat transfer coefficient

The calculation of the shell side heat transfer in a multi tubular reactor is not straightforward due to the complex flow conditions and many different approaches can be found in the literature. The method used here was developed by Bell-Delaware in 1963 [10] in which correction factors were introduced for the following elements:

1. Leakage through the gaps between the tubes and the baffles and the baffles and the shell, respectively (\( J_L \)).

2. Bypassing of the flow around the gap between the tube bundle and the shell (\( J_B \)).

3. Effect of the baffle configuration (\( J_C \)).
The method first calculates the ideal cross-flow heat transfer coefficient \( (\alpha_c) \) from the following equation:

\[
\alpha_c = \frac{Nu \times \lambda_{oil}}{D_o} = (0.273 \times Re^{0.653} \times Pr^{0.34}) \times \frac{\lambda_{oil}}{D_o}
\]

**Equation 3-29**

where:

\[
Re = \rho_{oil} \times V_{max} \times D_o / \eta_{oil}
\]

\[
Pr = \frac{C_P_{oil} \times \eta_{oil}}{\lambda_{oil}}
\]

The next step is to calculate the correction factors. The calculations are shown in Appendix B.

The shell side heat transfer coefficient is then given by:

\[
\alpha_s = \alpha_c \times J_c \times J_L \times J_B
\]

**Equation 3-30**

### 3.8.3 Tube side heat transfer coefficient

For the tube side heat transfer, a modified expression by Thoenes and Kramers is used, presented by J. Beek [11]:

\[
\alpha_T = \frac{Nu \times \lambda_{gas}}{d_p} = (2.58 \times Re^{1/3} \times Pr^{1/3} + 0094 \times Re^{0.8} \times Pr^{0.4}) \times \frac{\lambda_{gas}}{d_p}
\]

**Equation 3-31**

where:

\[
Re = \rho_{gas} \times V_{gas} \times d_p / \eta_{gas}
\]

\[
Pr = \frac{C_P_{gas} \times \eta_{gas}}{\lambda_{gas}}
\]

### 3.8.4 Tube wall heat transfer

The wall resistance depends on the inside and outside fouling factor and wall conductivity could be written as follow:
$1/\alpha_{wall} = F I_o + D_o \times \ln(D_o/D_I)/(2K_w) + D_o/D_I \times F I_I \quad \text{Equation 3-32}$

The value of the conductivity of the tube wall ($K_w$) is 0.0423 kW/m K [7]. The outside fouling factor, $F I_o$, and the inside fouling factor, $F I_I$, are set to 8.6e-5 m $K / K_w$ based on the plant design data.

### 3.9 HEAT OF REACTIONS

The heat of reactions is assumed to be independent of the pressure. Furthermore it is assumed that the heat of reactions is a linear function of the temperature. This gives the following heat of reaction:

\[
\Delta H_R = \Delta H_{R,298} + C_{p,i} \times dT_s \approx \Delta H_{R,298} + \Delta C_p \times \Delta T_s
\]

\[
\Delta C_{p,i} = \sum_{i=1-3} \frac{V_j}{V_{BASE(i)}} \times C_{p,i}
\]

\[
\Delta C_{p,1} = C_{p,C_2H_4O} - C_{p,C_2H_4} - 0.5 \times C_{p,H_2O}
\]

\[
\Delta C_{p,1}(25 \rightarrow 208^\circ C) = -7.405 \quad \text{kJ / kmol K}
\]

\[
\Delta C_{p,1}(25 \rightarrow 257^\circ C) = -6.66 \quad \text{kJ / kmol K}
\]

linear interpolation ⇒

\[
\Delta C_{p,1} = -7.405 + (T_s - 208) \times 0.0152
\]

and,

\[
\Delta C_{p,2} = 2 \times C_{p,CO_2} + 2 \times C_{p,H_2O} - C_{p,C_2H_4} - 3 \times C_{p,O_2}
\]

\[
\Delta C_{p,2}(25 \rightarrow 208^\circ C) = 7.31 \quad \text{kJ / kmol K}
\]

\[
\Delta C_{p,2}(25 \rightarrow 257^\circ C) = 6.426 \quad \text{kJ / kmol K}
\]
linear interpolation ⇒

\[ \Delta C_{p,2} = 7.31 + (T_s - 208) \times 0.0179 \]

The heat of reactions are therefore for the two first reactions with the standard heat of reactions from Vargaftik [7]:

\[ \Delta H_{R,298,1} = -104,600 \text{ kJ/kmol } C_2 H_4 \]
\[ \Delta H_{R,1} = -2 \times (104,600 + \Delta C_{p,1} \times \Delta T_s) \text{ kJ/kmol } O_2 \]

\[ \Delta H_{R,298,2} = -1,326,600 \text{ kJ/kmol } C_2 H_4 \]
\[ \Delta H_{R,1} = (-1,326,600 + \Delta C_{p,2} \times \Delta T_s) / 3 \text{ kJ/kmol } O_2 \]

Equation 3-33

Equation 3-34

Then reaction 1+ reaction 3 = reaction 2 we can calculate the heat of reaction of 3 as:

\[ \Delta H_{R,3} = 3 \times \Delta H_{R,2} - 0.5 \times \Delta H_{R,1} \text{ kJ/kmol } C_2 H_4 O \]

Equation 3-35

3.10 Reactor Parameters

The reactor length, \( L_R \) (tube length) is found from the supplied drawings to be 7.35 meter.

The void fraction \( e \) is assumed to be 0.45. The assumption is based on similar packing data (20 mm tube and 4.5 mm cylinders instead of actual 21 respectively. 5 mm dimensions).

The catalyst pellets are cylindrical with a diameter and length of 5 mm.

The gas constant \( R \) is 8.314 (kPa m³/kmol K).
3.11 PHYSICAL PROPERTIES

The heat capacities, viscosities and thermal conductivity are based on data from Vargaftik [12]. The data were approximated to a linear function of pressure and temperature in the actual range of the reactor conditions by linear regression. Excepted are the cooling oil physical properties which taken from the data provided by "Mobil Oil Australia" [13]:

**Heat capacities**

\[
C_{p,C_2H_4} = (0.0033 \times T_{gas} + 0.0057 \times P + 1.4629) \times 28.0 \text{ kJ/kmol °C}
\]
\[
C_{p,O_2} = (0.0003 \times (T_{gas} + 273) + 0.0004 \times P + 0.837) \times 32.0 \text{ kJ/kmol °C}
\]
\[
C_{p,C_2H_4O} = (0.0027 \times (T_{gas} + 273) + 0.000275 \times P + 0.3044) \times 44.0 \text{ kJ/kmol °C}
\]
\[
C_{p,CO_2} = (0.0006 \times T_{gas} + 0.0021 \times P + 0.7004) \times 44.0 \text{ kJ/kmol °C}
\]
\[
C_{p,H_2O} = (-0.0009 \times T_{gas} + 0.0155 \times P + 2.292) \times 18.0 \text{ kJ/kmol °C}
\]
\[
C_{p,N_2} = (0.0002 \times (T_{gas} + 273) + 0.0002 \times P + 0.9714) \times 28.0 \text{ kJ/kmol °C}
\]
\[
C_{p,Ar} = 20.77 \text{ kJ/kmol °C}
\]

\[
C_{p,oil} = 1/((0.860^{0.5})*(1.6844 + 0.003391*T_{oil})) \text{ kJ/kg °C}
\]

**Viscosities**

\[
\mu_{C_2H_4} = (0.2444 \times T_{gas} + 0.4498 \times P + 97.988) / 28E7 \text{ kmol/m s}
\]
\[
\mu_{O_2} = (0.3995 \times (T_{gas} + 273) + 0.1028 \times P + 100.18) / 32E7 \text{ kmol/m s}
\]
\[
\mu_{C_2H_4O} = (0.267 \times (T_{gas} + 273) + 0.194 \times P - 33.0) \text{ kJ/mol/m s}
\]
\[
\mu_{CO_2} = (0.352 \times T_{gas} + 0.147 \times P + 152.4) / 44E7 \text{ kmol/m s}
\]
\[
\mu_{H_2O} = (0.4213 \times T_{gas} + 0.0392 \times P + 152.4) / 18E7 \text{ kmol/m s}
\]
\[
\mu_{N_2} = (0.0002 \times (T_{gas} + 273) + 0.0002 \times P + 2.292) / 28E7 \text{ kmol/m s}
\]

\[
\mu_{oil} = 0.001 \times e(-4.3737 + 1990.13/(T + 273)) \text{ Ns/m}^2
\]
**Thermal Conductivities**

\[ \lambda_{\text{C}_2\text{H}_4} = (0.1444 \times T_{\text{gas}} + 0.0506 \times P - 22.269) \times 10^{-6} \text{ kW/m °C} \]
\[ \lambda_{\text{O}_2} = (0.0696 \times (T_{\text{gas}} + 273) + 0.0693 \times P + 4.685) \times 10^{-6} \text{ kW/m °C} \]
\[ \lambda_{\text{C}_2\text{H}_4\text{O}} = (0.00012 \times (T_{\text{gas}} + 273) + 0.00014 \times P + 4.685) \times 10^{-6} \text{ kW/m °C} \]
\[ \lambda_{\text{CO}_2} = (0.077 \times T_{\text{gas}} + 0.0154 \times P - 6.169) \times 10^{-6} \text{ kW/m °C} \]
\[ \lambda_{\text{H}_2\text{O}} = (0.11 \times T_{\text{gas}} + 0.12 \times P + 9.557) \times 10^{-6} \text{ kW/m °C} \]
\[ \lambda_{\text{N}_2} = (0.0573 \times (T_{\text{gas}} + 273) + 0.0203 \times P + 9.557) \times 10^{-6} \text{ kW/m °C} \]

\[ \lambda_{\text{oil}} = 1/0.86 \times (0.1175 - 6.286E-5 \times T_{\text{oil}}) \text{ kJ/kg °C} \]

**Oil density**

\[ \rho_{\text{oil}} = 860 - 0.65 \times T_{\text{oil}} \text{ kg/m}^3 \]

Temperature T is in °C and pressure P is in bar.

As it stated earlier, the reactor effluent is cooled in the gas-gas heat exchanger, compressed, and sent to the scrubber where EO is absorbed by the lean water and the remaining EO in the stream enters the cycle gas system and finally back to the reactor. The remaining EO in stream as an inlet to the reactor has a major effect on the reactor selectivity and overall product quality. Therefore, to analyse the effect of the scrubber operating conditions on the EO production process and in particular on the EO reactor, the EO scrubber needs to be modelled. The detail modelling of the EO scrubber, gas-gas heat-exchanger and hot oil cooler will be discussed in Chapter 5.

### 3.12 Computational Tools

Detailed modelling of the EO process is a complex undertaking not only because there are numerous unit operations present but also because of the complexity in their dynamics. In particular the EO reactor represents a difficult modelling task because of the highly non-linear nature of the model equations.
The simulation tools for the representation of the units of the EO plant have to be selected with care. An essential requirement is that any tool must have a software interface for the communication with an external client which will be discussed in chapter 5. It should further provide a powerful and expressive modelling language to represent the model in its full detail. The model should be efficiently solved by means of built-in algorithms with a user-specified accuracy. Other factors (user-friendly interface, presence of property databank, etc.) should be considered as well. It should also be accounted for whether the model is already available within the tool as a part of its model library or as a result of previous investigation.

On the conceptual level, and consequently on the numerical level, two approaches historically conflict in process modelling and simulation: the so-called model-oriented approach and the so-called equation-oriented approach.

The model-oriented approach is used in the majority of commercial software, such as Aspen Plus, PRO/II, HYSYS and ProSim. In this approach, the basic element in building the model of the process is the unit operation model, called module. This corresponds to the classical, and perhaps obsolete, view of a flowsheet. To model this process, the user selects the elementary standard modules from the simulator library, provides design and operating parameters and connects them by streams corresponding to material, energy and information flows circulating between units of the real process. The flowsheet is seen as a graph where the nodes are the modules and the arcs the streams. Modules have been developed by experts in modelling and the end user cannot really insert his own knowledge and the specificity of his process into them. The basic element for decomposing the process, the unit operation, corresponds to too large a scale and does not allow variety. These simulators suffer from their generality which, after having been their strong point, has proved to be ill-adapted to the present demand.

The equation-oriented approach is used in most dynamic simulators, such as gPROMS. These equation-based simulators appear above all as differential algebraic equation (DAE, differential algebraic equation) numerical solvers in an environment offering an advanced modelling language. They are renowned for their numerical
efficiency. Unfortunately, their unit-oriented model libraries are poor, and the user has to play the role of modeller. In the equation-oriented approach, the basic elements for building the process model are the equation and the variable, that is to say a numerical view of modelling. This numerical view limits access to these simulators to a small group of experts and not to process engineers.

Of the four units involved, the models of the gas-gas heat exchanger, the EO scrubber and the hot oil cooler consist of only standard balance and phase equilibrium equations. They can be represented by predefined models (model-defined software).

Hyprotech HYSYS has been chosen as a modelling tool for these units. HYSYS is a simulation and optimisation product family of Hyprotech Ltd. HYSYS is an integrated steady state and dynamic simulator. HYSYS contains a comprehensive model library for the standard process equipment as well as an extensive property databank with physico-chemical properties.

The model of the reactor, however, is neither available from the HYSYS model library, nor can they be easily implemented there. Hence, other tools need to be considered for its implementation. For the implementation of the EO reactor no dedicated simulator is known. Therefore, the process modelling tool gPROMS was selected in which the model can be written in its mathematical representation.

gPROMS is a advanced general purpose process modelling, simulation and optimisation software used for model-based decision support in process, product design and process operation. gPROMS is a suitable package for solving distributed parameter systems and has a simple and friendly language with strong numerical capabilities. It is the simulation language of choice because it also offers others facilities for process systems engineering, namely parameter estimation using the gEST function, dynamic optimisation, using the gOPT function, open architecture for communication with external objects and process, using gFOI and gFPI respectively. The PSE Advanced User Guide [14] offers detailed descriptions and instruction on these facilities.

Shahla Aryana
3.13 SUMMARY

In this chapter, a detailed treatment of the mathematical modelling of EO reactor is presented with the emphasis on the importance of the inhibiting effect of EDC on the reaction rates. The partial and total oxidation of ethylene as well as the oxidation of ethylene oxide are considered. The calculation of the shell side heat transfer is carried out based on the Bell-Delaware method [10]. For the tube side heat transfer and the heat transfer coefficient for catalyst pellet, respectively, a modified expression by Thoenes and Kramers and a correlation for the heat transfer based on the Chilton Colburn j-factor for 1 inch alumina balls developed by Hougen et al [8] are used. Pressure drop estimation is based on plant data, correlated as a function of the gas flow rate using Ergun equation for packed beds. The set of nonlinear kinetic expressions were coupled with heat and mass conservation equations and variable physical properties along the reactor length.

In the next chapter, the solution methods of the model are investigated with a focus on the discretisation technique as the solution choice. This was investigated and the model was subsequently solved using the modern modelling software gPROMS. The model prediction is validated against data from an industrial ethylene oxide reactor.
3.14 BIBLIOGRAPHY


13- Communications with Mobil Oil Australia, October (2003).


Chapter 4

4 Simulation and Model Validation

In this chapter, some aspects of the model validation experiment definition, the validation results and a critical examination of the outcome of the validation are presented.
4.1 INTRODUCTION

Simulation and modelling are powerful tools to understand complex physical systems. Simulation models of complex physical systems have been developed for years, generally using analytical methods. Recent advances in computer technology have influenced simulation techniques to become an effective approach to understand physical systems. Furthermore, modelling is an important step toward optimizing the operation of a given process.

The importance of ethylene oxide in industry has led to many investigations being carried out. However, most researches are focused on a better understanding of the reaction mechanisms and to improve the catalyst activity and selectivity.

The main purpose behind our mathematical modelling of EO units is to describe the dynamic behaviour of the units and use these models in simulation, sensitivity analysis, steady-state and dynamic optimisation. Mechanistic process models seem to be vital for the success of these model-based activities. Qualitative and quantitative knowledge gained from these advanced tools will ultimately lead to a continuous improvement of competitiveness, meeting higher productivity goals and tighter quality specifications.

In Chapter 3, the detailed mathematical model for EO reactor was presented. The model comprises coupled sets of algebraic equations and non-linear partial differential equations in both time and axial dimension.

In this chapter, the method of model is investigated with a focus on the discretisation technique as the solution choice. This is investigated and the model is subsequently solved using the modern modelling software, gPROMS. The simulation results are presented and benchmarked against the plant data.
4.2 gPROMS

General-purpose equation-oriented modelling (gPROMS) languages were originally conceived to solve lumped parameter systems (DAE systems) exclusively [1]. Soon after, they were extended to support the definition of distributed parameter systems (integro-partial differential equations systems, IPDAE) of regular geometry [2].

Now, these equation-oriented declarative modelling languages that allow the representation of general IPDAE systems subject to general initial and boundary conditions. In addition, the granularity, order and form of discretisation of the number distribution domains can be defined with great flexibility. Hence, from the perspective of representing and implementing complex mathematical models, state-of-the-art equation-oriented modelling languages assist the modelling process of systems of both lumped and distributed characteristics satisfactorily.

As stated in the previous chapter, the reactor model needs to be solved efficiently in an equation-oriented software environment. Process-engineering softwares such as gPROMS were originally developed as high-level equation-oriented declarative modelling tool for the steady-state and dynamic simulation of process systems. High-level indicates that the language is situated at a higher hierarchy than conventional procedural or object-oriented programming languages.

4.3 Model Solution

Spatial variations of the fundamental quantities cannot be neglected in a tubular reactor of the characteristics of a continuous EO reactor, and must be accounted for. When confronted with this situation, two mainstream approaches may be considered: a continuous or a discrete mathematical formulation. The first one will result in a distributed parameter system (a set of partial differential and algebraic equations, or PDAEs), where properties are homogeneous in the neighborhood of a differential volume element around a particular elevation of the reactor. The second will result in a lumped parameter system (a set of ordinary differential equations, DAEs), since properties are assumed to be homogeneous at a finite volume. The decision between
distributed parameter system and a lumped parameter system approximation is critical and has a significant effect on the modelling process.

A significant number of unit operations in chemical or biochemical process take place in distributed systems in which properties vary with respect to one or more spatial dimensions as well as time.

As seen in previous chapter, our reactor model is distributed in both time and axial dimension. The EO reactor model is required to be solved efficiently and accurately so as to allow advanced optimization to be implemented. Partial differential equations are the main means of providing mathematical models with distributed system along the size as well as time. Generally these models must be solved numerically.

Conventionally, the numerical solution of distributed parameter systems requires the spatial discretisation of the partial differential equations, PDEs, (or IPDAEs, in general) into a coupled set of ODEs, and algebraic equations, AEs (i.e. a set of DAEs). The later can be solved by a suitable numerical integration routine.

The advantage of this approach is that the grid spacing can be refined in response to a spatial gradient of the system. An immediate consequence of this is a better trade-off between the size of the resulting DAE system and solution accuracy. Equation oriented declarative languages such as gPROMS make use of the method-of-lines technique for discretisation of the distributed parameter system. Although the method of- lines family of numerical methods allows for different schemes of discretisation and different orders of curvature approximation, it is limited to uniformly spaced grids.

As a consequence of this, the trade-off between size of the system and solution accuracy is more subtle for these discretisation techniques. Non-uniform grids could be incorporated by means of a hierarchical sub-model decomposition approach, but at the expense of a greater modelling effort and more complicated model implementation.
Using discretised approach, the typical unsteady state model of the EO reactor comprises the following number of variables and equations at every time step:

**Variables**

<table>
<thead>
<tr>
<th>Known</th>
<th>61</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unknown</td>
<td>4560</td>
</tr>
</tbody>
</table>

**Model Equations:**

<table>
<thead>
<tr>
<th>Differential</th>
<th>399</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algebraic</td>
<td>4161</td>
</tr>
<tr>
<td>Initial condition</td>
<td>399</td>
</tr>
</tbody>
</table>

### 4.4 Model Evaluation

The purpose of an EO reactor is to produce ethylene oxide by the partial oxidation of ethylene. Since the partial oxidation of ethylene is accompanied by simultaneous reactions such as total oxidation of ethylene as well as oxidation of ethylene oxide, the most important variable for the assessment of the operational and economic performance of an EO plant are selectivity and work-rate.

The selectivity and the work-rate definitions we used are given as follows:

\[
Selectivity\% = \frac{EO\ produced}{Total\ ethylene\ consumed} \times 100 \quad \text{Equation 4-1}
\]

\[
Work - rate = EO\ produced \quad (T/\text{day}) \quad \text{Equation 4-2}
\]

The data required for this study was obtained from Huntsman Corporation Australia. The initial estimates of the model parameters in the ethylene oxide reactor model were calculated from the correlation available in the open literature. But it was necessary to validate the model against the industrial data to closely represent the industrial process.

_Shahla Aryana_
4.4.1 Input data

The data supplied from the industry could be classified into two categories: forecast data from the catalyst vendor and the plant operating data.

Forecast data from the catalyst vendor

The forecast data provided by the catalyst vendor comprise the optimal operational condition of ethylene oxide reactor based on the supplied catalyst. These data were used to evaluate the reactor model in early stage as well as estimate the catalyst deactivation parameters. The rate expressions (kinetics constants) are corrected based on the data from the catalyst vendor and using a modified dynamic model in gPROMS.

As stated in the previous chapter, the catalyst used in the reactor deactivates over the course of operation due to impurities in the feed and the catalyst sintering. The catalyst vendor suggested a rise in oil inlet temperature from the start of run (SOR) till the end of run (EOR) to compensate for the loss in catalyst activity under conditions in practice (Figure 4-1). Nevertheless, the selectivity would be decreased over the period of catalyst life time (Figure 4-2).

![Figure 4-1- The forecast data from catalyst vendor for oil inlet temperature during the catalyst life time](image)
Figure 4-2: The forecast data from catalyst vendor for selectivity during the catalyst lifetime.

**Plant operating data and initial condition**

The plant data contained the information about the following operating variables from the start of operation (fresh catalyst) to the end of operation of the ethylene oxide reactor:

1. Gas and coolant inlet flow rate.
2. Inlet and outlet composition (mol% of ethylene, oxygen, ethylene oxide and carbon dioxide).
3. Ethylene dichloride (EDC) flow rate.
4. Gas and coolant oil temperature (inlet and outlet).
5. Reactor pressure.
6. Selectivity and work-rate

The inlet data (comprising oil inlet flow rate and temperature, gas inlet flow, composition and temperature and EDC flow rate) used as input for the model.
Typically, a subset of input process variables was used to imitate the plant’s dynamic input behavior. Measurements of disturbances and manipulations were averaged using linear interpolation.

In general, a 3 years plant data set was used in model validation. This gives transparency to the entire validation procedure because the entire pool of process data available is used in this task.

To validate the model for 3 years operating time, the following variables were kept constant.

- Reactor pressure
- Gas inlet temperature
- Oil flow rate
- Water and argon inlet mole fraction

However, the others were changed dynamically. When plant data was unavailable or inconsistent (due to sensor failure or malfunction, for example), the simulation experiment was run with the modified values.

The inlet data used as input data to the model are presented in Appendix A.

4.4.2 Model parameter

A base case operating condition from the catalyst vendor data is selected at which the catalyst activity is assumed to be unity. The input variables to the parameter estimation are:

1. Gas and coolant inlet flow rate.

2. Gas inlet composition (mol% of ethylene, oxygen, ethylene oxide and carbon dioxide).

3. Ethylene Dichloride (EDC) flow rate.
4. Gas and coolant oil inlet temperature.

5. Reactor pressure.

Following data were compared between the model prediction and the forecast data:

1. Selectivity and work-rate

2. Gas and oil outlet temperature

3. Gas outlet composition

4.4.2.1 Correlation factors

The initial estimate of the model parameters in the ethylene oxide reactor model are calculated from the correlation available in the open literature. To ensure studying the issues faced in the industrial practice, it is necessary to benchmark the model against the industrial data to closely represent the industrial process.

To obtain a reasonable fit at the base case operating point, the rate expressions need to multiply by correlation factors (C(i)). The correlation factors are estimated in such a way for a given input variable of the base case data (from the catalyst vendor), the errors between the model predictions and the forecast data are minimised.

After calculating the correlation factor using the catalyst vendor, to ensure the reliability of model to predict the real process, the model predictions were validated against the EO plant data for first two month of operating time which the catalyst activity could be assumed as unity. The model prediction for the selectivity and work-rate was benchmarked against the data. The model showed the satisfactory prediction of the process data.

4.4.2.2 Catalyst deactivation parameters

As stated in chapter 3, the catalyst deactivation was modelled as a function of operating time and catalyst temperature which effects the first and second reaction.
The forecast data from the catalyst vendor (Figure 4-1 and Figure 4-2) were used to evaluate the catalyst deactivation parameters.

The following parameters were estimated:

- \( \alpha_{a_1} = 0.797 \quad K_{d,1} = 1.427 \times 10^{-3} \text{ (1/s)} \quad E_{a,1} = 1377 \text{ (K)} \)
- \( \alpha_{a_2} = 8.7 \times 10^{-2} \quad K_{d,2} = 5.13 \times 10^{-4} \text{ (1/s)} \quad E_{a,2} = 1462 \text{ (K)} \)

The temporal profiles of \( a_1 \) and \( a_2 \), the catalyst deactivation functions, introduced respectively in the partial and complete oxidation reaction rates of ethylene are illustrated in Figure 4-3 for the period of three years.

![Figure 4-3- Catalyst deactivation for period of three years operating time](image)

### 4.5 Model Validation

Of all the individual components of the industrial modelling process [5], conceptual modelling, model representation, and model validation are probably the most critical tasks to the final outcome of the entire process. Since the remaining steps are less well-defined and depend on the background and preferences of the model developer and sophistication of the modelling tools, they are of less relevance to the research community and industry.
In light of these facts, and given the intricacy of the industrial modelling process, this section will focus on the validation phases since the model validation is a mandatory task of the modelling process.

In theory, a validation procedure of a composite model should start from the bottom of the model hierarchy and progress towards the top, comparing the elementary models with plant data.

In practice, the fundamental model would usually be validated at a high level of the model hierarchy by exploiting the availability of process measurements from the plant data historian. This validation approach has been adopted in this thesis.

In EO reactor, one of the main manipulated variables is the cooling oil temperature. Cooling oil temperature is the key for process safety. For instance high cooling oil temperatures results in run away condition in the reactor. However, low oil temperature result the poor condition and low selectivity.

For better understanding of the reactor function and the model validity, the profiles of oil and gas temperature inside the reactor were considered. The results are shown in Figure 4-4 and Figure 4-5, respectively.

As observed, during the first half meter of the 7.35 meter long tubes, the model shows a significant rise in the gas temperature and slightly decrease in the oil temperature. The first half meter of the tubes have no catalyst which means no reaction, so, just heat exchange between the oil and gas take place. After this, a steady and slow increase in the oil temperature profile along the bed follows is observed with a sharp increase in the gas temperature because of the highly exothermic reactions.
Figure 4-4- The oil temperature profile along the reactor

Figure 4-5- The gas temperature profile along the reactor
Figure 4-6 shows the EO profile along the reactor. EO builds up as reactions take place and gas temperature increases.

The reactor temperature is one of the important variables that need to be predicted since it has a major effect on the reactor performance, catalyst aging and safety. Since no plant data are available for the catalyst temperature, the plant data for the oil and gas outlet temperature were used to validate the model. Figure 4-7 and Figure 4-8 show the oil and gas outlet temperatures of the model prediction against the plant data during 3 years of reactor operation. As seen, the model predictions are very good and follow very closely the transition during plant operation. Some discrepancies exist due to error in the plant data or error related to the discrepancy in the model's input data compare to the real data.

As stated previously, the oil inlet temperature is raised to compensate the loss in catalyst activity; consequently, rise in the oil and gas outlet temperature are expected from the start of run till the end of run (Figure 4-7 and Figure 4-8).
Figure 4-7- Comparison of the outlet oil temperature of the model against the plant data during 3 years

Figure 4-8- Comparison of the outlet gas temperature of the model against the plant data during 3 years

The other important parameters are selectivity and work-rate. These two parameters represent the EO reactor efficiency and product rate, respectively. Comparisons of the selectivity and the work-rate between the model prediction and the plant data are shown respectively in Figure 4-9 and Figure 4-10. The selectivity is decreasing over the period of catalyst life time due to loss in catalyst activity and the work-rate changes are related to the market demand.
In overall, the model predictions for the selectivity and the work-rate against the plant data are satisfactory. Whenever the plant data for the input variables were available and consistent, the model predictions were very close. However, due to unavailability or inconsistently of the plant data, the modified values were used; e. g. the linear interpolation technique was used to predict missing data. These modified values could cause a significant disagreement between the model prediction and the plant data. For example, in most of the time the EDC level which has an enormous effect on the selectivity and work-rate were not measured properly and the data were not reliable (refer to Appendix A for the input plant data).
As discussed earlier, the kinetic constants and the kinetic rates used in this model are empirical. Due to the empirical nature, they have some boundaries and limitations, which could cause error on the model predictions.

The comparison of gas outlet mole fractions for ethylene, oxygen, EO and $CO_2$ of the model prediction against the plant data are shown in Figure 4-11 to Figure 4-14, respectively.

**Figure 4-11** - Comparison of the outlet ethylene mole fraction of the model against the plant data during 3 years

**Figure 4-12** - Comparison of the outlet oxygen mole fraction of the model against the plant data during 3 years
**Figure 4-13** - Comparison of the outlet EO mole fraction of the model against the plant data during 3 years

**Figure 4-14** - Comparison of the outlet CO₂ mole fraction of the model against the plant data during 3 years

### 4.6 Discussion

The following equation was used to calculate the statistics that will serve as a guide to interpret the result of the model validation.
\[ E_{\text{mean}}^{rel} = \frac{1}{N} \times \sum_{i=1}^{N} (\tilde{Z}_i - Z_i) / (Z_i) \]  

Equation 4-3

\[ \| E \|_{l_{\text{mean}}}^{rel} = \frac{1}{N} \times \sum_{i=1}^{N} |(\tilde{Z}_i - Z_i) / |Z_i|| \]  

Equation 4-4

where \( \tilde{Z}_i \) is the model prediction and \( Z_i \) is the plant data.

Equation 4-3 denotes the relative error between the model prediction and the plant data; therefore, it is a rough estimation of the bias of the prediction. Equation 4-4 shows the mean relative distance between the plant data and the model prediction; thus, it is an indication of the accuracy of the prediction.

Table 4-1 shows the magnitude of these statistics for the validation/simulation experiment. These data show the error between the plant data and the model predictions for gas and oil outlet temperature, selectivity and work-rate for period of 3 years operating time.

The mean relative error and distance between the gas and oil outlet temperature between the plant data and the model prediction are less than 1% showing the model capability to express describe and predict the heat transfer behaviour inside the EO reactor during 3 years operating time.

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{mean}}^{rel} )</th>
<th>( | E |<em>{l</em>{\text{mean}}}^{rel} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Outlet Temp.</td>
<td>2.55E-2</td>
<td>9.67E-1</td>
</tr>
<tr>
<td>Oil Outlet Temp.</td>
<td>2.84E-2</td>
<td>8.74E-1</td>
</tr>
<tr>
<td>Selectivity</td>
<td>-1.62</td>
<td>3.24</td>
</tr>
<tr>
<td>Work-rate</td>
<td>-0.55</td>
<td>3.56</td>
</tr>
</tbody>
</table>

The relative mean distances for selectivity and for work-rate are 3.24% and 3.56%, respectively. However, the relative mean errors are -1.62% and 0.55%, respectively. As may be seen, the agreement between model predictions and the plant data of
selectivity and work-rate are good, especially considering that the validation was performed on an industrial process system. Indeed, not only there are no significant biases but also there are fairly good correspondence between selectivity trends and work-rate trends.

In spite of this, it is also evident that the model predictions for selectivity and work-rate show some disagreement with the plant data in some point (Figure 4-9 and Figure 4-10). It would be desirable to identify the causes for discrepancy of results, assess their importance and implications, and propose areas for future theoretical and experimental research.

There are three main factors to consider as possible causes for plant/model mismatch and they can be classified into two main categories: those related to the plant data; and those related to the mathematical model.

4.6.1 Sources of Error

When a process system is operating, the dynamic trajectories of input process variables (and possibly, rapidly changing parametric variables as well) must be input throughout the simulation period so that the output process variable trajectories can be compared adequately with dynamic plant data and/or used confidently to extract additional information on the status of the process.

As stated earlier, a subset of plant data was used as dynamic trajectories of input process variables to represent the real plant operation (Appendix A). However, they include errors between the actual plant operation and the input data to the model. Also, there are errors related to plant measurements.

These errors could have a major effect on the model predictions. For example, the EDC level which has a significant effect on the reactor performance; should vary between 1-2 ppm. However, it is difficult to measure accurately. It is observed that at some point the measured EDC level is >3 ppm, showing significant reading error. In such cases reasonable modifications were used for the model input.
Furthermore, some of the model input data were assumed to be constant due to unavailability of plant data e.g., inlet water mole fraction and reactor pressure.

The reaction expressions used in the model, have an empirical base and had been modified using the correlation factors. Thus these models are subject to errors related to experimental measurement.

Some assumptions have been adopted to simplify the model, e.g. radial dispersion neglected, which can cause errors between the model predictions and the plant data.

Despite the multiple sources of possible errors, the results show that the model predictions compared well with the plant data, thus, the model was validated.

4.7 SUMMARY

The development of a mathematical model for the oxidation reactor has important practical applications: (1) planning safe operational policies based on process knowledge and numerical simulation; (2) process optimization is feasible when a reasonably accurate dynamic model for the reactor is available; (3) an understanding of transient behavior of the reactor in order to design control strategies.

The mathematical model developed in the previous chapter, was discussed and different mathematical solution of the model was considered. The gPROMS simulation package was used to numerically solve the model using finite difference techniques.

The catalyst vendor data were used to calculate the correlation factors. Also, they were used to predict the catalyst deactivation for 3 years operating time of the plant.

The plant data from Huntsman EO reactor were used to validate the model. The results showed satisfactory agreement between the model predictions and plant data. No fitting parameters were used. Thus the model was validated for wide application.

Furthermore, the discrepancy between the model predictions and the plant data were discussed and plausible reasons for plant/model mismatch were assessed.
In the next chapter, firstly the other units in EO plant (EO scrubber, gas-gas heat exchanger and hot oil cooler) are modelled using HYSYS simulation package followed by developing a novel hybrid modelling environment to implement the EO reactor’s model by the other units in EO plant.
4.8 BIBLIOGRAPHY


Chapter 5

Hybrid Modelling Architecture

In this chapter, the EO scrubber, gas-gas heat exchanger and hot oil cooler unit are modelled using HYSYS simulation package followed by some background information on hybrid modelling and open software architecture. Finally the HYSYS model and the EO reactor model in gPROMS are connected using CAPE-OPEN environment.
5.1 INTRODUCTION

Detailed modelling of the EO plant is a complex undertaking not only because there are numerous unit operations present but also because of the complexity in their dynamics. In particular the reaction phenomena represent a difficult modelling task because of the highly non-linear nature. The HYSYS environment being well-suited for process flow and control modelling is used to simulate the EO scrubber as well as the utilities section including all heating and cooling flows, temperatures and pressures of the EO plant, while gPROMS complements HYSYS with its suitability for the simulation of the distributed process.

In previous chapters the EO reactor was developed and validated against the plant data. Also some results elucidating the phenomena were presented. The model thus far has been restricted, for simplicity, to the reactor unit operation; however, the other units in the EO plant (especially EO scrubber and hot oil cooler) also, have a significant effect in the reactor performance. To study the reactor performance, and at the same time to be able to adequately model a complete process with various unit operations another software (HYSYS) is used as an effective tool for studying process.

Figure 5-1 shows the demarcation between the different softwares in modelling the entire process. Inlets and outlets of the EO reactor are communicated between the softwares. The Inlet ports (Feed Gas and Oil Inlet) are provided by HYSYS and the outlet ports (Reactor Effluent and Oil Outlet) are calculated by gPROMS.

In this chapter, in the first section, the part of EO plant modelled using HYSYS simulation package, are presented and the simulation result are discussed. A novel hybrid modelling environment is constructed to establish the communication between the reactor model with the entire plant and shown to be a useful tool for modelling complex process.
5.2 EO SCRUBBER

Gas scrubbing, absorption and washing involves the dissolving a soluble component(s) of a gas mixture into a liquid, with generally no change in the chemical species present in the system [1]. Absorption is a member of the “equilibrium” category of chemical engineering unit operations, which includes process such as distillation and extraction. These operations are generally modelled using two major assumptions [1].

1. The process is carried out in a series of contacts
2. The streams leaving each stage are in equilibrium

Mass transfer is the primary phenomena of gas absorption. Specifically when designing an absorption column, the rate of diffusion of the gas into the liquid is of critical importance. Fick’s law, Equation 5-1, describes the rate of diffusion of solute into the solvent as a function of concentration driving force. Assumptions made by
Fick's Law describe steady state diffusion with a linear relationship between mass transfer rate and concentration gradient.

\[ N_A = -D_{AB} \frac{dC_A}{dy} \]  

Equation 5-1

Where:

\[ N_A = \text{molar flux of component A, mol.m}^{-2}\text{s}^{-1} \]
\[ D_{AB} = \text{diffusivity of A into component B, m}^2\text{s}^{-1} \]
\[ C_A = \text{concentration of component A, mol.m}^{-3} \]
\[ y = \text{distance in the direction of transfer, m} \]

Packed towers are commonly used in absorption process. The structure of a packed column is shown in Figure 5-2. The cylindrical column is oriented vertically, with the rich gas inlet and distributor placed along with a rich liquid outlet placed at the bottom of the column, and the weak liquid with distributor and weak gas outlet at the top. This allows for counter current flow through the packing, which gives a better vapor liquid contact and hence a higher mass transfer rate. The majority of the column is filled with a packing, which is either structured or randomly placed. The packing allows a larger surface area of contact within the column, hence a large area over which the liquid and gas are in contact.

The rich gas flows from its source up through the column, where it comes in contact with the weak liquor flowing down through the column. The soluble gas is transferred into the liquid and exits the column as the rich liquor stream. The remaining unabsorbed gas leaves the column as waste or is recycled back through the column.
There are four major components that make up the internals of an absorption column. These include Packing Supports, Liquid Distributors, Liquid Redistributors and Hold-down Plates [3]. Packing supports are what the name suggests as they are constructed to carry the entire weight of the wet packing, while also providing flow resistance to the two streams. Liquid distributors are critical to column performance as column performance is reliant upon not only uniform liquid flow through the column but also good initial liquid distribution. Liquid redistributors are used to collect and redistribute liquid that has migrated to the walls of the column, back to the packing to maintain uniform liquid flow throughout the cross section of the column. These can also have the added function of packing support if required. Hold-down plates are required when high gas flow-rates or surging commonly occurs within the column. They are used to prevent the top layer of the packing to become fluidised then continue to blow out of the column, which is a common occurrence under the previously mentioned conditions.
5.2.1 *Industrial EO scrubber*

Typically plants use two scrubbers, A and B, for the retrieval of EO. Originally the plant ran with the single A scrubber, however as production increased it was deemed necessary for a second to be implemented. The scrubbers are considered identical as there are negligible performance differences between the two.

Scrubber A and B are packed bed columns, each with an internal diameter of 1.828 m and a height of 19.812 m. The structured packing within the column is in three stages (beds). The first bed (top of column) is 5.04 metres of Mellapak 125Y structured packing. Bed 2 consists of 1.35m of Mellapak 250X and bed 3 being 3.78m of Mellapak 125Y. Figure 5-3 shows schematics of the EO scrubber.

![Diagram of EO scrubber](image)

**Figure 5-3- Schematic of the EO scrubber**

<table>
<thead>
<tr>
<th>Stream:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Reactor Effluent Gas</td>
</tr>
<tr>
<td>B</td>
<td>Lean Scrubbing Water</td>
</tr>
<tr>
<td>C</td>
<td>EO Rich Water</td>
</tr>
<tr>
<td>D</td>
<td>Scrubber Effluent Gas</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Packing:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mellapak 250X</td>
</tr>
<tr>
<td></td>
<td>Mellapak 125Y</td>
</tr>
</tbody>
</table>

Table 5-1 shows the physical specifications of the Huntsman scrubbers and Table 5-2 showing the average operating conditions of the EO scrubbers.
Table 5-1- Huntsman scrubber physical specifications

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Diameter</td>
<td>1.828m</td>
</tr>
<tr>
<td>Column Height</td>
<td>19.812m</td>
</tr>
<tr>
<td>Packing Height</td>
<td>10.170m</td>
</tr>
<tr>
<td>Packing Type</td>
<td>Mellapak 125Y &amp; 250X</td>
</tr>
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</table>

Table 5-2- Huntsman scrubber average operating condition

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Pressure (kPag)</td>
<td>1860</td>
</tr>
<tr>
<td>Gas Inlet Temperature (°C)</td>
<td>106</td>
</tr>
<tr>
<td>Lean Cycle Water Temperature (°C)</td>
<td>30</td>
</tr>
<tr>
<td>Gas Outlet Temperature (°C)</td>
<td>30.5</td>
</tr>
<tr>
<td>Rich Cycle Water Temperature (°C)</td>
<td>59</td>
</tr>
</tbody>
</table>

Table 5-3 shows average plant data that reflects common feed and output flow rates seen at the plant. It should be noted that Table 5-3 reflects the total flow rates of the combined streams for the two scrubbers. The amount of the flow each scrubber receives is half what is seen in the table above. Lean water represents the water entering the top of the column without any EO in stream. The rich water represents the water stream exiting the scrubber that contains the EO absorbed in the scrubber.

Table 5-3- Huntsman scrubber stream compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>MW</th>
<th>Gas Inlet (kg/hr)</th>
<th>Lean Water (kg/hr)</th>
<th>Rich Water (kg/hr)</th>
<th>Gas Outlet (kg/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>28.05</td>
<td>25564.2</td>
<td>-</td>
<td>58.4</td>
<td>25505.8</td>
</tr>
<tr>
<td>oxygen</td>
<td>32</td>
<td>8211.2</td>
<td>-</td>
<td>5.7</td>
<td>8205.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>28.02</td>
<td>108221.4</td>
<td>-</td>
<td>42.4</td>
<td>108179</td>
</tr>
<tr>
<td>EO</td>
<td>44.05</td>
<td>5017.7</td>
<td>2.6</td>
<td>5000</td>
<td>20.2</td>
</tr>
<tr>
<td>Water</td>
<td>18.02</td>
<td>1886.2</td>
<td>204569.9</td>
<td>206085.6</td>
<td>370.6</td>
</tr>
<tr>
<td>CO2</td>
<td>44.01</td>
<td>28248.9</td>
<td>-</td>
<td>351.7</td>
<td>27897.2</td>
</tr>
<tr>
<td>Glycol</td>
<td>62.07</td>
<td>-</td>
<td>10427.5</td>
<td>10427.5</td>
<td>-</td>
</tr>
<tr>
<td>argon</td>
<td>39.95</td>
<td>13112.4</td>
<td>-</td>
<td>9.9</td>
<td>13102.5</td>
</tr>
<tr>
<td>Total (kg/hr)</td>
<td>190262</td>
<td>215000</td>
<td>221981.2</td>
<td>183280.8</td>
<td></td>
</tr>
</tbody>
</table>
5.2.2 EO scrubber model

The HYSYS flowsheet representing the EO scrubber and the gas-gas heat exchanger is shown in Figure 5-4. The reactor effluent gas is cooled down by the gas entering the reactor in the gas-gas heat exchanger and sent to the scrubber. It should be noted that for the purposes of this study, the term lean water defines the scrubber inlet water stream that is free of EO, and rich water is water exiting the scrubbers with a relatively high proportion of EO. The gas exiting the top of the main scrubber is recycled back to the reactor with fixed percentage of that going to the CO₂ Removal unit.

The HYSYS package has a generic absorber simulator as a built in function. Therefore the critical aspect when creating a model using a simulation package with pre-defined generic functions is to ensure that all parameters and specifications of the unit operation being modelled are defined in the simulator. In the case of the EO scrubber absorber definition of the correct packing was one of the critical importance of the model development.

![Figure 5-4: HYSYS flowsheet representing the EO scrubber and the gas-gas heat exchanger](image-url)
HYSYS has a default setting of a 10 tray absorber and it was required to change this to a packed bed absorber with structured with the specifications seen in Table 5-1. This was done by adding the tray sizing utility to the scrubber simulation. The utility function allows the selection and alteration of specific packing sizes and designs to the column.

One of the important aspects of the EO scrubber model development was the selection of the correct thermodynamic package. HYSYS has a large number of fluid packages to choose from, ranging from EOS to activity models. For this particular simulation an activity model was required of which HYSYS has 8 pre-defined models. An Equation of State (EOS) Model was not suitable for this application as they are primarily used in systems that have majority non-polar or slightly polar components. Under these conditions EOS models are very reliable over a large range of operating conditions [4].

The selection of the proper thermodynamic can be performed in an iterative two step process [5]. Initially, the thermodynamic model should be chosen based on heuristics that provided a good starting scenario on which to build upon. The second step is to use the initial scenario and increase the accuracy of the thermodynamic model by further optimizing of other design parameters such as configuration specific unit operations and heat integration.

The individual activity coefficients for a system are obtained using the Gibbs free energy function in conjunction with the Gibbs-Duhem equation. Early activity models, such as Margules and van Laar, are limited by an empirical representation of the excess function [4]. The newer models such as Wilson, NRTL and UNIQUAC utilize the local composition concept and provide an improvement in their general application and reliability. All of these models involve the concept of binary interaction parameters and require that they be fitted to experimental data [4].

The Margules and van Laar models were not considered in the analysis as they generally give poor results for strongly non-ideal systems and systems containing dilute regions, such as EO system of concern. These models are less complex than the
Wilson, NRTL and UNIQUAC models therefore they require less CPU time for solving calculations, however this is not a concern due to the technology being used. Suppes [6], states that for systems dealing with aqueous organics the NRTL of extended NRTL model is the most suitable. However, the Wilson and Chien-Null models also produce accurate results under the given conditions.

Table 5-4 shows the results of the analysis of the different activity models in HYSYS. As the literature view suggests the most suitable models to this application are the Chien Null and the NRTL or Extended NRTL packages.

<table>
<thead>
<tr>
<th>Thermo Model</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Data</td>
<td>99.597%</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>99.31%</td>
</tr>
<tr>
<td>Wilson Ideal</td>
<td>99.19%</td>
</tr>
<tr>
<td>Chien-Null</td>
<td>99.83%</td>
</tr>
<tr>
<td>NRTL</td>
<td>99.83%</td>
</tr>
<tr>
<td>Extended NRTL</td>
<td>99.83%</td>
</tr>
</tbody>
</table>

5.3 GAS-GAS HEAT EXCHANGER

The reactor outlet gas prior to enter EO scrubber, enters the gas –gas heat exchanger where is cooled by heating the feed gas.

The gas-gas heat exchanger is modelled as a “shell and tube” heat exchanger with the specification presented in Table 5-5.

<table>
<thead>
<tr>
<th>Table 5-5- Gas-gas heat exchanger physical specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shell</strong></td>
</tr>
<tr>
<td>Internal Diameter (mm)</td>
</tr>
<tr>
<td>Number of</td>
</tr>
<tr>
<td>Length (m)</td>
</tr>
<tr>
<td>Fouling Factor (C m²/W)</td>
</tr>
<tr>
<td>TEMA Type (Appendix D)</td>
</tr>
</tbody>
</table>
5.4 SIMULATION RESULTS AND DISCUSSIONS

The purpose of the EO scrubber is to recover the ethylene oxide from the cycle gas by absorption with water. The most important variable for the assessment of the operational and economic performance of an EO scrubber is recovery (EO Rec%) that can be defined as follows:

\[
\% \text{EO Rec} = \frac{\text{EO in reach water (kg/hr)}}{\text{EO in reactor outlet gas (kg/hr)}} \times 100
\]

Equation 5-2

The developed model in HYSYS is required to be validated against a plant data for completeness, accuracy, and forecasting ability. The data used for this study were obtained from Huntsman Corporation Australia.

The input data which is average data from Huntsman’s plant fed to the model and output of the simulation model compared to the plant output in the same day (Table 5-6). As shown, the model prediction compare well with the plant data. The model predicts 99.91% recovery in EO compare to 99.65% EO recovery in plant data.

<table>
<thead>
<tr>
<th>Component</th>
<th>Gas Inlet Plant Data</th>
<th>Lean Water Plant Data</th>
<th>Rich Water Plant Data</th>
<th>Model Prediction</th>
<th>Recycle Gas Plant Data</th>
<th>Model Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>13.44</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>13.92</td>
<td>13.97</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4.32</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.48</td>
<td>4.48</td>
</tr>
<tr>
<td>EO</td>
<td>2.64</td>
<td>0.00</td>
<td>2.25</td>
<td>2.25</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>CO2</td>
<td>14.85</td>
<td>0.00</td>
<td>0.16</td>
<td>0.26</td>
<td>15.22</td>
<td>15.12</td>
</tr>
<tr>
<td>Water</td>
<td>0.99</td>
<td>95.15</td>
<td>92.86</td>
<td>92.75</td>
<td>0.20</td>
<td>0.13</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>56.88</td>
<td>0.00</td>
<td>0.02</td>
<td>0.02</td>
<td>59.02</td>
<td>59.14</td>
</tr>
<tr>
<td>Argon</td>
<td>6.89</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>7.15</td>
<td>7.16</td>
</tr>
<tr>
<td>Glycol</td>
<td>0.00</td>
<td>4.85</td>
<td>4.70</td>
<td>4.69</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Total Flow (kg/h)</td>
<td>190262</td>
<td>215000</td>
<td>221928</td>
<td>222335</td>
<td>183280</td>
<td>182926</td>
</tr>
<tr>
<td>EO Rec (%)</td>
<td>Plant Data</td>
<td>99.65</td>
<td>Model Prediction</td>
<td>99.91</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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For further investigation, the model result compared with plant data during 37 days operation. The input data chosen as model input are the average data for every day operation. Some of input data e.g. water flow rate and water content in the reactor effluent were missing, so it was required to estimate these data from the previous data or using the reactor model output.

The output of the HYSYS model was compared to the plant data during that time.

Figure 5-5 shows the EO recovery for period of 37 days operation. The average recovery calculated through the simulation model is 99.8% compared to the recovery range 99.4%-99.7% based on the plant data. Note that due to maintenance, plant data for 4 days were not available.

![Graph showing EO recovery over time](image_url)

**Figure 5-5- The EO recovery for period of 37 days of operation**

Figure 5-6 and Figure 5-7 show ethylene and $CO_2$ mole fraction in the scrubber gas outlet respectively. As shown in the figures, the model predictions are very good and follow very closely the transition during plant operation.
Figure 5-6- Comparison of ethylene mole fraction in the scrubber gas outlet of the model against the plant data during 37 days of operation

Figure 5-7- Comparison of carbon-dioxide mole fraction in the scrubber gas outlet of the model against the plant data during 37 days of operation

Table 5-7 shows the typical results for gas-gas heat exchanger. The reactor outlet gas to scrubber is expected to be in range of 100 °C -115 °C depends on the cycle gas temperature.

<table>
<thead>
<tr>
<th></th>
<th>Inlet temperature</th>
<th>Outlet temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Gas</td>
<td>59.5</td>
<td>198.0</td>
</tr>
<tr>
<td>Reactor Outlet</td>
<td>240.5</td>
<td>105.6</td>
</tr>
</tbody>
</table>

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5.5 Hot Oil Cooler

As it stated earlier, all three reactions in EO reactor, are strongly exothermic, thus the coolant oil, MobilTherm 607, was used to cool the reacting gas in EO reactor. A portion of the heated coolant is passed through a steam generator “hot oil cooler” to produce steam and the total coolant is recycled back to the shell side of the reactor. The hot oil cooler is a kettle boiler.

The hot oil cooler is playing important role in EO plant since it has a direct effect on the coolant temperature. As stated before, EO reactor operates close to both runaway and explosive conditions therefore control of the inlet coolant temperature are vital. A single-loop PID control system uses the flow rate of the coolant that is passed through the steam generator to maintain the internal temperature of the coolant to the reactor.

Modelling the hot oil cooler is an important step toward control of EO reactor. To model the hot oil cooler in HYSYS, the coolant oil is required to be defined. The oil characterization environment in HYSYS enables to characterize petroleum fluids by creating and defining Assay and Blends. The oil characterization procedure generates petroleum hypo-components for use in the fluid package.

HYSYS accepts five Standard laboratory analytical assay procedure:

- True boiling point distillation (TBP)
- ASTM D86 and ASTM D1160 distillation
- ASTM D2887 simulated distillation
- Equilibrium flash vaporization (EFV)
- Chromatographic analysis

In this model, the coolant oil, MobilTherm 607, is defined using ASTM D86 distillation data provided by “Mobil Australia”. HYSYS would convert the ASTM distillation curve to a TBP curve using standard method (API Data book) since the characterization procedure in HYSYS, performs its calculation based on an internally calculated TBP curve [7].

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Figure 5-8 shows the schematic of HYSYS assay property view and shows the oil typical properties calculated in HYSYS compare to the properties calculated using the equation provided by the producer (Mobil).

![Figure 5-8- HYSYS assay property view](image)

The hot oil cooler is modelled as a Kettle boiler with the specification presented in Table 5-8.

<table>
<thead>
<tr>
<th>Table 5-8- Hot-Oil Cooler physical specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Diameter (mm)</td>
</tr>
<tr>
<td>Number of</td>
</tr>
<tr>
<td>Length (m)</td>
</tr>
<tr>
<td>Fouling Factor (C m²/W)</td>
</tr>
<tr>
<td>TEMA Type (Appendix D)</td>
</tr>
</tbody>
</table>

As discussed earlier, the reactor model needs to be implemented by the other units in EO plant to improve the capabilities of the model. In the following sections, a novel
hybrid modelling environment is constructed and shown to be a useful tool for modelling complex process.

5.6 HYBRID MODELLING – THE CONCEPT

It has been stated that the developments in computer-aided process modelling can be classified into four groups; general modelling languages, process modelling languages, expert systems and interactive modelling environments [10]. General modelling languages can be viewed as equation oriented simulation languages. MODELICA [11], OMOLA [12] and the modelling languages of ASCEND [13] and gPROMS [14] are examples of general modelling languages.

Process modelling languages are similar to general modelling languages but they are designed to match the specific issues of a particular application domain. MODELICA [15] is an example of a language where the elements are tailored for chemical engineering.

The generality of the simulator can be used as another feature to characterise a simulation tool. At one end we have very generic tools such as Matlab [16], gPROMS or Modelica and at the other end we have very specialised tools for process simulation such as HYSYS [17], CADSIM Plus [18] or Apros/Apms [119].

Today, it clearly appears that the main hindrance to a larger use of simulation in the industrial community is the lack of models really suited to the user’s specific needs. Each program offers unique advantages and specialties, but there is to date no single program that incorporates all of the data and methods, which may possibly be used to solve every problem. Nor will there ever be an all encompassing process solver (Figure 5-9) that would be a solution to all chemical engineering modelling situations. As new hypotheses and theories are developed, process modelling tools will need to be restructured and improved. The field of engineering is already too broad for such a catch-all solver to be developed.
A way of overcoming this shortfall is to develop techniques to connect different software packages, enabling data communication across established links. For very large systems the very task of describing the relationship and connections between different components and subsystem becomes so cumbersome that it requires dedicated tools. Fortunately, the progress in software technologies offers possibilities for new kind of integration of simulation tools. For process simulation, integration means reuse of model configurations and parameter values, co-use of different simulation tools, easy extensibility of simulator functionality and closer interoperability between distributed control systems and dynamic process simulators. In order to achieve this kind of integration, a domain specific architectural specification is needed. The specification should take into account both data-centric and model-centric requirements. The main research problem of the thesis is therefore how to apply current information technologies to facilitate the use of process simulation and to enhance the benefits gained from using it. As a development task this means developing new software architecture for configuration and usage of process simulation models.

The hybrid architecture shown in Figure 5-9 facilitates the combining of the strengths of each particular program allowing powerful simulations to be developed. In this study the term ‘hybrid model’ will be used to describe a model that has parts built in separate but communicating simulation environments.
This architecture is an important, emerging field for chemical engineers. It is applicable for all situations, can be used to solve many complex problems and for modelling complex process. Despite this, only a limited level of research has been published in the development of this field. Perhaps unpublished work has been undertaken under commercially proprietary situations. The extent of these works is discussed below.

Figure 5-10 shows the open software vision which will enable hybrid simulations of complex process to be modelled. It acts as a bridge or communicator between different specialist 3rd-party software, to generate hybrid models and solutions.

There are a number of reasons for developing a more open architectural approach to process modelling tools [21]:

- Interaction between commercial softwares with the internally generated or proprietary software.
- Using third-party software to model different parts of the process.
- Incorporating the process modelling tools into an overall system. This is especially relevant for plant operations training, optimisation and control.

\[\text{Spreadsheet Models (e.g. Excel)} \quad \text{Solutions} \quad \text{PFD Models, CFD Models (e.g. HYSYS, Fluent)} \]

\[\text{Equation-based process modellers (e.g. gPROS, Matlab)} \quad \text{Solutions} \quad \text{Solutions} \quad \text{Solutions} \]

Future technologies (as yet undiscovered)

\[\text{Figure 5-10- The open software vision [20]}\]
The significance of this is that there is recognition that software interconnectivity is vital to modern chemical engineering.

5.7 Work to Date

Kulikov et al [22] presented a sequential modular strategy for the dynamic simulation of particulate process flowsheets. They focused on applying dynamic simulation algorithms for the software integration of different, existing process simulation tools which they pointed out several benefits for such an approach. A clear benefit is that if a certain process unit model is used within a mixed fluid-particulate process flow sheet, the unit model already implemented in some tool does not have to be re-implemented but can be reused directly. Also, the development of complex process models can be shared between different process specialists who use their preferred modelling and simulation tool, avoiding the usage of some general purpose tool which can hardly be found for all problem classes. Finally, the integration approach can take advantage of well-developed and highly specialized numeric in the particular software packages to increase solution robustness and efficiency.

Following that Kulikov [22] presented a case study (crystallization flowsheet). The flow sheet consists of four units, a mixer and an evaporator modelled with HYSYS, a crystallizer modelled using a specialized simulation tool Parsival and finally a hydrocyclone modelled using gPROMS (Figure 5-11). To integrate, they used CHEOPS integration platform which provides the generic class prototypes and interfaces for the integration of various tools, models and solver codes [23]. The platform is component-based and abstract classes are used to define and implement the integration framework in a generic way.
Mota et al (2004) [24], coupled a computational fluid dynamics (CFD) software package (Fluent) with their dynamic process simulator (AngTank) of an adsorption storage tank for methane fuelled vehicles. The two solvers run as independent process and handle non-overlapping portions of the computational domain. The codes exchange data on the boundary interface of the two domains to ensure continuity of the solution and of its gradient. They developed a software interface to dynamically suspend and activate each process as necessary, and be responsible for data exchange and process synchronization. This hybrid computational tool has been successfully employed to accurately simulate the discharge of a new tank design and evaluate its performance.

Abbas (2003) [20] developed a model for an ammonium sulfate system. The model was based on the population balance theory which describes the evolution of crystals for batch cooling crystallisation. gPROMS was used to solve the crystallisation model and HYSYS software platform, was used to simulate the utilities unit of the pilot facility. An 'open' simulation architecture was then created to model and simulate the entire pilot facility in dynamic mode bringing together the capabilities of a number of softwares to solve the many facets of the process. The integrated software tools (HYSYS, gPROMS and Excel) communicated seamlessly in this environment and showed the strength of the 'open' simulation architecture in providing solution analysis. This unique environment has potential to be extended to other process where complex dynamics require multiple tools to generate a solution.
Zorzetto et al. [25] dealt with the development of a modelling program, where 'hybrid' was defined as the mix between an equation-based approach to process modelling, much like gPROMS, and a modular, "black box" approach to process modelling, like HYSYS. The work of Zorzetto and co-workers was aimed at creating a new, self-contained and more comprehensive hybrid modelling tool. This paper demonstrates the value of hybrid modelling via the construction of a model that harnesses the strengths of different tools.

While Zorzetto et al. [25] seek to develop an all-inclusive modelling tool, Kakhu et al. [21] present a different approach. Kakhu et al. consider mechanisms for supporting openness within process modelling tools. They commented that there is a general and serious lack in the ability of existing software to interact. Hence, it can be concluded that there is a need for links to be built between different process modelling tools. Kakhu et. al. focused mainly on the gFOI (foreign object interface) and gFPI (foreign process interface) capabilities of gPROMS.

Two works [26, 27] have dealt with the linking of gPROMS with Computational Fluid Dynamics (CFD) simulations. CFD and process simulators are highly complimentary, and there are benefits to be gained by their integration [26]. This is relevant to many process, such as reactive crystallisation (precipitation), where both fluid dynamics (the degree of mixing) and particle size distribution must be taken into account. Urban and Libers [27] stated that by integrating two different modelling environments, it is possible to achieve value that cannot be created by either of them alone. They used gPROMS to model both a crystalliser and a number of close unit operations and fed the gPROMS output data to the CFD package, where the CFD package returned to gPROMS a more-defined model of the reactor hydrodynamics. They reported that, upon validation against plant data, the hybrid simulation was able to predict accurately the performance of industrial scale equipment, and was able to assist in the improvement of process operation. Similarly, the paper by Bezzo and coworkers [26] dealt with the interaction between the gPROMS process simulator and the Fluent CFD package (Fluent, Inc.) to describe the behaviour of a reacting system. Bezzo et al. stressed the importance of combining process simulators in accounting
for the spatial variations of properties within unit operations. These two works demonstrate the benefits of hybrid modelling in achieving a higher degree of detail and predictive accuracy in process modelling.

Sequeira et al. [28] reported the integration of Excel, Matlab and HYSYS to create a hybrid physical/economic model of a plant to enable real-time optimisation. They used HYSYS to model the chemical process, Matlab as the search engine in the economic optimisation and finally Excel, having the main job of communication between the former two programs, is responsible for data manager. ActiveX is used for the connection between HYSYS and Excel while the Matlab-Excel connection was established via the Dynamic Data Exchange (DDE) service.

Another study while aimed at academic educational applications, also presented the HYSYS-Excel-Matlab connection. Van Der Lee et al. [29] argued that graduate courses teaching the fundamentals of process control steer clear of advanced process control topics like model-predictive control because of the lack of integrated modelling environments. They demonstrated the usefulness of hybrid modelling in teaching and learning by presenting a HYSYS process simulation model of a distillation column being controlled by algorithms in Matlab.

Marchetti et al. [30] presented some of the issues in designing a simulation environment, which combines a sequential modular simulator to an equation oriented package. A thorough literature search was done for other articles on linking; however, it appears that there are no works that report the development of a hybrid model between HYSYS and gPROMS. Therefore, it is fit and proper that the gap between these programs be bridged.

It has been envisaged that the implementation of the vision of software connectivity will have a number of effects on the discipline of chemical engineering [31]. These include:

- The increasing ease of modelling chemical process;
• The increasing rate of model improvement, verification and application within the chemical process industries as models become compatible in different software packages;

• The accelerated rate of software development in a more competitive and fluid software development environment;

• The increasing diversity of software developers due to the fact that specialist models can be developed quickly and with a fraction of the resources required, as developers need not develop a new software package to build a specialist model. Developers just need to ensure that they are compliant with the connectivity standard;

• The increasing specialisation of software which is both relevant to a more specialist number of users and compliant with the global software connectivity standard;

• The use of software models as marketing tools for equipment vendors, since specialist models can be developed by equipment vendors which comply with the connectivity standard to enable potential buyers to use in their decision-making.

5.8 CAPE-OPEN AND GLOBAL CAPE-OPEN

As the computer-aided process engineering (CAPE) [32] community continues developing and validating individual process models, the incentive behind developing and implementing model-based technologies grows. In the mid 1990s, developers and end-users were confronted with the reality that high-level definition of process models is language-dependent, restricting general accessibility and usability of model descriptions embedded within modelling environments. Also, however using CAPE tools is essential for getting products and process quickly to the market, but the incompatible and proprietary nature of commercial simulators has resulted in a number of significant deficiencies:

• hard to include company specific models and process knowledge,
• need for multiple simulators, with additional license fees, training, and error prone data transfer,

• hard to incorporate the expertise of researchers and specialist companies in simulations,

• difficulty in integrating niche software products from small and mid-size enterprises.

To address this problem, the CAPE community initiated the CAPE-OPEN (CO) (CAPE-OPEN Consortium, 2000) and Global CAPE-OPEN (GCO) (Global CAPEOPEN Consortium, n.d.) projects. Global CAPE-OPEN was funded by European Community under the Industrial and Materials Technologies Programme (Brite-EuRam III), for developing standards for interoperability in process simulation. When this project finished in 2002, the participants and other interested parties decided to continue the development and maintenance of the standards. The CAPE-OPEN Laboratories Network (CO-LaN) was established as neutral industry and academic association promoting open standards in simulation software. It is committed to make CAPE tools easier, faster and less expensive to use by working towards interoperability of commercial CAPE tools.

The objective of the Global CAPE-OPEN project is to deliver the power of component software in CAPE. CAPE-OPEN promoted the advent of open-standard interfaces for process simulation, which allow users of compliant simulators to employ elements from other suppliers directly in their simulations, without any programming or the production of special versions, and allow covering the full process life-cycle with compatible simulation.

The original CAPE-OPEN standard for Unit Operations catered only for steady-state unit operations. It was therefore a natural extension to produce a standard for dynamic components. A voluntary working group was established within CO-LaN, containing members from both end-user companies (Shell and Norsk Hydro) and vendors (RSI, PSE Ltd, VTT and Fantoft Process Technologies). It was decided that the working group would concentrate first on supporting sequential dynamic simulators, rather
than equation-based simulators. This was done because sequential simulators are still the most widely used for dynamic simulation. However, many of the needs of an equation-oriented simulator can be met by applying this standard and the CAPE-OPEN equation solving standards together.

The dynamic unit operations interface is designed to support the scenario where a model of a specialized piece of equipment, such as a chemical reactor, needs to be included in a dynamic model, typically a training simulator. The reactor model is often proprietary, and is developed as stand-alone code, in a model in CFD software and/or in an equation-based simulator like gPROMS.

There are two other major global software standardisation activities, namely pdXi and OPC. The major United States initiative, pdXi, is the AIChE Process Data Exchange Institute. This initiative is described in greater detail in [33]. Meanwhile, the OPC Foundation is the Object Linking and Embedding (OLE) for Process Control. Its activities are aimed at utilising Microsoft's OLE/COM middleware capabilities to develop standard methods for accessing control systems. It is believed that this initiative and the GCO program are complementary activities [31].

Global CAPE-OPEN has the following key objectives:

- To develop additional standard interface specifications for other components of process simulation: kinetics, complex materials, databases of physical properties, optimisation, data reconciliation, distributed systems, costing;
- To consolidate the CAPE-OPEN results by setting up a management environment for the standard itself, and for the labeling of compliant components, the CAPE-OPEN Laboratories Network, or "CO-LaN";
- To mature the compliant environments to a degree that a number of reference success stories in real process engineering tasks can be created as a basis for the world-wide adoption of the standards;
- To explore the broader context of process simulation in order to ensure coherence of CAPE-OPEN with other process engineering standards;
• To ensure that CAPE-OPEN is "future-proof" by exploring changes in the user environment (e.g. higher emphasis on batch), in the precision of modelling tools (e.g. subunit modelling) and in the technical environment (e.g. Java Beans, XML).

5.9 gPROMS - HYSYS Model Development

This section outlines the way in which a dynamic link was established between gPROMS and HYSYS using CAPE-OPEN to create a hybrid modelling architecture.

5.9.1 gPROMS facilities for CAPE-OPEN Units

The full set of capabilities of gPROMS related to CAPE-OPEN comprises three major components:

- gO:CAPE-OPEN itself, a software wrapper that executes the gPROMS model within the target environment.

- CAPE-OPEN Thermodynamics, software socket within gPROMS that allows gPROMS models to make use of any CAPE-OPEN compliant physical properties packages.

- Export to CAPE-OPEN facilities in the gPROMS ModelBuilder. These allow the user to specify all the information required to execute the model in the target environment, then to export it at the push of a button – no programming is required.

gO:CAPE-OPEN in fact wrappers all the solution software required to solve the gPROMS Integro-Partial Differential Algebraic (IPDAE) set of equations and execute it within the target environment. This means that any model that runs in gPROMS will execute identically in, for example, HYSYS. Thus models can contain any of the features for which gPROMS is typically used, such as distributions with respect to space or particle size, detailed rate-based heat and mass transfer relationships, or complex reaction kinetics.
gPROMS model can be exported for execution by gO:CAPE-OPEN within a CAPE-OPEN compliant simulator. The model can use its own physical properties, or call the physical properties package of the target simulation environment via the gPROMS CAPE-OPEN properties socket.

5.9.2 ASPEN HYSYS facilities for CAPE-OPEN units

HYSYS is built upon proven technologies, with more than 25 years experience supplying process simulation tools to the oil & gas and refining industries. It provides an intuitive and interactive process modeling solution that enables engineers to create steady state models for plant design, performance monitoring, troubleshooting, operational improvement, and business planning and asset management.

Aspen HYSYS 2004 version 1.0 has following features to support CAPE-OPEN Interfaces:

- CAPE-OPEN Unit Operation Socket – sequential modular
  - Allows any CAPE-OPEN Unit to be used in a HYSYS Simulation
  - Supports both 0.93 and 1.0 versions of the standard.
- CAPE-OPEN Thermodynamics Socket - via COMThermo
  - Allows CAPE-OPEN Property Packages to be used to provide property calculations in HYSYS simulations.
- CAPE-OPEN Thermodynamics Plug – via COMThermo
  - Use HYSYS (or any COMThermo client) to create CAPE-OPEN Property Packages based on COMThermo Compounds and Property Methods. To run a

To run a gPROMS model in HYSYS is needed to perform five steps:

1. Configure the gPROMS model for use in a flowsheeting simulator;
   Ensure that the streams conform to the CAPE-OPEN stream structure. In order to link the gPROMS model correctly within the CAPE-OPEN flowsheeting
package, the streams used in the model must conform to the standard CAPE-OPEN definition.

gPROMS is supplied with a “CAPE-OPEN_Unit” library that contains a CO Material stream type definition. To make your model CAPE-OPEN compliant, simply define inlet and outlet ports (with connection type “CO_Material”) using the standard gPROMS port definition mechanism.

2. Export the gPROMS model;

3. Insert the gPROMS model as a unit within HYSYS;

4. Configure the gPROMS unit within HYSYS;

5. Execute the model in HYSYS and examine the results.

5.10 SIMULATION CONSTRUCTION AND RESULTS: HYBRID MODEL

As described earlier, the central unit operation of the EO plant is the EO reactor, which is cooled by an oil stream flowing through its jacket. The heated oil is then sent to a heat exchanger called Hot Oil Cooler. The temperature of the oil inlet to the reactor is controlled by the oil flow into the hot oil cooler. The reactor outlet is cooled in a recuperative heat exchanger by heating up the reactor inlet. The cooled reactor outlet then sent to the EO scrubbing system to recover the EO product by absorbing it with the lean recycle water.

Detailed modelling of this process is a complex undertaking not only because there are numerous unit operations present but also because of the complexity in their dynamics. In particular the reaction phenomena represent a difficult modelling task because of the highly non-linear nature. The HYSYS environment being well-suited for process flow and control modelling is used to simulate the EO scrubber as well as the utilities section including all heating and cooling flows, temperatures and pressures of the EO plant, while gPROMS complements HYSYS with its suitability for the simulation of the distributed process.
Figure 5-1 shows the breakdown of responsibilities between the different softwares to model the entire process. Inlets and outlets of the EO reactor are communicated between the softwares.

The inlet and outlet ports required to be defined in gPROMS in order to export to Cape-Open. Figure 5-12 shows topology of the EO reactor model in gPROMS. As may be seen, Feed gas and Oil inlet are the inlet ports and Reactor Effluent and Oil outlet are the output ports.

![Schematic of model topology in gPROMS](image)

*Figure 5-12- Schematic of model topology in gPROMS*

The inlet and outlet ports need to be defined prior to export to Cape-Open. The ports are defined in gPROMS interface (Figure 5-13). The Inlet ports (Feed Gas and Oil Inlet) are provided by HYSYS and the outlet ports (Reactor Effluent and Oil Outlet) are calculated by gPROMS (Figure 5-14).

Shahla Aryana
Figure 5-13- gPROMS model interface

Figure 5-14- Schematic of exporting to Cape-Open in gPROMS
The variables required for each port are temperature, pressure, composition, flow rate and specific enthalpy. The exported EO reactor model is inserted into the HYSYS as a Cape-Open object. Inlet and outlet ports in the CAPE-OPEN object are configured to reflect the arrangement in gPROMS and HYSYS. Figure 5-15 shows the material connection of EO Reactor (the Cape-Open's object) in HYSYS. Figure 5-16 shows schematic of the EO plant model in HYSYS. The EO reactor model in gPROMS and the plant model in HYSYS communicated through the ports. The feed gas (FeedGas port) and the coolant (OilInlet port) are defined in HYSYS. The CAPE-OPEN object (EO reactor model in gPROMS) acts as a unit in HYSYS. The outputs of the CAPE-OPEN unit are the reactor effluent (ReactorEff ports) that enters the cycle gas loops and the coolant oil (OilOutlet port) that enters the coolant oil loop. Any change in HYSYS input will affect the output result of gPROMS model.

Figure 5-15- The Cape-Open object in HYSYS
Figure 5-16- Schematic of EO plant model in HYSYS

Figure 5-17 shows the report of the EO reactor result in HYSYS. The results between HYSYS and gPROMS are compared in Table 5-9. The results are similar; however there are some discrepancy in temperature results due to different thermodynamic package used by HYSYS and gPROMS.
**Figure 5.17- Connection results in HYSYS**

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>FeedGas</th>
<th>OilInlet</th>
<th>OilOutlet</th>
<th>Reactor E</th>
</tr>
</thead>
<tbody>
<tr>
<td>TotalFlow</td>
<td>[mol/s]</td>
<td>1736.77</td>
<td>2657.67</td>
<td>2657.67</td>
<td>1722.4</td>
</tr>
<tr>
<td>Temperature</td>
<td>[K]</td>
<td>471.15</td>
<td>509.15</td>
<td>512.211</td>
<td>513.69</td>
</tr>
<tr>
<td>Pressure</td>
<td>[Pa]</td>
<td>2.071e+006</td>
<td>2.16e+006</td>
<td>2.16e+006</td>
<td>1.9272e+0</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>[J/mol]</td>
<td>-5455.28</td>
<td>-7041.78</td>
<td>-700247</td>
<td>-1082</td>
</tr>
<tr>
<td>Fraction</td>
<td>[mol/m³]</td>
<td>0.175121</td>
<td>0</td>
<td>0</td>
<td>0.1561</td>
</tr>
<tr>
<td>Ethylene</td>
<td></td>
<td>0.0610421</td>
<td>0</td>
<td>0</td>
<td>0.041701</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td>1.00069e-005</td>
<td>0</td>
<td>0</td>
<td>0.026617</td>
</tr>
<tr>
<td>CO²</td>
<td></td>
<td>0.0498344</td>
<td>0</td>
<td>0</td>
<td>0.057944</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>0.00310214</td>
<td>0</td>
<td>0</td>
<td>0.0010823</td>
</tr>
<tr>
<td>Nitrogen</td>
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<td>0</td>
<td>0</td>
<td>0.63516</td>
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<tr>
<td>Argon</td>
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<td>0</td>
<td>0</td>
<td>0.081628</td>
</tr>
<tr>
<td>EGlycol</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>&gt;</td>
</tr>
</tbody>
</table>

**Table 5.9- Comparison between HYSYS and gPROMS results**

<table>
<thead>
<tr>
<th></th>
<th>gPROMS Results</th>
<th>HYSYS Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Outlet Temperature (°C)</td>
<td>240.0</td>
<td>239.1</td>
</tr>
<tr>
<td>Gas Outlet Temperature (°C)</td>
<td>241.2</td>
<td>240.5</td>
</tr>
<tr>
<td>Outlet EO Molar Flow (kgmol/hr)</td>
<td>6.26E-02</td>
<td>6.26E-02</td>
</tr>
</tbody>
</table>

5.11 Simulation Issue

The main advantage of CAPE-OPEN is that this standard enables hybrid simulation. Because this is described mainly in unpublished drafts, the standard is currently considered not to be stable enough for hybrid co-simulation. This work shows that the standard is robust for continuous co-simulation. However, the standard is quite
complex and far from trivial to implement. Also, simulators such as HYSYS do not support the dynamic simulation for CAPE-OPEN object.

5.12 SUMMARY

The EO scrubber, gas-gas heat exchanger and hot oil cooler unit were modelled using the HYSYS simulation package. The model predictions for the EO scrubber show satisfactory agreement with plant data providing validation for the model.

Computational architecture for the modelling of complex process has been introduced. Separate sections of a process were developed separately in different software environments. The EO reactor model in gPROMS was linked with the EO plant model in HYSYS using the CAPE-OPEN environment. The results obtained from the HYSYS and gPROMS softwares were compared. The results showed satisfactory agreement.

The significance of the above result is that a model of a process can be built in parts, using a number of programs, and then connected to create a dynamic hybrid model that can be simulated under different operating conditions and schedules. This model can then be redesigned and maintained easily, enabling modelling to be accomplished with increased speed and conclusions reached with greater confidence.

Results from the hybrid model and the sensitivity analysis are presented in the next chapter with optimisation of the EO reactor.

Shabia Aryana
5.13 BIBLIOGRAPHY


Chapter 6

Sensitivity and Optimisation Study

A series of sensitivity analyses are performed on selected variables and parameters of the EO reactor model and the EO scrubber model to determine their influence on the models. Objective functions of the EO process are developed and the EO reactor model is optimized.
6.1 INTRODUCTION

It is well known that chemical reactors sometimes go out of control after a minor upset in some critical operating parameters. Run away conditions might occur and burn out a new set of expensive catalyst. All of these situations are particularly important in industry such as ethylene oxide production, where highly exothermic reactions are carried out.

A sensitivity analysis is the process of varying model input parameters over a reasonable range (range of uncertainty in values of model parameters) and observing the relative change in model response. Consequently, the importance of sensitivity analysis for the reactor cannot be emphasized strong enough.

There are several ways to undertake a sensitivity study of a reactor. The most obvious and probably most frequent used method had been experimental using a laboratory or pilot-plant reactor. However, with increasing computing power, the choice has been shifted to computer simulation due to economic and time advantages.

In this section, the validated model of the EO reactor and the EO scrubber are used to conduct a sensitivity analysis. The outcome of the sensitivity analysis aided the understanding of the process behaviour. The variables having significant impact on work-rate and selectivity are identified and used as control variables for optimisation studies.

6.2 SENSITIVITY ANALYSIS OF EO REACTOR

Analysis has been undertaken to check the sensitivity of the reactor performance to a number of process variables:

- Coolant and feed temperature
- EDC concentration
- Reactant concentrations
Also, effects of EO scrubber unit on the reactor performance have been investigated.

6.2.1 Coolant and feed temperature

For the EO reactor, it is desirable to limit the coolant temperature in order to achieve safe operation. The bulk coolant temperature below must be kept its saturation temperature so that no bulk boiling occurs. The coolant temperature is kept sufficiently low such that the heat transfer capability of the coolant is maximized. Regardless of the manner in which the heat is generated and removed from the reactor, there are other special problems which must be considered. There is a practical matter and it is the maximum temperature allowable for the coolant.

For the case of the coolant used in the EO reactor (Mobiltherm 603) in a closed system the temperature is 285 °C. There is also limitation on the allowable temperature rise of the coolant as it passes through the reactor. On one hand, it is advantageous for the temperature to rise sufficiently enough to allow efficient heat transfer in the secondary heat exchanger for steam generation, but there is also strong motivation to minimize this temperature rise in order to reduce thermal shocks in the reactor. For instance, in the oxidation reactor the coolant typically rises from an entrance temperature of 235 °C to an exit temperature of 242 °C, a temperature increase of only 7 °C. This is achieved due to the high flow rate of the coolant (1,174 kg/s).

It should be noted that while such temperature limitation set upper limits on the temperatures achieved in the core of the catalyst bed, there are also lower limits imposed on the inlet coolant temperature. At the entrance of the oxidation reactor, the coolant releases heat which is absorbed by the gas flow containing recycled and fresh regents. This heat is used up to initiate of oxidation reactions. Since the oxidation reactions are highly exothermic, a great deal of heat is released and it is gained back by the coolant.

Therefore, the inlet temperature of oil as coolant is one of the important control variables which could control possible thermal runaways as well as the reactor
performance. In this context, the effect of oil inlet temperature on the reactor performance was studied.

Figure 6-1 shows the effect of increasing (+5%) the oil inlet temperature on the gas temperature profile along the reactor. The disturbance propagates in a linear fashion. The transition time is less than 100 sec due to the high gas velocity and the fast reactions.

![Figure 6-1: Temperature profile along the reactor in response to a +5% step-change in oil inlet temperature](image)

Figure 6-2 shows the effect of increasing (+5%) the oil inlet temperature on the work-rate and selectivity. It shows that with increasing oil temperature, the work-rate increases by about 12% while selectivity decreases by 2.5%. These results should be expected, since the reaction rates of all the three reactions involved increase with temperature and the work-rate increases with increasing oil temperature. However, a decrease in selectivity is expected due to stronger effect of temperature on the undesired reactions (total ethylene and EO oxidation) than the desired one (partial ethylene oxidation).
Figure 6-2: Selectivity and work-rate in response to a +5% step-change in oil inlet temperature

Figure 6-3 shows the oil and gas outlet temperature increase as expected. However, in practice, there is concern for step-change increase and linear-change which needs more investigation.

For further investigation, the amount of heat transferred between the tube wall and the coolant oil is shown in Figure 6-4. This graph shows that in the beginning, the amount of transferred heat drops dramatically due to the step increase of shell side temperature (oil inlet temperature). Consequently, the bedside temperature starts to increase enhancing the reactions thereby increasing the released heat by reactions and the reactor inside temperature. Thus, heat transfer starts to increase.

The dramatic decrease in heat transfer could lead to thermal runaway condition and catalyst damage.
During industrial operation, use of a linear-change is better suited than a step-change. Figure 6-5 shows the modification of oil inlet temperature according to a linear increase and the amount of heat removed from tube side.

Figure 6-6 shows the selectivity and work-rate in response to a linear-change. Results in both cases show that the final outcomes are similar but the reactor performance is
expected to be better in case of linear increase. So, to avoid any runaway condition, linear increase is suggested.

![Graph showing the transferred heat between oil and tube wall in response to a +5% linear-change in oil inlet temperature.](image)

**Figure 6-5** - The transferred heat between oil and tube wall in response to a +5% linear-change in oil inlet temperature

![Graph showing selectivity and work-rate in response to a +5% linear-change in oil inlet temperature.](image)

**Figure 6-6** - Selectivity and work-rate in response to a +5% linear-change in oil inlet temperature

A step change in inlet gas temperature has a much smaller influence on the process, because of the less stored thermal energy in the gas compared with the oil (Figure 6-7). As Figure 6-7 shows that gas outlet temperature changes very slightly.
6.2.2 EDC level

As stated in earlier chapters, the 1, 2-dichloroethene (EDC) is used as an inhibitor agent and it works at the catalyst level to enhance the process selectivity for ethylene oxide production. It is assumed that the inhibitor agent reduces the availability of active sites on the silver/alumina catalyst. However, the partial oxidation of ethylene in the presence of EDC is not understood in detail.
From the operational point of view, the inhibitor agent has two major effects on the process: (1) it moderates the overall reaction avoiding the total oxidation of the ethylene oxide to undesirable products thereby increasing the selectivity; (2) it dampens the reaction rate, leading to an effective increase in EO reactor temperature, with the negative effect of hastening the deactivation/aging of the catalyst. These effects have important practical implications due to the trade-off between the process throughput and plant safety.

This enhancement of the ethylene oxide selectivity is very attractive from the production point of view. However, the addition of EDC is restricted by the fact that there is a permissible limit for the oxygen concentration profile along the reactor. An acceptable limit of oxygen concentration is below 7% mol. The operation of the reactor above this permissible limit in the concentration of oxygen will lead to flammable mixtures and the unstable behavior of the reactor.

The most difficult aspect on the use of EDC as inhibitor agent is on how to control its concentration in the reactor. The amount of inhibitor required is 3 ppm (parts per million). Controlling the inhibitor addition is very challenging in industry. Therefore, in practice it is not easy to quantify the effect of the inhibitor for various scenarios of operation. Nevertheless, the inhibitor concentration along the reactor is a critical variable to understand and manipulate.

Figure 6-9 shows the effect of EDC level on the selectivity and work-rate, the disturbance propagates in a nonlinear fashion. With the addition of EDC, there is a shift in the rates of reactions, resulting in a relatively small decrease in the amount of EO formed. Thus, the selectivity for EO increases, although the work-rate decreases.

Figure 6-10 shows the production rates of ethylene oxide and carbon dioxide decrease with increasing level of EDC, which for ethylene oxide decreases to a smaller extent. This results in a decreased load on the downstream separation units.
6.2.3 Reactant

In the next step, the influences of reactant concentrations were studied. Data for an oxygen range (5-8%) were obtained for a constant 17.5% ethylene. Also, simulation for a constant 6.16% oxygen and varying ethylene (15-19%) was carried out. The disturbance propagates in a linear fashion.
As shown in Figure 6-11, with increasing molar concentration of oxygen in the feed, work-rate increases significantly while selectivity decreases about 4%. On the other hand, with increasing ethylene concentration in the feed, work-rate increases considerably and selectivity increases slightly (Figure 6-12).

![Figure 6-11- The influences of inlet oxygen on work-rate and selectivity](image)

![Figure 6-12- The influences of inlet ethylene on work-rate and selectivity](image)

### 6.2.4 Scrubber effect

As stated earlier, the cooled reactor outlet enters into the scrubber to recover the valuable EO product by absorbing it with recycle lean water. The gas coming out at the top of the scrubber along with the remaining EO are recycled (i.e. recycle gas) back to the reactor. It is the source of EO in the reactor feed.
The EO mole fraction in feed is assumed to be less than 0.01%. In this section, the effect of EO on reactor performance is investigated.

An increase in the EO being fed back into the reactor causes a shift in the equilibrium between the ethylene epoxidation and the EO oxidation, leading to the amount of ethylene being converted to carbon dioxide and water to increase.

Although the mass of EO exiting the reactor is not greatly affected by a rise in inlet EO, there is a significant drop in selectivity due to a drop in ethylene conversion (Figure 6-13). An increase in molar concentration of EO in the feed from 0% to 1% causes selectivity to decrease by 8%. This is a significant waste of product and a decline in efficiency.

![Work-rate and Selectivity Graph](image)

**Figure 6-13 - The influence of EO inlet on the selectivity and the work-rate**

The EO scrubber as a unit responsible for removing EO has a strong impact on the reactor performance. On the other hand, more EO in feed causes more EO in product that means more EO toward the scrubber, affecting the scrubber and the separation unit.
6.2.5 Results

Results of sensitivity analysis show that:

- By increasing the EDC level in the feed, ethylene conversion decreases monotonically while the selectivity to ethylene oxide increases. However, raising the temperature to compensate for the fall in work-rate would lead to a faster aging of catalyst.

- With increasing oxygen and ethylene inlet concentrations, the work-rate improves. On the other hand, with oxygen addition, selectivity decreases significantly, while negligible effect is observed with ethylene addition.

- The oil inlet temperature has a strong effect on reactor performance while the gas inlet temperature has no significant effect on the work-rate and selectivity.

- With a rise in EO concentration in the recycle gas resulting from a poorly performing scrubber system, the selectivity decreases significantly, while the work-rate remains largely unchanged. Thus EO scrubber performance has a strong impact on the reactor performance.

- In case of linear-change and step-change, the final outcomes are similar but the reactor performance is expected to be better in case of linear increase. So, to avoid any runaway condition, linear increase is suggested.

The outcome of the sensitivity analysis aided the understanding of the process behavior. The variables having significant impact on work-rate and selectivity were identified and were used as control variables for optimisation studies. These are the EDC level, ethylene and oxygen concentration in the feed and oil inlet temperature.

6.3 Sensitivity Analysis of EO Scrubber Model

As discussed earlier, the EO content of the reactor feed stream has a negative effect on the work-rate and the selectivity, thus it is imperative for the scrubber to be
performing at its optimum capacity to ensure the maximum recovery of EO, minimising the amount being recycled back to the reactor.

The following analysis is to study the sensitivity of the following operational variables on overall scrubber performance:

- Operating pressure
- Scrubbing inlet water temperature
- Scrubbing water flow-rate
- Scrubbing inlet gas temperature

The scope of the analysis is to study the effect of the scrubber operational parameters on EO recovery only. Other constituents of the stream which are removed later in the process, are assumed to affect the scrubbing operation.

6.3.1 Operating pressure

Figure 6-14 shows the influence of the scrubber operating pressure on the overall recovery of EO. In the range of 1500-2000 kPa, the operating pressure decreases the recycled EO mass flow rate consequently increase the EO recovery. Since, with increasing pressure, the EO solubility in water increases means the amount of EO that is been recovered improves.
However, the normal operating pressure is 1960 kPa cannot be easily changed during operation. Therefore, it can be assumed during the normal operation, the scrubber pressure has no significant effect on the EO recovery.

### 6.3.2 Scrubbing inlet water temperature

The current conditions indicate a lean water temperature of 30°C with analysis performed over a range of 0 °C- 40 °C. Figure 6-15 shows that decreasing inlet water temperature lead to the increase of EO being recovered. Also, it shows the EO recovery is adversely affected by high temperature.
Antoine equation [1] (Equation 6-1), shows the relationship between temperature and saturation vapor pressure.

\[
\log_{10} p^*_s = A - \frac{B}{T + C}
\]

**Equation 6-1**

Where \( p^*_s \) = saturated vapor pressure, mmHg  
T = temperature, °C  
A = 7.40783  
B = 1181.31  
C = 250.6

It should be noted that the constant values are relevant for EO only.

Equation 6-1 shows that decreasing inlet water temperature lead to the increase of the saturation pressure of EO which it means further increasing of EO being recovered. The inlet water temperature and EO recovery has an exponential relationship, that means the EO recovery is greatly affected at higher temperatures and in the lower temperature the difference is negligible.

Figure 6-16 shows the effect of increasing +30°C step-change of inlet water temperature on the EO recovery.

![Figure 6-16- EO recovered in response to a 30°C step-change in the water temperature](image-url)
Currently cooling water is being used to cool scrubber inlet water, however there are significant seasonal variations in cooling water temperature resulting variations in recovery of EO, with higher recoveries during the cooler months, and possibly even significant fluctuations from the daily average when comparing figures from recovery of day and night.

6.3.3 Scrubbing water flow rate

Figure 6-17 shows that as flow rate of inlet scrubbing water (lean water) is increased, recovery of EO is increased. This is due to the larger amount of water coming into contact with the inlet gas allowing for a higher amount of absorption to occur.

It can be assumed the lean water flow rate is the most important parameter influencing the overall recovery of EO as it is relatively easy to control and effects would be instantly noticed.

Figure 6-17- Influence of scrubber inlet water flow rate on EO recovery
The analysis shows that a gas inlet stream containing 2500kg/hr EO coming into contact with the current lean water flow rate of 102,000kg/hr allows 12kg/hr of EO back into the reactor. If the gas inlet stream has an increased EO content, for example 3000kg/hr, then the amount of EO in the scrubber overheads being recycled back to the reactor increases to 14.98 kg/hr. This dramatically impacts the selectivity and work-rate of the reactor as discussed in chapter 3.

Currently there is no control scheme to link the EO level of the scrubber gas inlet stream to the lean water flow rate. The lean water flow rate could be used as a control variable to minimising the fluctuations on EO returning to the reactor as well as increasing the EO recovery past its current levels. This control scheme would have to be put in place with consideration of the effect on scrubber flooding and effect of the increased/decreased amount of water present in the system on the operations downstream of the scrubber, particularly the stripping section.

6.3.4 Scrubber inlet gas temperature

Another parameter which could have effect on the scrubber operation is the temperature of the scrubber gas inlet stream. Figure 6-18 shows that the temperature of the scrubber gas inlet stream has no effect on the EO recovery.

![Figure 6-18: Influence of scrubber inlet gas temperature on EO recovery](image)
6.3.5 Results

Results of sensitivity analysis show that:

➤ With increasing pressure, the EO solubility in water increases leading to an increase EO recovery. However, the normal operating pressure is 1960 kPa and it has a very small variation during operation.

➤ By decreasing inlet water temperature, the EO recovery improves. The EO recovery is greatly affected at temperatures greater than 25°C.

➤ With increasing inlet scrubbing water flow rate, the EO recovery increases due to the larger amount of water coming into contact with the inlet gas allowing for a higher amount of absorption to occur.

➤ The temperature of the scrubber gas inlet stream has no effect on the EO recovery.

➤ The variables having significant impact on EO recovery are the lean water temperature and flow rate. The lean water flow rate is relatively easy to control and effects would be instantly noticed.

6.4 Optimisation of EO Reactor

Optimisation is a procedure used for finding the maximum or the minimum of a function, usually termed the objective function. Industrially, optimisation is an important step in the design of equipment where optimal process design parameters are identified.

Equally as important in process operation, optimisation can minimise the operational costs and maximise process profitability. As such, optimisation is regarded as a fundamental step in process design and operation.

Optimisation is commonly performed at steady state conditions so called “point optimisation” where optimal steady state parameters are found. This is very well
suited for continuous and stable process design and operation. Steady state optimisation does not address the issues related to start-up, shut-down and operation upsets. These transient process require more complex treatment and fall in the category of “dynamic optimisation”.

Even though advances in the mechanistic modelling of EO reactor and the acceptance of these fundamental models by the research community and industry should have motivated numerous studies to improve the operating conditions of industrial ethylene epoxidation, only scattered evidence of model-based optimisation of EO reactor can be found in the open literature.

Most of researches were, and still are, focused on probing the mechanism of the reaction on silver catalysts for the purposes of developing more efficient silver catalysts [2–4] and more reliable reaction kinetics [5–7]. As an exemplary process, ethylene epoxidation has also been served as the reaction system for modelling studies and non-linear behavior analysis [8, 9]. Besides, it has been frequently the object of process intensification [10, 11].

Due to its great importance in industry and large scale of production, process optimization of ethylene epoxidation is undoubtedly another important research topic. However, papers contributed to this topic are very scarce.

Baratti et al. [12] proposed a strategy to maximize the reactor performance by optimizing the catalyst distribution in the pellets or in the reactor, without consideration of the operating condition on the optimization performance.

The article by Zhu (1992) [13], which was closely related to process optimization of ethylene epoxidation, was only descriptive and more concerning the significance of optimization of this process, rather than a practicable optimization.

Perhaps the first substantial contributions in this area are from Gudekar et al. (2005) [9] and Zhou et al (2005) [14]. Kishor et al, in their work, performed an open-loop and closed-loop nonlinear stability analysis of an industrial ethylene oxide reactor using bifurcation techniques. They developed stable control regions of the ethylene
oxide reactor system as a function of operating temperature, catalyst activity, controller tuning, and disturbance direction and magnitude. They simulated a reactor runaway event, from which it is shown that eliminating the oxygen in the feed to the reactor can be used to prevent reactor runaway. However, the effect of EDC and EO oxidation were neglected in their model.

Zhou et al [14], developed a steady state, one dimensional model to determine optimal feed composition, feeding rate and operation pressure for EO fixed-bed reactor. Also, they found that the optimal performance obtained by the dynamic optimization policy with time-dependent inlet EDC concentration is very close to that of the constant EDC addition policy.

In this study, the EO reactor model developed in Chapter 3, is used in this subsequent process optimisation. The point and dynamic optimisation are carried out to achieve the desired process objective. The objective of the optimisation is to maximize the reaction rate up to the “flammability” limit - the fundamental limit of the reactor after which the ethylene burns and the reaction can run away.

Because the EO process is non-linear and exhibits transient behaviour, the operational optimisation of this process is a non-linear dynamic one with constraints. gPROMS offers gOPT – an optimisation facility which is chosen for the dynamic optimisation of the EO process in this study. The choice of this tool is motivated primarily by the fact that the model simulation solution is performed in the gPROMS environment. Secondly the implementation of the optimisation in gOPT is very simple. Furthermore the gOPT code employs piecewise control variable definition as per the control vector parametrisation technique [15] allowing for optimal control variable profiles to shape the optimal solution. The implementation of the optimisation problem in gOPT is described next.
6.4.1 Point optimisation

There are a number of ingredients that constitute the optimisation formulation. These are the process model, the initial conditions, the objective function, the decision variables and variable constraints.

The process model is the mathematical representation of the process and along with the initial conditions completely describes the transient nature of the process. These have been explicitly described in previous chapters.

The objective function is a mathematical function formulated around the optimisation objective. It usually describes a process condition that is either maximised or minimised. This condition may be a process variable or a relation defining a certain condition to be optimised. A generic formulation of the objective function is given in Equation 6-2

\[ \text{Max } J(x_i, x_{i+1}, \ldots, x_n) \quad i = 1, 2, \ldots, n \]  

Equation 6-2

In the relation \( J(x_i, x_{i+1}, \ldots, x_n) \), \( \bar{x} \) is a vector representing the adjustable parameters or what is termed decision variables. These are the parameters subjected to successive (iterative) variation during the optimisation solution search. A number of iteration is required before reaching the optimum. An initial guess is supplied to provide an initial estimate of the decision variables so that optimisation is initiated. The constraints of the problem are the bounds imposed on the variables of the process. These constraints usually represent physical bounds in the process or limitations in operational conditions. For instance the temperature in a reactor may be bounded between a minimum where the reaction is not viable and a maximum where safety considerations are taken into account. There are a number of different types of constraints that may be formulated and these include equality and inequality constraints as well as algebraic and differential ones.

In EO reactor, the objective function is to maximize conversion of ethylene to EO (selectivity) within the flammability limit which the reactor can operate safely.
As results of sensitivity analysis, the coolant temperature, EDC level, and reactant concentration in the feed which have significant effect on the reactor performance, can be manipulated for a maximal profit. EO has a significant negative effect on the selectivity and work-rate. However, in practice, its concentration is kept as small as possible. The inlet feed temperature has only a small effect on the productivity and the bed temperature, and therefore, not to be used as manipulated variable.

The flammability is the major constraint of the EO reactor. The flammability limit gives the proportion of combustible gases in a mixture, between which limits this mixture is flammable. It is known that in actual practice in order to remain outside the flammability limit of the gas mixture the concentration of oxygen has to be lowered as the concentration of ethylene is raised. The actual safe operating ranges depend, along with the gas composition (reactants and balance gases), also on individual plant conditions such as temperature and pressure. Therefore in each individual plant a so-called flammability equation is used to determine the concentration of oxygen which may be used with any given concentration of ethylene. This flammability equation can be expressed graphically in a so-called flammability curve.

The flammability limit is calculated based on the maximum allowable oxygen limit using equation provided by Scientific Design Company [16].

Objective function is to maximize the selectivity. Depend on the EO market demand, the required production rate varies.

The point optimisation is carried out for 2 case studies:

- **First case study**: Low production rate (110 Ton/day EO)
- **Second case study**: High production rate (130 Ton/day EO)

**gPROMS**: gOPT facility is used to maximise the objective function (Selectivity) using the control variables with respect to the all constraints.
The set up constraints and the final value for first and second case study are shown in Table 6-1 and Table 6-2, respectively. The main constraint is the flammability limit which is set to > 0.3. The other constrains are the oil outlet temperature and the gas outlet temperature which are respectively set to less than 280 °C and 275 °C. The reaction initiation temperature is set to minimum 220 °C.

<table>
<thead>
<tr>
<th>Constraint</th>
<th>Optimum Value</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work-rate (Ton/day)</td>
<td>111</td>
<td>110</td>
<td>111</td>
</tr>
<tr>
<td>Oil Outlet Temperature (°C)</td>
<td>237.6</td>
<td>200</td>
<td>280</td>
</tr>
<tr>
<td>Gas Outlet Temperature (°C)</td>
<td>239.8</td>
<td>200</td>
<td>275</td>
</tr>
<tr>
<td>Initiate Temperature (°C)</td>
<td>223</td>
<td>223</td>
<td>270</td>
</tr>
<tr>
<td>Flammability Limit (%)</td>
<td>0.6</td>
<td>0.3</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Control Variable</th>
<th>Optimum Value</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Inlet Temperature (°C)</td>
<td>233.8</td>
<td>230</td>
<td>260</td>
</tr>
<tr>
<td>Ethylene Inlet (Mol. Frac. %)</td>
<td>17.5</td>
<td>15</td>
<td>17.5</td>
</tr>
<tr>
<td>Oxygen Inlet (Mol. Frac. %)</td>
<td>6.48</td>
<td>5</td>
<td>7.5</td>
</tr>
<tr>
<td>EDC Level (ppm)</td>
<td>1.5</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Objective Function Value (Selectivity %)</td>
<td>81.7%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The control variables and their optimum values the first and second case studies are shown in Table 6-3 and Table 6-4, respectively. The EDC level, ethylene and oxygen concentration in the feed and oil inlet temperature are chosen as control variables.

<table>
<thead>
<tr>
<th>Constraint</th>
<th>Optimum Value</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work-rate (Ton/day)</td>
<td>130</td>
<td>129</td>
<td>131</td>
</tr>
<tr>
<td>Oil Outlet Temperature (°C)</td>
<td>242.0</td>
<td>200</td>
<td>280</td>
</tr>
<tr>
<td>Gas Outlet Temperature (°C)</td>
<td>244.0</td>
<td>200</td>
<td>280</td>
</tr>
<tr>
<td>Initiate Temperature (°C)</td>
<td>225.406</td>
<td>223</td>
<td>240</td>
</tr>
<tr>
<td>Flammability Limit (%)</td>
<td>0.3</td>
<td>0.3</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 6-4- Control variables for high level of work-rate

<table>
<thead>
<tr>
<th>Control Variable</th>
<th>Optimum Value</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Inlet Temperature (°C)</td>
<td>234.141</td>
<td>223</td>
<td>260</td>
</tr>
<tr>
<td>ethylene Inlet (Mol. Frac. %)</td>
<td>19</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>oxygen Inlet (Mol. Frac. %)</td>
<td>7.05</td>
<td>5</td>
<td>7.5</td>
</tr>
<tr>
<td>EDC Level (ppm)</td>
<td>1.5</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>Objective Function Value (Selectivity %)</td>
<td></td>
<td></td>
<td>81.0%</td>
</tr>
</tbody>
</table>

In the start of run, the results show in both cases the ethylene concentration and the EDC level act as active bounds. Furthermore, in low production rate (first case) the initial temperature acts as lower active bound. However, in high production rate (second case), the oxygen concentration acts as lower active bound in response to a flammability point.

Also the results show that the optimum selectivity in first case (low work-rate) is higher than the second case (high work-rate). To increase the work-rate, the oil inlet temperature has to be increased to enhance the reaction rates, the penalty being a decrease in the selectivity.

In the next section, firstly the concept of dynamic optimisation is discussed. The results of the point optimisation are used as an initial point to carry out dynamic optimisation.

6.4.2 Dynamic optimisation

The mathematical description of a dynamic optimisation problem is summarised as follows:

\[
\max_{t_f, u(t), v \in [0, t_f]} \quad (z(t_f))
\]

\[
F(\dot{x}(t), x(t), y(t), u(t), v) = 0, \quad t \in [0, t_f]
\]  \hspace{1cm} \text{Equation 6-4}

\[
l(\dot{x}(0), x(0), y(0), u(0), v) = 0
\]  \hspace{1cm} \text{Equation 6-5}

\[
t_f^{\min} \leq t_f \leq t_f^{\max}
\]  \hspace{1cm} \text{Equation 6-6}
\[ u_{\text{min}}(t) \leq u(t) \leq u_{\text{max}}(t) \quad , \quad t \in [0,t_f] \]

Equation 6-7

\[ v_{\text{min}} \leq v \leq v_{\text{max}} \]

Equation 6-8

\[ w_{ei}^\text{min} \leq w(t_f) \leq w_{ei}^\text{max} \]

Equation 6-9

\[ w_{ee}(t_f) = w_{ee}^\text{qr} \]

Equation 6-10

\[ w_{i}^\text{min}(t) \leq w(t) \leq w_{i}^\text{max}(t) \quad , \quad t \in [0,t_f] \]

Equation 6-11

\[ w_{j}^\text{min}(t) \leq w(t) \leq w_{j}^\text{max}(t) \quad , \quad t \in [0,t_f] \]

Equation 6-12

Equation 6-3 indicates that the optimisation (maximisation) is performed considering the variable \( z(t_f) \) as performance measure or objective function. Without any loss of generality, the objective function is simply the magnitude of a variable \( z(t) \) evaluated at the end of the optimisation horizon \( t = t_f \). In addition, Equation 6-3 denotes the fact that the decision variables of the optimisation problem are the time horizon \( t_f \) (a scalar) and a subset of variables given by the vectors \( u(t) \) and \( v \). The former denotes control variables that are allowed to vary in response to a functionality \( u(t) \) over the span of the time horizon \( [0,t_f] \). The latter indicates parametric variables that are fixed at a value \( v \).

Equation 6-4 simply denotes the set of differential-algebraic equations (DAEs) encompassing the fundamental process model, while Equation 6-5 symbolises a set of additional equations (initial conditions) that must be satisfied at the beginning of the optimisation horizon. In these equations \( x \) and \( y \) denote differential and algebraic variables respectively, and \( \dot{x} \) indicates the time derivatives of the former.

There a number of different types of constraints that may be formulated and these include equality and inequality constraints as well as algebraic and differential ones. Equation 6-6, Equation 6-7 and Equation 6-8 denote lower and upper bounds on the decision variables, indicated by the superscripts min and max respectively. These
constraints on the decision variables are stated explicitly since they can be handled very efficiently by modern optimisation algorithms.

There are also other types of constraints and importantly those which bound the decision variables and in some cases the time horizon of the process. Further constraints are in the form of interior point constraints, path constraints and end-point constraint.

End-point constraints are those which impose a condition on the process that must be satisfied at the end of the operation. For example the end product concentration must be higher than 99% - being a purity demand. This constraint can be formulated as inequality one where a the constrained condition must be less than a desired value (Equation 6-9), greater than a desired value or even inside a desired region or it may be formulated as an equality one where the final value of the constrained condition must equal a desired value (Equation 6-10).

Equation 6-11 denotes interior-point constraint variables, which are used to enforce process variables to lie within the defined upper and lower bounds at any other time but the end of the optimisation horizon. By definition these are inequality constraints. Although the inclusion of these constraints is not strictly necessary, the work of Vassiliadis et al. [17] demonstrated that adopting them could increase the robustness and efficiency of solution algorithms handling inequality path constraints. Equation 6-12 symbolises the inequality path constraints mentioned above.

There are two standard mathematical solvers available in gPROMS for solving dynamic optimisation problems [18].

The first (default) implements a control vector parameterisation algorithm based via single-shooting (CVP_SS).

The second solver is an implementation of control vector parameterisation via multiple-shooting (CVP_MS).
In general, CVP_MS is more suited than CVP_SS for solving dynamic optimisation problems with relatively few differential variables but a large number of control variables and/or control intervals.

Two case studies have been carried out as follows:

- **First case study**: The optimal profile for the coolant temperature during 3 years operating time.
- **Second case study**: The optimal profile for the coolant temperature and ethylene for transient between low production rate (110 Ton/day) to high production rate (130 Ton/day).

**First case study**

The results from point optimisation presented in Table 6-5 are used as an initial condition for the dynamic optimisation.

Since the catalyst decays continuously, the production process is essentially dynamic and a dynamic optimization strategy should be used. However, it is not feasible to simultaneous change all the variables dynamically. Also experience shows that the improvement of the optimization performance with more than one variable in dynamic optimization is minor over that when only one variable is varied dynamically while others are fixed to constant sub-optimal values [19]. The variable that is most sensitive to dynamic behavior is bed temperature, which is most responsible for thermal sintering and catalyst decay.

Activity losses are attributed to a decrease of the catalyst surface area, by poisoning or sintering, and a monotonic decline in selectivity is implicated as the temperature is increased to obtain a desired total reaction rate (work-rate).

Figure 6-19 shows the oil inlet temperature optimal profile to obtain the desired work-rate (127 Ton/day) for the 3 year operation according to maximise selectivity. As it seen, the oil inlet temperature needs to be increased by 15 °C to compensate the catalyst deactivation.
By increasing oil inlet temperature, the selectivity is expected to decrease gradually during operating time. Figure 6-20 shows the loss of selectivity in response to an optimal condition for the 3 years of operation.

The forecast data from catalyst vendor shows that oil inlet temperature is required to increased by 18 °C (Figure 4-1) and selectivity will decrease by 4.5% (Figure 4-2). However, the optimisation results show that the oil inlet temperature is required to increase by 15 °C (Figure 6-19) and selectivity will decrease by only 2% (Figure 6-20).

This is partly due to different assumption in initial condition. Nevertheless, the results show that the EO reactor performance can be improved by more than 2% in selectivity. This means less ethylene burns and more EO produced which is the ultimate goal of this thesis.

![Figure 6-19 - The optimal oil inlet profile for 3 years operating time](image-url)
Second case study

Due to market demand, plant is required to shift work-rate from high production rate (130 Ton/day) to low production rate (110 Ton/day) and vice versa. This case study has been carried out to achieve maximum selectivity during transition time with respect to safety.

As it seen in Table 6-2 and 6-4, inlet oxygen concentration was upper active bond for high production rate. Also, temperature was playing a major role in both cases. Therefore, in this case study, oil inlet temperature and oxygen inlet concentration are used as control variables to shift work-rate from 110 (Ton/day) to 127 (Ton/day) and objective function is to maximize selectivity. The ethylene inlet concentration and the EDC level are kept constant of 17.5% and 1.5 ppm, respectively. Also, it is assumed the transition operation will take place in 2 hours.

As results of sensitivity analysis, to avoid any runaway condition linear increase was suggested. Therefore, piecewise-linear control was used for the oxygen inlet concentration and the oil inlet temperature.
The results obtained from point optimisation- first case study have been used as an initial point. Figure 6-21 shows the optimal transition profiles for the oil inlet temperature and Figure 6-22 shows the optimal transition profiles for the oxygen concentration.

The results show that to increase the work-rate from 110 (Ton/day) to 127 (Ton/day), the oil inlet temperature and the oxygen concentration are required to increase by 4 °C and 0.5%, respectively.

Increasing oil temperature results in enhancing the catalyst activity and increasing oxygen concentration will help the reactions take place. Therefore, the work-rate will be increased; however, selectivity would be lost. Figure 6-23 shows the change in work-rate during the transition period. Figure 6-24 shows a decline in selectivity by 1.2% which is the consequence of increasing oil inlet temperature.

Figure 6-21- Optimal transition profiles for the oil inlet temperature
Figure 6-22- Optimal transition profiles for the oxygen inlet concentration

Figure 6-23- Work-rate transition
6.5 SUMMARY

In this chapter, the validated model of the EO reactor and the EO scrubber developed in previous chapters, were used to conduct a sensitivity analysis.

Using the validated EO reactor model, the effect of the oil and gas inlet temperature, the EDC level, the ethylene and oxygen inlet concentration and the EO scrubber performance on the reactor performance were investigated. The results showed that showed that the EDC level and oil inlet temperature have a major effect on the both selectivity and work-rate and the gas inlet temperature has negligible effect on the reactor. The ethylene and oxygen concentration in the feed have only effect on the work-rate and the selectivity, respectively. By increasing EO concentration in the recycle gas, the selectivity decreases significantly, while it has negligible effect on the work-rate.

Furthermore, the effects of the operation variables on the EO scrubber performance were studied. The result showed that by increasing scrubber pressure or decreasing the inlet water temperature the EO recovery improves, however the normal operating
pressure is 1960 kPa and it has a very small variation during operation. Also, the flow rate of the inlet scrubbing water has direct effect on the EO.

Point and dynamic optimisation in general were discussed and different scenario of optimisation of the EO reactor was studied. The EDC level, the oil inlet temperature and the ethylene oxygen inlet concentration were used as control variables. The flammability limit, the fundamental constraint in the EO reactor and other constrains were introduced to the system. The objective function in all scenarios was to maximize the selectivity. The results showed that by using optimum profile, the selectivity could be improved by more than 2%. 
6.6 Bibliography


16- Scientific Design Company


Chapter 7

Conclusion and Future Directions

This chapter provides a brief summary and the main conclusion of this thesis. Also, recommendations for further research are presented.
Ethylene oxide is one of the most versatile chemical intermediates species used in chemical manufacturing and processing.

Ethylene oxide production is complex in nature and is known to be highly non-linear, thus posing difficulties in its modelling and control. In addition, EO reactor operates close to both runaway and flammability limits. Any unanticipated disturbances during process operation could lead to runaway condition and catalyst damage. Compounding the problem is to control key factors such as addition of EDC which can have a major effect on the EO reactor performance.

Dynamic modelling and optimisation of EO reactor and EO plant are in centre of this project which are main contributions of this thesis.

7.1 CONCLUSION

In this work, the emphasis has been centered on the following research areas:

➢ Dynamic Modelling of EO Reactor

In this thesis, a one-dimensional heterogeneous dynamic model of the EO reactor was developed. The EO reactor model consists of a set of nonlinear kinetic expressions coupled with heat and mass conservation equations and variable physical properties along the reactor length. The calculation of the shell side heat transfer was carried out based on the Bell-Delaware method. For the tube side heat transfer and the heat transfer coefficient for catalyst pellet, respectively, a modified expression by Thoenes and Kramers and a correlation for the heat transfer based on the Chilton Colbun j-factor for 1 inch alumina balls developed by Hougen et al were used. The pressure drop estimation was based on plant data, correlated as a function of gas flow rate using Ergun equation for packed beds.

The solution method of the model was investigated with a focus on the discretisation technique. This was investigated and the model was subsequently solved using gPROMS.
The catalyst vendor data were used to estimate the kinetics constants. Also, they are used to predict the catalyst deactivation over 3 years of plant operation. The plant data from Huntsman EO reactor were used to validate the model. The results showed satisfactory agreement between the model prediction and plant data. Furthermore, the discrepancy between the model predictions and the plant data were discussed and reasons for plant/model mismatch were discussed.

The key features of the EO reactor model are that the model covers EO oxidation as well as partial and total ethylene oxidation, with emphasis on the importance of the inhibiting effect of EDC on the all reaction rates. Furthermore, no fitting data from plant data was used to estimate the model parameters. The results showed acceptable agreement with the plant data, thus model was validated. The model has the capability to represent the reality.

- **Dynamic Modelling of the Other Units of EO Plant**

The other units in the EO plant (especially EO scrubber and hot oil cooler) could have a major effect on the reactor performance. To investigate the effect of the other units in the EO plant on the reactor performance, dynamic model of the EO scrubber, gas-gas heat exchanger and hot oil cooler were developed in HYSYS simulation package. The model prediction for the EO scrubber was benchmarked against the plant data. The model prediction results showed satisfactory agreement with the plant data. Thus the model was validated and it could be used to represent the plant.

- **Hybrid Modelling of EO Plant**

Architecture for the modelling of complex process has been introduced. Separate sections of such process were built in each program. The EO reactor model in gPROMS was linked to the EO plant model in HYSYS using CAPE-OPEN environment. The results between the HYSYS and gPROMS were compared. The results showed satisfactory agreement.
The significance of the above result is that the model of a process can be built in parts, using a number of programs, and then connected to create a dynamic hybrid model that can be used to simulate plant, under different operating conditions and schedules. This model can be redesigned and maintained easily; enabling integrated process modelling to be accomplished with increased speed and greater confidence.

- **Sensitivity Analysis of EO Plant**

The validated model of the EO reactor and the EO scrubber were used to conduct a sensitivity analysis to determine suitable control variables. Results of sensitivity analysis for the EO reactor showed that the EDC level and oil inlet temperature have major effects, on both selectivity and work-rate. However ethylene concentration’s main effect is on the work-rate and oxygen concentration’s is on the selectivity. The gas inlet temperature has negligible effect on the reactor. The EDC level, oil inlet temperature, ethylene and oxygen concentration in feed are suitable as control variables.

Results of sensitivity analysis for the EO scrubber showed that the lean water temperature has an inverse effect on EO recovery. However, the flow rate of lean water has a direct effect on EO recovery. The temperature of the scrubber gas inlet stream has no significant effect on the EO recovery. The variables having significant impact on EO recovery are the lean water temperature and flow rate. Lean water flow rate is relatively easy to control and its effects would be instantly noticed.

The sensitivity analysis of the EO plant showed that the EO scrubber has strong effect on the reactor performance. By increasing the EO concentration in the recycle gas, the selectivity decreases significantly which this is a waste of product and a decline in efficiency.
Optimisation of EO Reactor

The variables having significant impact on work-rate and selectivity were identified by the sensitivity analysis study, and used as control variables for optimisation. These are the EDC level, ethylene and oxygen concentration in the feed and oil inlet temperature. The objective of the optimisation is to maximize the selectivity with respect to the operational and physical constrains. The point and dynamic optimisation with different scenarios were carried out. The outcomes of point optimisation were used as initial conditions for the dynamic optimisation.

The results from point optimisation study showed that the ethylene concentration and the EDC level act as active bounds. At high production rates, the oxygen concentration acts as a lower active bound in response to a flammability point.

In dynamic optimisation, firstly, the oil inlet temperature was used as a manipulated variable to compensate for the catalyst activity losses during 3 years operating time. The oil inlet temperature optimal profile was calculated to obtain the desired work-rate (127 T/day) in order to maximise selectivity. The results were compared with the vendor data and we concluded that the selectivity could be improved by more than 2%. Thus, less ethylene will burn and more EO will be produced; these are the key goals of this thesis.

Furthermore, optimal transition profiles for oil inlet temperature and oxygen concentration were estimated to shift the work-rate from 110 (Ton/day) to 127 (Ton/day) which maximising the selectivity. The results show that in order to increase the work-rate, the oil inlet temperature and the oxygen concentration require to be increased by 4 °C and 0.5 mol%, respectively. Consequently, the selectivity would decrease by 1.2%. The validated model of the EO reactor and the EO scrubber were used to conduct a sensitivity analysis to determine the control variables. The results of the sensitivity analysis for the EO reactor showed that the EDC level and oil inlet temperature have major effects on the
both selectivity and work-rate. However ethylene concentration mainly affects the work-rate and oxygen concentration only affects the selectivity. The gas inlet temperature has negligible effect on the reactor. The EDC level, oil inlet temperature, ethylene and oxygen concentration in feed are considered as main manipulated variables in order to achieve optimal control.

7.2 Recommendations and Future Research Directions

The work presented in this dissertation could be extended further and amalgamated with complementary research topics. The following represent key areas worthy of review and attention:

➤ Modelling of CO2 removal and separation unit

Carbon dioxide is one of the ethylene oxide reactor effluents and recycle streams. CO₂ should be removed as a gas contaminant from the mixture. The removal of carbon dioxide (CO₂) from reactor effluents and recycle streams, using absorption with chemical reaction technique, is one of critical importance for EO operation, where the primary purposes range from prevention of ethylene oxide catalyst poisoning, enhancing the quality of the final products to reducing greenhouse gas emissions from ethylene and oxygen reaction. CO₂ absorption occurs when a gas phase containing CO₂ is brought into direct contact with a liquid phase under appropriate conditions. This takes place in a CO₂ absorption unit.

As stated earlier, the cooled reactor outlet is sent to the EO scrubbing system to recover the EO product by absorbing it with the lean recycle water. Rich cycle water from EO scrubber is heated and flashed to a low pressure before entering the Stripping Column. The flashing feed releases most of the EO and other gases. Steam is used to drive off the remaining EO. The separation unit is responsible for the final purity of the product.
The CO₂ removal and separation units are required to be modeled, validated and connected to the EO plant model presented in this thesis.

➢ Develop dynamic hybrid model

The hybrid modelling environment in this work were developed using CAPE-OPEN environment. However, CAPE-OPEN described mainly in unpublished drafts, the standard is currently not combined to be stable and accessible enough for dynamic hybrid co-simulation. There are other method by which the architecture can be combined, as there are a number of options available to establish the link between the different softwares. Since both gPROMS and HYSYS are capable of importing and exporting data into Excel, it is suggested that, Excel as the connection bridge, be used as the link between gPROMS and HYSYS.

Also, the hybrid modelling simulation environment developed in this work may be extended to bring in other capabilities into the picture namely computational fluid dynamics (CFD) modelling. Communication between gPROMS and CFD software will need to be established within the modelling environment to study heat transfer in the EO reactor in more details.

➢ Control of EO reactor

This work could be used to develop a model based (multi layer) framework for advanced operation of EO reactor. An MPC (Model Predictive Control) strategy may be implemented to provide the optimal oil inlet temperature trajectories to regulatory control layer. The MPC must be based on the EO plant model developed in this thesis to implement an advanced control strategy for the optimal operation of the reactor.

With this strategy, the cost factor, production capacity targets, raw material availability and production schedule may be determined by the scheduling layer which would run on a plant wide information management system.
Expert system

It is desirable to design a framework that will intelligently drive the EO operation independent of the operator. The quest for automation requires the assembly of a real-time expert system which acts as a commander residing above the two-layer control structure proposed. The development of such a system will require the integration of the predictive control, statistical monitoring, fault diagnosis and identification tools.
Appendix A

Inlet Data
Figure A-1- The inlet oil temperature of the plant data during 3 years plant data

Figure A-2- The inlet feed volume of the plant data during 3 years plant data

Figure A-3- The inlet ethylene concentration of the plant data during 3 years plant data

Shahla Aryana
Figure A-4- The inlet oxygen concentration of the plant data during 3 years plant data

Figure A-5- The inlet CO2 concentration of the plant data during 3 years plant data

Figure A-6- The inlet EDC level of the plant data during 3 years plant data
Appendix B

Shell Side Heat Transfer
The shell side heat transfer coefficient in the reactor is calculated using Bell-Delaware Method. In Bell' method, some correlation factors were applied to the ideal cross-flow heat transfer value.

The first step is to calculate the cross-flow heat transfer coefficient. The Reynolds number Re is defined by Equation B-1.

\[ \text{Re} = \rho V_{\text{max}} \frac{D_o}{\eta} \]  
\textbf{Equation B- 1}

where 
- \( \rho \) = Fluid density 
- \( \eta \) = Fluid viscosity 
- \( D_o \) = Tube outside diameter 
- \( V_{\text{max}} \) = Maximum fluid velocity

\( V_{\text{max}} \) is defined as the maximum fluid velocity between the tubes near the centerline of the flow and is given by Equation B-2.

\[ V_{\text{max}} = \frac{\dot{M}}{\rho S_m} \]  
\textbf{Equation B- 2}

\( S_m \) is the flow area near the centerline and for triangular pitch is calculated by Equation B-3.

\[ S_m = \frac{1}{\alpha} (D_s - D_{on} + \frac{D_{on} - D_o}{0.5P_T} (P_T - D_o)) \]  
\textbf{Equation B- 3}

The value \( \alpha \) is got by rearranging Equation B-4 and determining the value of the Nusselt and Prandtl numbers by Equations B-5 and Equations B-6, respectively.

\[ \text{Nu} = \frac{\alpha D_o}{\lambda} \]  
\textbf{Equation B- 4}

\[ \text{Nu}_c = 0.273 \times \text{Re}^{0.635} \times \text{Pr}^{0.34} \]  
\textbf{Equation B- 5}

\[ \text{Pr} = \frac{C_p \mu}{\lambda} \]  
\textbf{Equation B- 6}
The next step is to calculate the Correction factors. Bell introduced the Correction factors for the following elements:

1. Leakage through the gaps between the tubes and the baffles and the baffles and the shell, respectively (\(J_L\)).
2. Bypassing of the flow around the gap between the tube bundle and the shell (\(J_B\)).
3. Effect of the baffle configuration (\(J_C\)).

The correction factor for leakage (\(J_L\)) is related to the shell-to-baffle and tube-to-baffle leakage areas, \(S_{sb}\) and \(S_{sb}\), respectively. \(S_{sb}\) and \(S_{sh}\) are calculated using Equation B-7 and Equation B-8, respectively.

\[
S_{sb} = D_o \delta_{sb} \left[ \pi - \cos^{-1} \left(1 - \frac{2L_C}{D_o} \right) \right]
\]  \hspace{2cm} \text{Equation B-7}

\[
S_{sh} = \pi D_o \delta_{sh} N_T \left(1 + F_c \right)/2
\]  \hspace{2cm} \text{Equation B-8}

Where \(\delta_{sb}\) and \(\delta_{sh}\) are the radial clearance between the baffle and shell and the tube and baffle, respectively. \(J_L\) is related to \((S_{sb} + S_{sh})/S_m\) with \(S_{sh} / (S_{sb} + S_{sh})\) as a parameter. The value of \(J_L = 0.54\) was obtained from the graph presented by Bell (1973).

The correction for bypass in the bundle-shell gap (\(J_B\)) is given as a function of \(F_{sp}\), the fraction of the cross-flow area available for bypass flow. \(F_{sp}\) is calculated by Equation B-9.

\[
F_{sp} = \frac{(D_o - D_{on})L_B}{S_m}
\]  \hspace{2cm} \text{Equation B-9}

The value of \(J_B = 0.90\) was obtained from the graph presented by Bell (1973). The parameter in the graph is the ratio of the number of pairs of sealing strips (\(N_d\)) to the number of cross rows (\(N_c\)). \(N_c\) was estimated using Equation B-10.
\[ N_c = \frac{D_s (1 - 2 L_c / D_s)}{P_{TP}} \quad \text{Equation B-10} \]

The correction for baffle configuration \((J_c)\) is expressed as a function of the fraction \((F_c)\) of tubes in cross flow (Equation B-11). \(F_c\) is calculated using Equation B-12.

\[ J_c = 0.55 + 0.72 F_c \quad \text{Equation B-11} \]

\[ F_c = \frac{1}{\pi} \left[ \pi + \frac{2(D_s - 2L_c)}{D_{OTL}} \sin^{-1} \left( \frac{D_s - 2L_c}{D_{OTL}} \right) - 2 \cos^{-1} \left( \frac{D_s - 2L_c}{D_{OTL}} \right) \right] \quad \text{Equation B-12} \]

is the baffle cut distance calculated be Equation B-13.

\[ L_B = B_c D_s / 100 \quad \text{Equation B-13} \]

where \(B_c\) is the percentage baffle cut. The value of \(J_c = 1.1722\) was obtained from Equation B-11.

Finally, the shell-side heat transfer coefficient \((\alpha_s)\) is calculated using Equation B-14.

\[ \alpha_s = \alpha_c \times J_L \times J_B \times J_c \quad \text{Equation B-14} \]
Appendix C

gPROMS Optimisation Output
The following process are available:

EO_DYNAMIC

Requesting gOPT_1 license from server.
License granted by server(s) 129.78.12.29.
gPROMS array initialisation took 0 seconds.
There are 4482 variables in this process.
Performing PRESET RESTORE "primeEO1301", "primeEO130state1",
"primeEO130algebraic1" ...
Restoring data from primeEO1301.gSTORE ...
The number of variables in the saved process is 4483
A total of 4482 variables have been restored.
Restoring data from primeEO130state1.gSTORE ...
The number of variables in the saved process is 4483
A total of 402 variables have been restored.
Restoring data from primeEO130algebraic1.gSTORE ...
The number of variables in the saved process is 4483
A total of 4067 variables have been restored.
75241 active expression nodes created (48 bytes each).

Building mathematical problem description took 2 seconds.
Parsing input/EO_OPTIMISE_CASE1.gOPT
Solving NLP Optimisation...
Integrating...

<table>
<thead>
<tr>
<th>No. of Step</th>
<th>No. of Objective</th>
<th>Current Constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iterations</td>
<td>Functions</td>
<td>Length Function</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>38953.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No. of Step</th>
<th>No. of Objective</th>
<th>Current Constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iterations</td>
<td>Functions</td>
<td>Length Function</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>38953.6</td>
</tr>
</tbody>
</table>

The NLP optimal point:
Current Values of Optimisation Decision Variables
([*] denotes an active bound)

<table>
<thead>
<tr>
<th>Decision Variable</th>
<th>Type</th>
<th>Value</th>
<th>Lower Bound</th>
<th>Upper Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time horizon</td>
<td></td>
<td>4.81E+006</td>
<td>4.75E+006</td>
<td>4.85E+006</td>
</tr>
<tr>
<td>Control Interval #1</td>
<td></td>
<td>2.405E+006</td>
<td>2.399E+006</td>
<td>2.405E+006[*]</td>
</tr>
<tr>
<td>Control Interval #2</td>
<td></td>
<td>2.405E+006</td>
<td>2.399E+006</td>
<td>2.405E+006[*]</td>
</tr>
</tbody>
</table>

1. R101.TOIL_IN (piecewise linear)
Control At Interval Start At Interval End
Interval Value Lower Bound Upper Bound Value Lower Bound Upper Bound
#1 234.75 234.75[*] 2350 235.254 235 236
#2 235.3 235.3[+] 236 235.9 235.9[+] 236.5
Objective function: 38953.6

Current Values of Constrained Variables
([*] denotes violation of constraint)

Constrained Variable Type Time Value Lower Bound Upper Bound
R101.AAWR_OUT Interior 0 127.285 127 129
R101.AAWR_OUT Interior 2.405E+006 127 127[*] 129
R101.AAWR_OUT Endpoint 4.81E+006 127.022 127 129
R101.WR_LIMIT Endpoint 4.81E+006 2.73174E-010 0 1

*************
* * SOLUTION FOUND *
* *
*************

Computational Statistics

Total CPU Time : 49.688 seconds

CVP_SS Optimiser Statistics
  CPU Time : 0.015 seconds (0.030188 % of total time)
  Number of MINLP Iterations : 0
  Number of NLP Iterations : 2
  Number of NLP Line Search Steps : 2

DASOLV Integrator Statistics
  CPU Time : 29.719 seconds (59.811218 % of total time)
  CPU Time Spent on State Integration Only : 4.531 seconds (15.246134 % of DASOLV time)
  127 steps, 152 residuals : 1.42599 seconds
  45 Jacobians : 0.373005 seconds
  CPU Time Spent on Sensitivity Integration Only : 25.188 seconds (84.753866 % of DASOLV time)
  258 steps, 312 residuals : 2.373 seconds
  352 Jacobians : 3.377 seconds
  Mean (Sensitivity+State)/(State) CPU Ratio : 6.55904

Returning gOPT_1 license to server.
License returned to server.
Returning gSRV_1 license to server.
License returned to server.
Disconnected from license server.
Appendix D

TEMA Designation
The Tubular Exchanger Manufacturers' Association (TEMA) produce the most widely known standard in the heat transfer business, which is on shell-and-tube heat exchangers. They currently update the standards every 10 years with "TEMA 98" having been published slightly late, in 1999.

An overview of the TEMA designation describing type of Heat Exchangers.

<table>
<thead>
<tr>
<th>Front End Stationary Head</th>
<th>Shell Type</th>
<th>Rear End Stationary Head</th>
</tr>
</thead>
<tbody>
<tr>
<td>A CHANNEL AND REMOVABLE COVER</td>
<td>E ONE PASS SHELL</td>
<td>L FIXED TUBESHEET, LIKE 'A' STATIONARY HEAD</td>
</tr>
<tr>
<td>B BONNET (INTEGRAL COVER)</td>
<td>F TWO PASS SHELL WITH LONGITUDINAL BAFFLE</td>
<td>M FIXED TUBESHEET, LIKE 'B' STATIONARY HEAD</td>
</tr>
<tr>
<td>C CHANNEL INTEGRAL WITH TUBE-SHEET AND REMOVABLE COVER</td>
<td>G SPLIT FLOW</td>
<td>N FIXED TUBESHEET, LIKE 'C' STATIONARY HEAD</td>
</tr>
</tbody>
</table>

Shown: Removable Tube Bundle only
C  CHANNEL INTEGRAL WITH TUBE-SHEET AND REMOVABLE COVER
  Fixed Tube sheet only

D  SPECIAL HIGH PRESSURE CLOSURE

H  DOUBLE SPLIT FLOW

I

P  OUTSIDE PACKED FLOATING HEAD

J  DIVIDED FLOW

K  KETTLE TYPE REBOILER

S  FLOATING HEAD WITH BACKING DEVICE (SPLIT RING)

T  PULL THROUGH FLOATING HEAD

U  U-TUBE BUNDLE

W  PACKED FLOATING TUBE SHEET WITH LANTERN RING
Some examples of the TEMA designation for Heat Exchangers

Bonnet (Integral Cover), One Pass Shell, Fixed Tubesheet Bonnet

Fixed tubesheet heat exchanger. This is a very popular version as the heads can be removed to clean the inside of the tubes. The front head piping must be unbolted to allow the removal of the front head, if this is undesired this can be avoided by applying a type A front head. In that case only the cover needs to be removed. It is not possible to clean the outside surface of the tubes as these are inside the fixed part. Chemical cleaning can be used. Shown is a version with one shell pass and two tube passes.

This is the same type of heat exchanger as above, but with one tube pass.

Channel with Removable Cover, One Pass Shell, Fixed Tubesheet Bonnet

This is almost the same type of heat exchanger as the first BEM, the removable cover allows the inside of the tubes to be inspected and cleaned without unbolting the piping.
Channel and Removable Cover, One Pass Shell, Floating Head with Backing Device

Floating Head Heat Exchanger. A floating head is excellent for applications where the difference in temperature between the hot and cold fluid causes unacceptable stresses in the axial direction of the shell and tubes. The floating head can move, i.e. provides the possibility to expand in the axial direction.

Note that the bundle can not be pulled from the front end. For maintenance both the front and rear end head, including the backing device, must be disassembled. If pulling from the front head is required a type AET should be selected.