Kinetic Parameter Determination and Commercial Reactor Optimisation

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Graduation Project
(June 2000-February 2001)
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The Strategic Arts are
First, measurements;
Second, estimates;
Third, analysis;
Fourth, optimisation;
Fifth, success;

The Conditions give rise to measurements.
Measurements give rise to estimates.
Estimates give rise to analysis.
Analysis gives rise to optimisation.
Optimum gives rise to success.

The Art of War
Sun Tzu (300 B.C)

Abstract

Methods for kinetic parameter determination and economic reactor optimisation had been developed for the following kinetic case:

P	+	Q	$\leftrightarrow$	I			(1)
I	+	Q	$\leftrightarrow$	R	+	S	(2)

Kinetic parameter determination was applied for elucidating the kinetic behaviour of the reacting system and it involved two statistical techniques: parameter estimation and experimental design techniques. The parameter estimation technique was utilised for obtaining maximum information from the experimental data while the experimental design method dealt with effectively selecting information rich experimental region. Due to highly non-linear characteristic of the kinetic models, sequential procedure of estimation and design of experiments had to be applied. Although only the first sequence of the procedure was carried out in this project, the developed methods are reproducible.

The quality of the estimates produced in this first sequence of work is poor. Principal component analysis of the result revealed that some of essential kinetic parameters could not be determined firstly due to the presence of hidden parameter dependency in the kinetic model. Secondly, the previous experimental method is not suitable for determining kinetic parameters of the reversible reactions. D-optimum approach for designing experiments for parameter estimation, which was strongly based on the kinetic model, was proposed. However, since the kinetic model was found to be inadequate, no design based on that model could be constructed by D-optimum approach.

Using the preliminary kinetic model, the economic optimisation of the adiabatic commercial reactor was carried out by minimising total cost per ton product. Optimisation result indicated that the economic optimum may be found at a higher operational temperature and therefore in the near future the kinetic model should incorporate the by-product formation and catalyst deactivation model. More experiments at higher experimental temperature should be conducted.

Acknowledgments

This project was started in the summer of 2000, and has been contributed immensely to the very educational years that I have spent at TU Delft. There are many people who have kindly contributed their knowledge and expertise to this project, to who I am deeply indebted for the completion of this project.

Firstly, I am very grateful to Jan Harmsen, primarily for taking me on board of his team. This project has great potential to make a contribution to the process development in the future and I feel privileged to have been a part of his research group. I also thank him for his tremendous support and guidance throughout the course of the project, and for never failing in infecting me with his enthusiasm.

I am also very grateful Peter Verheijen for designing this interesting graduation project for me. It was really a privilege to be able to work with him, to benefit from his experience and great knowledge in parameter estimation and experimental design. His interesting comments and sharp observations made me alert and challenged all the time.

To Peter Schmal for his support and friendship. He enthusiastically provided a most necessary help in process simulations and reviewing my reports. His cheerfulness has somehow helped me to see the sunnier side of the project.

To Jean Paul Lange who was always well equipped with his practical tricks to help me. I have profited a lot from his originality and experience in conducting experiments. To Jaap Peenstra, who never hesitated in giving me help. I really enjoyed working with him.

Special thanks to Prof. Johan Grievink, Mart Valentijn, Gerard Beijnon and Les Chewter for their deep interest in the project and for giving me a lot of valuable inputs on parameter estimation.

My thanks are also addressed to all staff for their help in organising the project. To my friends for making my study time so rich and rewarding.

This acknowledgement wouldn't be complete without saying a big thank you to my family for giving me supports and so much happiness.

Thank you.

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Nomenclature

Latin alphabets:

A	The inlet area	m^2
$AbsErr$	Absolute error of an measurement	-
C_1	Fixed cost constant	fl/ ton S
C_2	Reactor cost constant	fl/ ton S
C_3	Separation cost constant	fl/ ton S
$Capex_{Ssection}$	Capital expenditure of S section	fl/ ton S
$Capex_{Psection}$	Capital expenditure of P section	fl/ ton S
C_{BP}	By product values	fl/ ton S
C_i	Molar concentration	$kmole/m^3$
$C_{i,in}$	inlet molar concentration	$kmole/m^3$
$Capex_R$	Capital expenditure of S reactor	fl/ ton S
C_R	Raw material cost	fl/ ton S
$Capex_S$	Capital expenditure of S separation	fl/ ton S
$Capex_{Total}$	Total capital expenditure	fl/ ton S
c_{pi}	Heat capacity of component I	kJ/kmole/K
$C_{U,Total}$	Total utility cost	fl/ ton S
$C_{U,Psection}$	Utility cost of P section	fl/ ton S
$C_{U,Ssection}$	Utility cost of S section	fl/ ton S
D	Reactor Diameter	m
D_1	Fixed cost constant	fl/ ton S
D_2	Reactor cost constant	fl/m^3
D_3	Separation cost constant	fl/ton Q
DirectFixedCost	Direct fixed cost	fl/ ton S
d_p	Catalyst diameter	m
E_a	Activation energy	kJ/kmole
F_i	Molar flow of component i	kmole/h
F-Matrix	Information matrix	-
$F_\alpha(p, n-p)$	F-value	-
$FR_{molar,in}$	Inlet molar ratio	kmole Q/kmole P
H	Volumetric enthalpy flow	kJ/m^3
h_f	Enthalpy of the fluid	kJ
ΔH	Heat of reaction	kJ/kmole

Nomenclature

h_I	Enthalpy of pure component	kJ/kmole
k	Rate constant	m^6/kmole/kg_{cat}/h
k_o	Pre-exponential factor	m^6/kmole/kg_{cat}/h
k_o'	Transformed pre-exp. factor	m^6/kmole/kg_{cat}/h
Ke	Equilibrium constant	$kg_{cat}h/m^3$, kmole $kg_{cat}h/m^6$
Ke'	Transformed eq. constant	-
L	Active reactor length	m
LHSV	Liquid hourly space velocity	$m^3_{liq}/m^3_{reactor}$/h
MW_i	Molecular weight of component i	kg/kmole
n	Number of data	-
NC	Number of components	-
NF	Number of factorial points	-
NR	Number of reactions	-
NU	Number of experiments	-
p	Number of parameter	-
P	Pressure	bar
ProdRate	Mass production rate	kt/ ann
Heat	Heat loss	kJ/h
Q	The sum of squares relative deviations of the responses	-
$\tilde{Q}$	The approximated sum of squares relative deviations of the responses	-
r	reaction rate	kmole/kg_{cat}/h
R_g	Gas constant	kJ/kmole/K
S	Circumference of the reactor pipe	m
ΔS	Entropy	kJ/kmole/K
ΔS_{To}	Transformed entropy	kJ/kmole/K
$ScaleC$	Error scale factor	-
$SS(\bar{\theta})$	Sum of squares of residuals	-
$SS(\overline{\theta^0})$	Sum of squares of residuals	-
t	time	h
T	Temperature	K or C
T_0	Ref. experimental temperature	K or C

Nomenclature

T_{in}	Inlet temperature	K or C
T_{out}	Outlet temperature	K or C
T_{ref}	Reference temperature	K
v	Liquid velocity	m/h
V_R	Reactor Volume	m^3
w	Element of W-Matrix	-
W	Catalyst weight	kg
WHSV	Weight hourly space velocity	kg fee/ kg cat/ h
W-Matrix	Weight matrix	-
u_i	eigenvector i	-
U	Matrix of eigenvectors	-
x	Axial position	m
x_i	coded variable i	-
y	Measured response	-
z	Standardised axial position	-

Greek alphabets:

β	The difference between the estimate and the real parameter value	-
λ	Eigenvalue	-
Λ	Diagonal matrix of eigenvalues	-
ε	Bed voidage	m^3 void/ m^3 R
η	Calculated response	-
θ	Parameter estimate	-
θ^*	Real parameter values	-
θ_0	Initial estimates	-
ρ_{cat}	Catalyst density	kg/m^3
ρ_i	Density of component i	kg/m^3
$\hat{\sigma}^2$	Approximated variance of the measurement error	-
υ_{ij}	Stoichiometric coefficient for component I in reaction j	-
ω	Constant relative variance	-
ξ	Experimental condition	-

Chapter 1

Introduction

1.1 Project Objective and Specifications

The objective of this graduation project is to determine an economic optimum design of a commercial fixed bed reactor. Given the initial state of the project, in which the kinetic knowledge was still absent, this project engaged extensively in winning maximum kinetic information from the experimental data. The steps followed are:

1. Kinetic Parameters Determination

The parameter determination involves the application of statistical methods in two phases:

A. Parameter estimation
B. Experimental design

As the kinetic models involved fall under the class of non-linear models, statistical sequential parameter determination is required. First in each sequence is the parameter estimation and then followed by the experimental design to improve the accuracy of the next kinetic estimates. The speed of convergence to the accurate estimates depends on the quality of each step, good estimates will lead to a good experimental design and this will results in even better estimates. Preliminary experiments had been performed and the results were used in this project to produce the initial estimates. Given the limited time and data, only the first sequence of parameter determination could be carried out. The focus is more on the development of the reproducible parameter determination methodology for the near future application.

2. Shell Reactor Optimisation

By employing kinetic estimates produced in the first part of the work and a cost function developed under the present economic knowledge, a region of minimum cost was searched by manipulating the inlet variables. Since the kinetic, reactor and economic knowledge applied here are still being developed; the optimisation result should not be considered as a truly optimum reactor design. However, it can give an indication for the region that has most of the economic interest, where the kinetic models should be best validated, i.e. it can define the next experimental design region.

Two types of plug flow reactor were involved in this project. Isothermal lab scale plug flow reactor was utilised for experimental design and parameter estimation. The optimised commercial scale reactor is an adiabatic plug flow reactor. The mathematical models were developed for both reactors and implemented in gPROMS simulation software. gEST and gOPT, which are special features of gPROMS were employed for parameter estimation and reactor optimisation respectively.

1.2 Report Outline

This report is organised in six chapters. In the following chapter, the theoretical background of parameter determination is given and followed by one of reactor optimisation as the third chapter. The fourth chapter presents the reactor mathematical model developments. Results and discussions are placed in the fifth chapter. The final chapter presents the conclusion and recommendations for future works.

Chapter 2

Kinetic Parameter Determination

2.1 Introduction

When prior kinetic information is very scarce or unavailable in any publications, chemical kinetic parameters should be estimated from the experimental data. The estimation involves the application of statistical methods in two phases: parameter estimation and experimental design. For many people, the importance of experimental design is neglected and only the parameter estimation is carried out. However, one should realise that the value of the information contained in the data is actually established when the experiment is designed and even a very careful estimation is unable to recover information that is not present in the data. Much of the data could be obtained with considerable less effort by proper choice of experimental conditions. Furthermore, the quality of the experimental data greatly determines the quality of the parameters obtained in terms of precision and accuracy. This is of outmost importance if chemical model parameters are then used in process design.

The objective of this chapter is to present both techniques of parameter estimation and experimental design as applied on the kinetic model under the study. It is outside the scope of this project to discuss in detail the statistical theory and only some concepts, which are playing an important role in the process of parameter estimation and designing experiment in this case, are mentioned. Direct implementations on the case can be found throughout this chapter. There are three big parts within this chapter, with parameter estimation as the first part. Sensitivity analysis, a special feature of parameter estimation is placed on the third part, right after the experimental design.

First explained here is the complexity of the kinetic parameter determination, which is sourced from the non-linearity behaviour of the kinetic mathematical models. It will be clear from this explanation that the sequential procedure is the only effective approach to determine kinetic parameters. In general the experimental response can be formulated as follows:

$$\bar{\eta} = f(\bar{\xi}, \bar{\theta}) \qquad (2.1)$$

$\bar{\eta}$, $\bar{\theta}$ and $\bar{\xi}$ denote a vector of responses, parameters and experimental conditions respectively. A model is non-linear if at least one derivative of the response with respect to the parameters includes at least one of those parameters. Generally, kinetic model formulated in terms of algebraic and differential equations displays highly non-linear behaviour in the parameters and because there is no close expressions for these parameters, iteration procedures are needed for the determination of the optimal estimates.

In addition to that, designing experiments for non-linear models is complicated by the fact that the design depends upon the parameter values, which are unknown in the beginning. This loop of parameter estimation and experimental design in non-linear case is clearly illustrated by Atkins (1992) using the simplest example of kinetic models, the exponential decay of A to B according to the following reaction scheme:

$$A \rightarrow B \tag{2.2}$$

The response model is the concentration of A as the exponential function of the experimental variable ξ and the parameter θ.

$$\eta(\xi,\theta) = \frac{C_A}{C_{A0}} = exp(-\theta\xi) \tag{2.3}$$

Consider time as the experimental variable here. The profile of the concentration decreases exponentially with time is depicted on figure 2.1. It is clear from this figure, that the measurements at time near zero or very large may not provide any kinetic information. Near zero, the concentration is approximately one and the kinetic parameter value could take any value. At very large time, the reactants are finished and the reaction stops. Nothing valuable about the kinetic can be measured.

Measurements where the expected response is closer to one-half might be expected to be more informative, but the value of the experimental variable for such response values will depend on the parameter itself. Consequently, in order to determine at which level of experimental variable the measurement should be taken, we need to know the parameter value, which is usually unknown in the beginning. Therefore, a good set of initial parameter estimates should be made available before starting designing experiments for non-linear model. In cases where no initial information is available, preliminary experiments have to be performed.

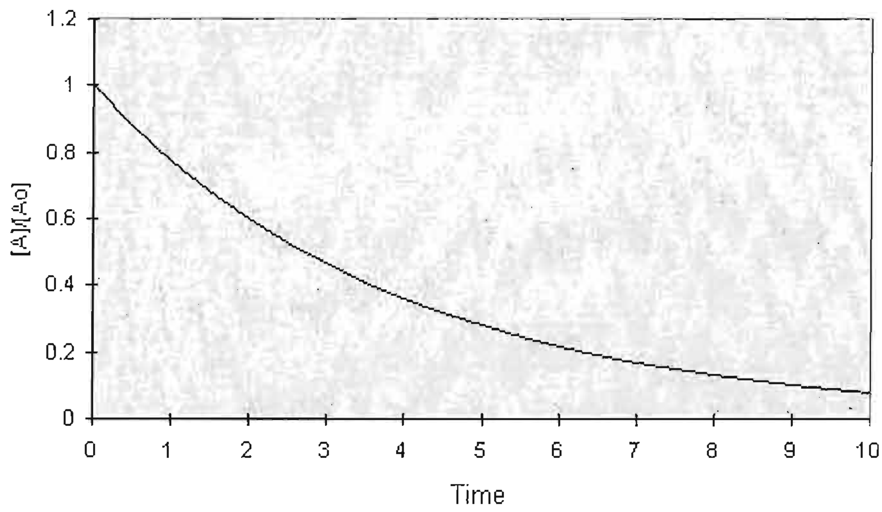


Figure 2.1: Exponential Decay of A to B.

2.2 Parameter Estimation

2.2.1 The Kinetic Models

The experiments were performed in a heterogeneous isothermal plug flow reactor. The reaction is taking place in liquid-solid phase environment. Based on the chemistry insight, the following reaction scheme has been proposed:

$$P + Q \leftrightarrow I \qquad (2.4)$$

$$I + Q \leftrightarrow R + S \qquad (2.5)$$

Although the formation of by products was observed at the highest experimental temperature, the number of recorded data is insufficient for allowing by-product kinetic model to be incorporated. For the time being, its formation is considered to be negligible, as what was observed under most of the experimental conditions. However, experiments on different or even extreme conditions in the future may help in elucidating the by-product formations. The kinetic models of these equilibrium reactions are:

$$r_1 = k_1(C_P C_Q - \frac{1}{Ke_1} C_I) \qquad (2.6)$$

$$r_2 = k_2(C_I C_Q - \frac{1}{Ke_2} C_R C_S) \qquad (2.7)$$

The inlet conditions varied in the experiments are given in table 2.1.

Table 2.1: Experimental inlet variables

DEFINITIONS	INLET VARIABLES
Inlet temperature [K]	T_{in}
Inlet molar feed ratio (C_Q/C_P)	$FR_{molar,in}$
Liquid hourly space velocity [/h]	LHSV

2.2.2 Transformation of Kinetic Parameters

In general, the dependency of the rate constant on the temperature can be described by the Arrhenius equations:

$$k_j = k_{oj} \exp\left(-\frac{E_{aj}}{R_g T}\right) \quad , \quad j = 1,\ldots,NR \tag{2.8}$$

The forward and the reverse rate constants are related by equilibrium constant, which is in turn is related to the thermodynamic free energy, enthalpy, etc.

$$Ke_j = \frac{k_j}{k_{-j}} \quad , \quad j = 1,\ldots,NR \tag{2.9}$$

$$Ke_j = \exp\left(\frac{\Delta S_j}{R_g} - \frac{\Delta H_j}{R_g T}\right) \quad , \quad j = 1,\ldots,NR \tag{2.10}$$

However, these reaction rates have highly dependent parameter structure, resulting in large correlations and large inaccuracies ranges of the estimated parameters. Any inaccuracy experienced by one of the parameter significantly manifests in another. Furthermore, ill-conditioned parameters would hamper the optimisation process of parameter estimation. Parameter transformation is therefore necessary in order to reduce the correlation and fix this ill behaviour.

Watts (1994) suggested model reformulation and parameter transformation that produce kinetic model with well-behaved estimates. To break the correlation between activation energy (E_{aj}) and the pre-exponential constant (k_{oj}) and to improve the behaviours of the estimates, Arrhenius equation is reformulated to:

$$k_j = k_{oj}' \exp\left[-\left(\frac{E_{aj}}{R_g}\right)\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \quad , \quad j = 1,\ldots,NR \tag{2.11}$$

$$\text{with } k_{oj}' = k_{oj} \exp\left(-\frac{E_{aj}}{R_g T_0}\right) \quad , \quad j = 1,\ldots,NR \tag{2.12}$$

T_0 is a reference temperature. In this project, the middle experimental temperature is chosen as the reference temperature. By centring temperature about a reference value, the behaviour of the parameter estimates is improved. The parameter behaviour approaching linear behaviour and solver based on linear approximations can work well. Also reported by Watts (1994) that the logarithms of pre-exponential parameters behave extremely linearly, so they recommended fitting the log rate constants.

$$k'_j = \ln k_{oj}' - \frac{E_{aj}}{R_g}\left(\frac{1}{T} - \frac{1}{T_o}\right) \quad , \quad j = 1,...,NR \qquad (2.13)$$

$$k_j = \exp(k'_j) \quad , \quad j = 1,...,NR \qquad (2.14)$$

The fitted parameters are $\ln k_{oj}'$ and E_{aj}. The first advantage from applying this model is that the transformation reduces the magnitude of the reaction constants. Initialisation of fitting process becomes easier as the suitable initial guess can be quickly located. For information on how to find the initial guesses see section 2.2.4. Secondly, log rate constants also obey the theoretical constraint on rate constants, that is, no matter what the values of Ea and $\ln k_{oj}'$ are, the rate constant will be positive. The same method is applied to equilibrium constants. It is transformed to:

$$Ke_j = \exp\left(\frac{\Delta S_{Toj}}{R_g} - \left(\frac{\Delta H_j}{R_g}\right)\left(\frac{1}{T} - \frac{1}{T_o}\right)\right) \quad , \quad j = 1,...,NR \qquad (2.15)$$

with

$$\frac{\Delta S_{Toj}}{R_g} = \frac{\Delta S_j}{R_g} - \frac{\Delta H_j}{R_g T_o} \quad , \quad j = 1,...,NR \qquad (2.16)$$

The same logarithmic trick is also applied:

$$Ke'_j = \frac{\Delta S_{Toj}}{R_g} - \left(\frac{\Delta H_j}{R_g}\right)\left(\frac{1}{T} - \frac{1}{T_o}\right) \quad , \quad j = 1,...,NR \qquad (2.17)$$

$$Ke_j = \exp(K'_j) \quad , \quad j = 1,...,NR \qquad (2.18)$$

2.2.3 Error Scale Factor

Inlet variables such as inlet concentrations are treated as measurements, which are not error free. Mathematically, inlet concentrations can be formulated as follows:

$$C_{i,z=0} = ScaleC * C_{i,in} \quad , \quad i = 1 \cdots NC \qquad (2.19)$$

In case the measurements are error free, the error scale factor is one, the real inlet concentrations take the measured values. By including this factor as an estimated parameter, the prediction of the estimates becomes better and the flexibility in the fitting process is increased. Please note that fitting an error scale factor is allowed only for relative error. There is no need to estimate absolute error whose value is already fixed and known.

Liquid hourly space velocity (LHSV) also contains relative error associated with the pump debit. However, error scale factor for this variable is not included into the fitting as LHSV is employed on converting the experimental data from molar flow rate into molar concentration.

$$C_i = \frac{F_i}{(LHSV)V_R} \tag{2.20}$$

Its error therefore is contained in the inlet concentration value. Table 2.2 shows the set of fitted parameters.

Table 2.2: The fitted parameters

EQUATIONS	PARAMETERS
Equilibrium constant of reaction j, (2.17) and (2.18s)	ΔS_{Toj}
	ΔH_j
Forward rate constant of reaction j, (2.13) and (2.14)	$\ln k_{oj}'$
	$E_{a,j}$
Inlet concentrations (2.19)	ScaleC

2.2.4 Initial Guesses of Parameter Estimates

In non-linear mathematical models such as these rate models, obtaining good initial guesses of parameters is important for successful estimation. Without a good initial guesses, the initialisation of the parameter estimation will fail or the algorithm will not converge to the solution. In this case, where there are 9 parameters to be estimated (2 reactions each with 4 parameters and the scale factor of the inlet concentrations) finding a good set of initial guesses in one go is very difficult. The following steps were taken in order to obtain initial guesses:

1. Fitting only the log rate and equilibrium constants

For each reaction temperature, fit the log rate and equilibrium constants, i.e. fit $\ln k_j(T)$ and $\ln Ke_j(T)$, and error scale factor (ScaleC). Doing so reduced the number of parameters to 5 and made the initialisation of parameter optimisation easier. Most given sets of initial guesses could initialise the fitting process.

2. Plotting the constants against transformed temperature

a) Plot $\ln k_j(T)$ against transformed reaction temperature $\left(\frac{1}{T}-\frac{1}{T_o}\right)$ to obtain the log of the reference pre-exponential factor $\ln k_{oj}'$ as the intercept and the activation energy $E_{a,j}$ as the slope.

b) Plot $\ln Ke_j(T)$ against $\left(\frac{1}{T}-\frac{1}{T_o}\right)$ to obtain the value of the transformed entropy $\Delta S_{T0,j}$ as the intercept and ΔH_j as the slope.

3. Fitting the complete set of parameters

Compute the values of $\ln k_{oj}', E_{a,j}, \Delta H_j$ and $\Delta S_{T0,j}$ obtained earlier as the initial guesses.

2.2.5 The Parameter Estimation Tool, gEST

gPROMS and its feature for parameter estimation gEST were utilised in the parameter estimation. gEST uses the maximum likelihood estimator. For further information about the optimised objective function, the readers are referred to gPROMS Advanced User's Guide. For the mathematical model of isothermal plug flow reactor is referred to Chapter 5.

2.2.6 Assessing the Adequacy of the Model

2.2.6.1 Goodness of Fit

Having found the parameter estimates does not mean that the fitted model is adequate, i.e. the model is right. The term, which is used to show how well the model can predict the response, is "Goodness of Fit", van den Bleek (1996). One way to assess the adequacy of the model is by analysing the residuals. Estimation of model parameters requires the assumption that the errors are uncorrelated random variables with mean zero and constant variance. The validity of this assumption can be checked after the fitting procedure by plotting the residuals against the predicted or the observed response values. If the assumption is correct than there should be no pattern appears on the scatter plot.

2.2.6.2 Confidence Region

After finding the estimates assumed to be associated with the global minimum, it is useful to define a region in which the true parameters can be found. One way to accomplish this is with a region estimate called a confidence region. In non-linear models, the magnitude of the non-linearity determines the form of the region, van den Bleek (1996). The kinetic models, which are usually highly non-linear, have an asymmetric confidence region. In case that the true variance of the measurement error is unknown, this region can be constructed by using the following formula:

$$\frac{(SS(\overline{\theta_0}) - SS(\overline{\theta}))/p}{SS(\overline{\theta})/(n-p)} \sim F_\alpha(p, n-p) \tag{2.21}$$

The estimates ($\overline{\theta}$) and the sum of squares of the residuals ($SS(\overline{\theta})$) are the result of the fitting process of p parameters with n data points. The sum of squares of the residuals is minimised during the fitting process and is given as:

$$SS(\overline{\theta}) = \sum_1^n \left(\frac{(y_i - \eta_i)}{\omega y_i} \right)^2 \tag{2.22}$$

ω is the relative variance introduced to gEST input file. ω is to be determined by the optimisation or a given value by the experimenter.

The value in the denominator of Equation (2.20) is the estimate of the variance of the measurements error.

$$\hat{\sigma}^2 = SS(\overline{\theta})/(n-p) \tag{2.23}$$

The ratio in Equation (2.17) follows the F-distribution with p degrees of freedom in the numerator and (n-p) degrees of freedom in the denominator. The resulting confidence region is called a $100(1-\alpha)$ percent confidence region, and $(1-\alpha)$ is called the confidence coefficient, set by the analyst. The value of $F_\alpha(p, n-p)$ can be obtained from the statistic table or from the estimation statistic file generated by gEST at the end of the fitting process. The confidence area is:

$$SS(\overline{\theta_0}) \le SS(\overline{\theta}) + p\hat{\sigma}F_\alpha(p, n-p) \tag{2.24}$$

The interpretation of a confidence interval is that, if a number of parameter sets are obtained through several iterations and a $100(1-\alpha)$ percent confidence region is constructed for each set of parameters, then $100(1-\alpha)$ percent of these regions will contain the set of true parameters. For example, if this were a 95 percent confidence region, in the long run only 5 percent of the regions would fail to contain the set of true parameters.

Another interpretation is that the observed region enclosed the true values of parameters with confidence $100(1-\alpha)$. The larger the region, the less information about the true parameter values becomes.

2.3 Experimental Design

2.3.1 Experimental Design Problem Outline

A single experiment consists of measuring the values of the response. In the case, the measured response is the concentration of the reactants. The response model specifically in chemical kinetics is non-linear. Its general representation is given as follows by Box and Lucas (1959):

$$\eta = f(\xi_1, \xi_2, \ldots, \xi_k; \theta_1, \theta_2, \ldots, \theta_p) = f(\overline{\xi}; \overline{\theta}) \quad (2.25)$$

It is a function of k variables $\xi_1, \xi_2, \ldots, \xi_k$ elements of vector $\overline{\xi}$ and of p parameters $\theta_1, \theta_2, \ldots, \theta_p$ elements of vector $\overline{\theta}$. The experimental variables and parameters of the kinetic models are given in Table 2.1 and 2.2 respectively. Box and Lucas (1959):

"The problem here is that of selecting a program of trials, such that they may be expected to provide results from which the parameters can be estimated with high accuracy. The experimental design may be defined by an Nxk matrix design, $D = \{\xi_{iu}\}$, with N as the number of trials and k as the number of the variables. The uth row of this matrix with elements $\xi_{1u}, \xi_{2u}, \ldots, \xi_{ku}$ provides the level of the k variables at which the response is to be observed in the uth trial." The experimental region can be defined by a series of inequalities in ξ's such as

$$\xi_i(\min) \le \xi_i \le \xi_i(\max) \qquad (i=1,2,\ldots,k) \quad (2.26)$$

The choice of experimental variables or conditions is generally not unrestricted. For examples, mole fractions can only range from zero to one and the temperature of liquid is constrained between its freezing point and boiling points. One of important aspects that should also be considered when defining the experimental region is the ability of measurement apparatus to detect the response. The experiments at low temperature in combination with for example a short residence time may result in the experimental response below the detectable limit. For high reaction temperature the catalyst stability and by-product formation may be the problems. Experimentalist could provide valuable information about the feasibility of the experimental region.

2.3.2 Locally D-Optimum Design (Theory)

Locally D-optimum designs for non-linear models were introduced by Box et al. (1959). They started by denoting the observed response at the *u*th set of experimental conditions by y_u:

$$E(y_u) = \eta_u = f(\overline{\xi}; \overline{\theta}) \quad (2.27)$$

The true values of the parameters are denoted by $\theta_1^*, \theta_2^*, \ldots, \theta_p^*$, the elements of vector $\overline{\theta^*}$. Taylor expansion of η_u around $\overline{\theta^*}$ results in the linearisation

$$\eta_u = f(\overline{\xi_u};\overline{\theta}) = \eta(\overline{\xi_u};\overline{\theta^*}) + (\theta_1 - \theta_1^*)\frac{\partial \eta(\overline{\xi_u};\overline{\theta^*})}{\partial \theta_1} + (\theta_2 - \theta_2^*)\frac{\partial \eta(\overline{\xi_u};\overline{\theta^*})}{\partial \theta_2} + \cdots$$
$$+ (\theta_p - \theta_p^*)\frac{\partial \eta(\overline{\xi_u};\overline{\theta^*})}{\partial \theta_p} + rest \qquad (2.28)$$

The relation with the linear models is emphasised by rewriting the equation as:

$$\eta(\overline{\xi_u};\overline{\theta}) - \eta(\overline{\xi_u};\overline{\theta^*}) = \overline{\beta} F(\overline{\xi_u}) \qquad (2.29)$$

where $\overline{\beta} = \{(\theta_1 - \theta_1^*) \quad (\theta_2 - \theta_2^*) \quad \cdots \quad (\theta_p - \theta_p^*)\}$ (2.30)

and

$$F(\overline{\xi_u}) = \left\{ \frac{\partial \eta(\overline{\xi_u};\overline{\theta^*})}{\partial \theta_1} \quad \frac{\partial \eta(\overline{\xi_u};\overline{\theta^*})}{\partial \theta_2} \quad \cdots \quad \frac{\partial \eta(\overline{\xi_u};\overline{\theta^*})}{\partial \theta_p} \right\} \qquad (2.31)$$

The complete information matrix F looks like as follows

$$F = \begin{bmatrix} \frac{\partial \eta(\overline{\xi_1};\overline{\theta^*})}{\partial \theta_1} & \cdots & \frac{\partial \eta(\overline{\xi_1};\overline{\theta^*})}{\partial \theta_p} \\ \vdots & \ddots & \vdots \\ \frac{\partial \eta(\overline{\xi_{NU}};\overline{\theta^*})}{\partial \theta_1} & \cdots & \frac{\partial \eta(\overline{\xi_{NU}};\overline{\theta^*})}{\partial \theta_p} \end{bmatrix} \qquad (2.32a)$$

$\overline{\xi_u}$ denotes a vector of experimental conditions for the u-th trial, whose elements are the k-variables ξ_{1u}, ξ_{2u},..., ξ_{ku}. $\overline{\theta^*}$ represents the vector of the true parameter values. Since the true parameter values are unknown at the beginning, the preliminary estimates ($\overline{\theta_0}$) are used. Thus the F-matrix looks as follows:

$$F = \begin{bmatrix} \frac{\partial \eta(\overline{\xi_1};\overline{\theta_0})}{\partial \theta_1} & \cdots & \frac{\partial \eta(\overline{\xi_1};\overline{\theta_0})}{\partial \theta_p} \\ \vdots & \ddots & \vdots \\ \frac{\partial \eta(\overline{\xi_{NU}};\overline{\theta_0})}{\partial \theta_1} & \cdots & \frac{\partial \eta(\overline{\xi_{NU}};\overline{\theta_0})}{\partial \theta_p} \end{bmatrix} \qquad (2.32b)$$

It is known that the least square estimates $\hat{\beta}$ and equivalently $\hat{\theta}$, minimises the sum of squares

$$\sum_{u=1}^{N} \{\eta(\overline{\xi}_u;\overline{\theta}) - \eta(\overline{\xi}_u;\overline{\theta}_0)\}^2 \tag{2.33}$$

and have a variance covariance matrix which is approximated by $(F^T F)^{-1} \sigma^2$ where, in general, σ^2 is unknown. F is called the information matrix. Mathematically, F^TF represents the square of the Jacobian matrix, which transform the coordinates in the sample space to coordinates in parameter space, which is related to the contour of the confidence region in the parameter space. The higher the determinant value of F^TF (denoted as $|F^TF|$), the smaller the confidence region and the higher the accuracy of the estimates will be.

To maximise the amount of information gained by the experiments, it is wished to select the experimental conditions in such a way that the uncertainty is minimised. If the design criterion is to minimise the generalised variance of the parameter estimates, then the design matrix (D) should be chosen as such that $|F^TF|^{-1}$ is made as small as possible or $|F^TF|$ is made as large as possible. This design criterion is known as D-optimality.

In chemical kinetics, the response functions are presented in terms of a series of differential equations, which may have no analytical solution. So the functions in matrix F, the derivatives of the response function with respect to the θ's at $\theta=\theta_o$, cannot be given explicitly. Numerical methods may then be employed.

2.3.2.1 Initial Estimates

The quality of experimental designs for non-linear models depends on the matrix F whose elements are the values of the derivatives of the response function with respect to the θ's at $\theta=\theta_o$. That is to say that for a non-linear model, the selection of experimental conditions depends on the values of the parameters themselves, which is initially unknown. To obtain reliable estimates of the parameters, a sequential strategy is usually needed. Initially, some experimental runs need to be performed in order to get the first parameter estimates. As the investigation proceeds and better estimates become available, better experimental conditions can be determined. See Section 2.2 for the explanation on the parameter estimation.

2.3.2.2 Weight Matrix

The assumption of constancy of variance enters the optimum experimental design through the information matrix F. This assumption is often unsatisfactory for the following reasons:

1. The various variables may represent entities having different physical dimensions or measured on different scales. For instance, the mole fractions of the components may take values in the range zero to one, while the temperature may take a value in the range 500-1000. The error of the temperatures are likely to dominate those of the mole fractions and any information contained in the latter will be lost.

2. Some observations may be known to be less reliable than others. The parameter estimates should be less influenced by those than by the more accurate ones

Atkinson et al. (1992) recommended the use of NxN diagonal matrix of weights W. This matrix depends on the error distribution and the link between them. By taking into account different type of errors of different type of measurements, it is possible to combine data from different sources like temperatures and concentrations.

$$W = \begin{bmatrix} w_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & w_k \end{bmatrix} \tag{2.34}$$

The *ith* diagonal element of matrix W is:

$$w_i = \frac{1}{AbsErr^2} \tag{2.35}$$

with *i* as the type of measurements, e.g. temperature, concentration and time. By taking the inverse of the square of the error, the difference in the measurement scale has been cancelled.

Then the new D-optimality design criterion says:

A design is D-optimum if it maximises the value of $|F^T WF|$, i.e. the generalised variance of the parameter estimates is minimised, Atkinson (1992).

2.3.3 The Application of D-Optimum Design Approach

2.3.3.1 Practical Limitations of D-optimisation

In the following are practical problems associated with finding the optimum design, i.e. finding the maximum value of $|F^T WF|$:

1. The maximum of the design criterion is usually located on the boundary of the feasible region, Atkinson and Hunter (1968). The extreme values of the experiments may be far removed from the region of interest. There is also the danger that the properties of the model under investigation are not the same at the boundary as in the centre of feasible region. On the basis of this practical reason, Bard (1974) recommended that experiments should be chosen in the interior of the region, even when not prescribed by the design criterion.

2. There are usually several local maxima. In many cases, the number of maxima tended to be close to the number of unknown parameters in the models, Bard (1974). An attempt to find the real maximum of the design criterion is therefore computationally laborious and complex. If we wish to obtain the most information in each experiment, the maximisation procedure must be repeated before each experiment is performed. It is often more practical to perform standard but less efficient experiments.

Due to these impracticalities, the original D-optimum design could not be applied on The case. However, D-optimum theory provides a good technique for judging the design quality by looking to the determinant value. This approach was applied on the study case.

2.3.3.2 Determining the Experimental Region

The measurement points were not produced by the design D-optimisation, but chosen systematically in the experimental region determined by:

1. The economic optimum region
   It is much more interesting to validate the kinetic models on the region where the economic is optimum. Therefore, after estimating the kinetic parameters, the reactor optimisation should be carried out first. Optimisation would identify the economic optimum region, where next experimental program should be designed.

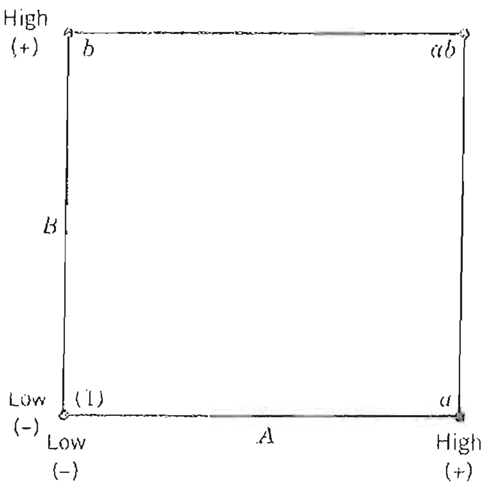
2. The experimentalist
   The experimentalist should definitely be contacted. The feasibility of the economic optimum region obtained from the reactor optimisation (see number 1) should be conformed by him. His experience may tell different or even better choice of experimental region.

Then several sets of measurement points (or experimental designs) within the region were developed. The value of $|F^TWF|$ of each design was calculated and compared to each other. The one that has the highest determinant value would be proposed as the next experimental design.

2.3.3.3 Effectively Exploring the Experimental Space With Factorial Experimental Design

After the experimental region or space has been determined, the next problem is finding an effective and systematic method for choosing the measurement points. The experimental space should be fully explored without having too many unnecessary measurement points. When several variables are of interest in an experiment, a factorial experimental design should be used. In these experiments variables are varied together. By a factorial experiment it is meant that in each complete replicate of the experiments all possible combinations of the levels of the variables are investigated. Normally, factorial experimental design is applied for studying the magnitude and direction the experimental variables (factors). This design could be modified further for the purpose of parameter estimation, for helping the experimentalist in exploring the experimental region effectively and systematically.

The approach was explained by Montgomery (1998) as follows: "If an investigator selects l levels for each of k variables and then runs experiments with all possible combinations, such factorial design is called as l^k factorial design. The simplest type is 2^k designs. There are 2 levels for each variable, low and high level. In 2^k design it is customary to denote the high and low levels of the variables by the signs – and +, respectively. This is sometimes called the geometric notation for the design. A special notation is used to label the combinations of the levels of the variables. In general, a combination is represented by a series of lowercase letters. If a letter is present, then the corresponding variable is run at the high level in that combination; if it is absent, the variable is run at its low level. The combination with all variables at lower level is represented by [1]." If there are 2 variables, say A and B, with 2 levels for each of variable, we have here 2^2 factorial design and it has four runs or combinations. Geometrically, the design is a square as shown in Figure 2.2, with four runs forming the corners of the square.



Treatment	A	B
(1)	–	–
a	+	–
b	–	+
ab	+	+

Figure 2.2: Geometric presentation of factorial design.

The systematic exploration of the experimental space can be further extended by applying central composite design. Central composite design is normally applied for process optimisation. Like the factorial design in this estimation work, central composite design is not really applied for its real purpose, but only its systematic geometric method is followed. Corner points of the design square are positioned on the same distance with respect to the centre point, which is the approximated optimum point. The geometrical representation of the design is shown on figure 2.3. The design gives equal interest in departures in any direction from the approximated optimum point.

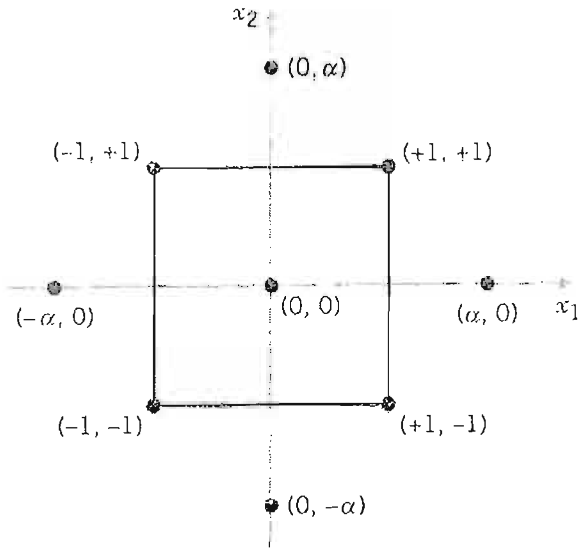


Figure 2.3: Central Composite Design

It is convenient to scale the variables with respect to the centre point. The variables at the corner points would take values between –1 and +1. The coded variables are defined by:

$$x_i = \frac{\xi_i - \xi_{i,o}}{\Delta\xi} \tag{2.36}$$

$\Delta\xi$ is the difference between the minimum or maximum value of the variable and its value at the centre point.

$$\Delta\xi = |\, \xi_{i,max} - \xi_{i,o} \,| \tag{2.37}$$

This design has the desirable property of being rotatable around the centre point and additional measurements of overall curvature are available. It may be made rotatable by proper choice of the axial spacing from the centre point. For rotatability choose the distance equal to $(NF)^{1/4}$, where NF is the number of points in the factorial part of the design. Notice that the contours are concentric circle.

2.3.3.4 The Construction of F- and W-Matrices

Factorial design or central composite design provides a systematic way of selecting experimental points within a certain experimental space. However, it does not say anything about the quality of those points. To determine whether those points contain enough information for parameter estimation $|F^TWF|$ should be calculated.

W-matrix can be calculated from the result of the initial estimation process. After a set of initial parameter estimates was obtained, a statistic file is generated by gEST (STAT). It contains the value of the *absolute error* of each measured concentration, denoted as *sigma*. Inserting these sigma values into Equation 2.35 results in the elements of W-matrix. In one experiment where there are 5 concentrations measured, the weight matrix looks as follows:

$$W = \begin{bmatrix} w_P & 0 & 0 & 0 & 0 \\ 0 & w_Q & 0 & 0 & 0 \\ 0 & 0 & w_I & 0 & 0 \\ 0 & 0 & 0 & w_R & 0 \\ 0 & 0 & 0 & 0 & w_S \end{bmatrix} \qquad (2.38)$$

F-matrix had to be constructed numerically by gPROMS and Microsoft Excel, see Appendix G. Consider the following ij-th element of the F-matrix:

$$F_{ij} = \frac{\partial \eta(\overline{\xi_i};\overline{\theta_0})}{\partial \theta_j} \qquad (2.39)$$

The interpretation of this element is the change in the response (concentration) at i-th combination of the experimental conditions brought about by a variation in the parameter j. If in i-th experiment there are 5 measured concentrations, such in the study case, Equation 2.39 refers to a 5x1 vector. A complete F-matrix for one experiment, with 5 measured concentrations and 8 parameters, has a size of 5x8. If one wishes to combine a number of experiments, say 8 experiments, then the F-matrix size becomes (8x5)x8. The increase in the size of F-matrix is followed by the increase in the size of W-matrix. In this case, W-matrix becomes (8x5)x(8x5).

$$F - Size = NM \times NP \qquad (2.40)$$

$$W - Size = NM \times NM \qquad (2.41)$$

NM is the number of measurements taken and NP is the number of parameters. In order to get the numerical value for the ij-th element of F-matrix, one simulation with a small perturbation in the value of parameter j, while the other parameters are held constant at their estimated values, is carried out in gPROMS. The ratio of the response change to the perturbation in the parameter j, forms ij-th element of the F-matrix:

$$F_{ij} = \frac{\eta(\theta_j + \Delta\theta_j) - \eta(\overline{\theta_0})}{\Delta\theta_j} \qquad (2.42)$$

So $\eta(\theta_j + \Delta\theta_j)$ and $\eta(\overline{\theta_0})$ are generated by gPROMS. Then the ratio 2.42 is calculated in Excel.

For example, if the concentration is P's, the j-th perturbed parameter is Ea_1 and the experiment is carried out at i-th combination of temperature, feed ratio and liquid velocity, then the element looks as follows:

$$F_{iEa1} = \frac{C_P(Ea_1 + \Delta Ea_1) - C_P(\overline{\theta}_0)}{\Delta Ea_1} \qquad (2.43)$$

Special attention has to be given to the amount of perturbation. Small values of $\Delta\theta_j$ yield in large numerical inaccuracies in the calculation of $\eta(\theta_j + \Delta\theta_j)$ and $\eta(\overline{\theta_0})$ in gPROMS. The subtraction of two quantities subject to numerical inaccuracies in the nominator already will yield an inaccurate result, which will be further increased by division of the small values of $\Delta\theta_j$. Therefore relatively large values of $\Delta\theta_j$ should be applied. In this case $\Delta\theta_j$ was selected to be 50% of the standard deviation of parameter j. Perturbation less than 50% of the standard deviation was found to cause large inaccuracies. The values of the standard deviation were obtained from the initial estimation process. Presented in the STAT-MR files, which are generated at the end of the estimation process in gEST, are the variance matrices. The square roots of the diagonal elements of these matrices are the standard deviations of the estimates.

The calculation of the determinant value, $|F^TWF|$, was assisted by Matlab.

2.4 Parameter Identifiability Problem

2.4.1 Illustration of the Problem

Often not all parameters can be uniquely estimated or identified from the data. This kind of problem appears when there is hidden parameter dependency. The problem can be illustrated by looking to the next example.

Suppose the following consecutive reaction:

$$A \xrightarrow{k1} B \xrightarrow{k2} C$$

The rate of decomposition of A is:

$$\frac{dC_A}{dt} = -k_1 C_A \qquad (2.44)$$

The net rate of formation of intermediate B is:

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \qquad (2.45)$$

The product C is formed by the decay of B:

$$\frac{dC_C}{dt} = k_2 C_B \qquad (2.46)$$

The analytical solutions for Equations 2.44 to 2.46 are:

$$C_A = C_{Ao}\exp(-k_1 t) \tag{2.47}$$

$$C_B = C_{Ao}\frac{k_1}{k_2 - k_1}\{\exp(-k_1 t) - \exp(-k_2 t)\} \tag{2.48}$$

$$C_C = C_{Ao}\left\{1 + \frac{k_1\exp(-k_2 t) - k_2\exp(-k_1 t)}{k_2 - k_1}\right\} \tag{2.49}$$

Suppose now that $k_1 << k_2$. Then it can be assumed that during the major part of the reaction, the rates of change of the intermediate concentration is negligibly small:

$$\frac{dC_B}{dt} = 0 \tag{2.50}$$

This assumption is known as pseudo steady state assumption. The Equation 2.44 can be written as follows:

$$C_B = \frac{k_1}{k_2}C_A \tag{2.51}$$

Shown here is that at any time of measurements, only the combination of $\frac{k_1}{k_2}$ that can be estimated from the experimental results.

2.4.2 Principal Component Analysis

Vajda (1985) reported that sensitivity analysis in terms of the eigenvectors and eigenvalues of the matrix F^TWF can uncover the hidden dependencies among the parameters in the kinetic models and can confirm or deny the validity of simplifying kinetic assumptions (such as quasi steady-state hypothesis) under the considered experimental conditions. This theory is often called as principal component analysis. For detail mathematical derivations the readers are referred to Vadja (1985). Further in this section only the main formulae and the interpretation of the theory are presented.

Mathematically, the eigenvectors and eigenvalues of the matrix F^TWF can describe the effect on the model behaviour brought about by a variation in the parameter values. The response surface that describe the model behaviour as a function of parameter changing is defined by:

$$Q(\overline{\theta}) = \sum_{j=1}^{q}\sum_{i=1}^{m}\left[\frac{\eta_{i,j}(\overline{\theta}) - \eta_{i,j}(\overline{\theta_0})}{\eta_{i,j}(\overline{\theta_0})}\right]^2 \tag{2.52}$$

j denotes the selected combination of experimental conditions and i denotes the measured concentration. $\overline{\theta_0}$ denotes the set of the real parameter values. $Q(\overline{\theta})$ is thus the sum of squared relative deviations of the observed concentrations. To study the effect of parameter variation the following approximate response function can be used, Vadja (1985):

$$Q(\overline{\theta}) \approx \tilde{Q}(\overline{\theta}) = (\Delta\overline{\theta})^T F^T WF(\Delta\overline{\theta}) \tag{2.53}$$

with

$$\Delta\overline{\theta} = \overline{\theta} - \overline{\theta_0} \tag{2.54}$$

To see how $\tilde{Q}$ changes with $\overline{\theta}$ the eigenvalues of F^TWF have to be examined. The function $\tilde{Q}$ is most sensitive to change in $\overline{\theta}$ along the principal axis corresponding to the largest eigenvalue and is least sensitive to change in $\overline{\theta}$ along the principal axis corresponding to the smallest eigenvalues of the matrix F^TWF. The eigenvalues and eigenvectors can be obtained by diagonalization of the matrix F^TWF.

$$F^T WF = U\Lambda U^T \tag{2.55}$$

Λ is a diagonal matrix formed by the eigenvalues of F^TWF on the diagonal.

$$\Lambda = \begin{bmatrix} \lambda_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \lambda_p \end{bmatrix} \tag{2.56}$$

Note that although the number of eigenvalues is the same as the number of the parameters, it does not refer to a specific parameter. The diagonal elements are arranged so that:

$$\lambda_1 \geq \lambda_2 \geq \cdots \lambda_p \geq 0 \tag{2.57}$$

and U denotes the matrix of eigenvectors.

$$U = [u_1 \quad u_2 \quad \cdots \quad u_p] \tag{2.58}$$

A column vector u_i is an eigenvector. These eigenvectors are called the principal components. The first principal component is the eigenvector corresponding to the largest eigenvalue. The second principal component is the eigenvector corresponding to the second largest eigenvalue, and so on.

The whole action from Equation 2.55 to 2.58 could be interpreted as an attempt to find a new coordinate system. What happens after the transformation by Equation 2.55 is that the coordinate in the parameter space is changed as such that the variation in $\tilde{Q}$ along each of the new axis is the symmetric. The new coordinate does not change the behaviour of $\tilde{Q}$ in the parameter space but it gives a new view of $\tilde{Q}$. The meaning of this principal axes theory can be better illustrated geometrically.

Suppose that we are dealing with a model that has 2 parameters, θ_1 and θ_2. In the parameter space, the axis perpendicular to $\Delta\theta_1$ and $\Delta\theta_2$ axes is $\tilde{Q}(\overline{\theta})$ axis. Consider that we are looking to the inequality $\tilde{Q}(\overline{\theta}) \leq \varepsilon$ and the projection of the contour of $\tilde{Q}(\overline{\theta}) \leq \varepsilon$ on the plane spanned by the other axes is an ellipsoid, see Figure 2.4. u_1 and u_2 are the new principal axes. The corresponding eigenvalues are λ_1 and λ_2 respectively. These eigenvalues can be interpreted as the slopes or the variations of the response surface $\tilde{Q}(\overline{\theta})$ along the corresponding principal axes. The higher the eigenvalues, the steeper the slope becomes and a local minimum of the response surface $\tilde{Q}(\bar{\theta})$, which corresponds to the unique set of parameter solutions, can be found. When the eigenvalue is very small or approaching zero, the response surface $\tilde{Q}(\bar{\theta})$ along the corresponding principal axis is very flat and there is no unique parameter solutions can be found in that direction.

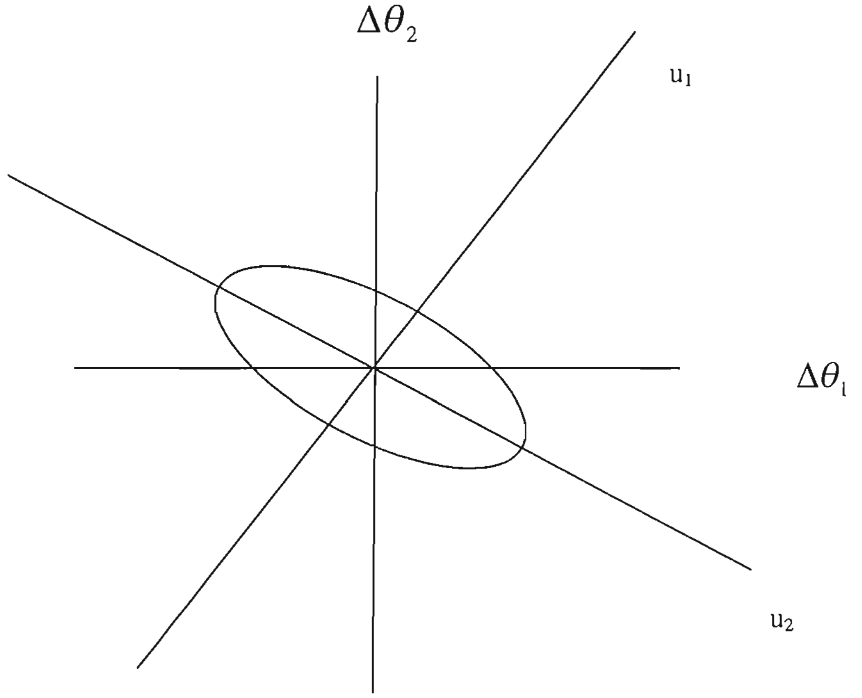


Figure 2.4: An approximate region defined by $\tilde{Q}(\bar{\theta}) \leq \varepsilon$ with the principal axes.

Which parameters cannot be determined can be found by looking to some significant nonzero components of the eigenvector corresponding to a small eigenvalue. The parameters correspond to these components have no unique solutions. When there is a fixed ratio between nonzero components of the eigenvector corresponding to a small eigenvalue, there is hidden dependency among the corresponding parameters. These parameters can only be determined as a group of parameters. Further information on how this analysis was performed in Matlab is given in Appendix D.

Chapter 3

Economic Optimisation of the Commercial Scale Reactor

3.1 Introduction

It is imprudent to say that the final result of this optimisation is a real optimum design for a commercial reactor. Reactor economic optimisation requires much information, not only about the reactor unit itself, but also about how the reactor would behave as the result of interactions with other units in the plant, and about the consequence of this reactor behaviour on the economics of the plant. Most of that essential information was not available at the moment this project was carried out.

However, before moving on to the experimental design, it is very practical to look first for the economically optimal operating region of the process. It is practically unrewarding to conduct the experiments in the region, which is far away from commercial interest. Incorporating the economic optimisation into parameter determination can increase the effectiveness of the whole project. The result may not give a precise reactor design, but it can be expected to give a good approximation for the boundaries of the experimental region, based on the economic considerations. For that purpose and armed with the current modest reactor, kinetic and economic information, economic optimisation on the reactor is possible.

The reactor unit under the study is a part of a complete process whose simplified block is shown on Figure 3.1. The process consists of two steps:

1. P production from X and Y (its reactor and separation units are denoted by R1 and S1 respectively).

2. The conversion of this P plus Q into S and its co-product R (denoted by R2 and S2). The developed kinetic model in this work belongs to R2.

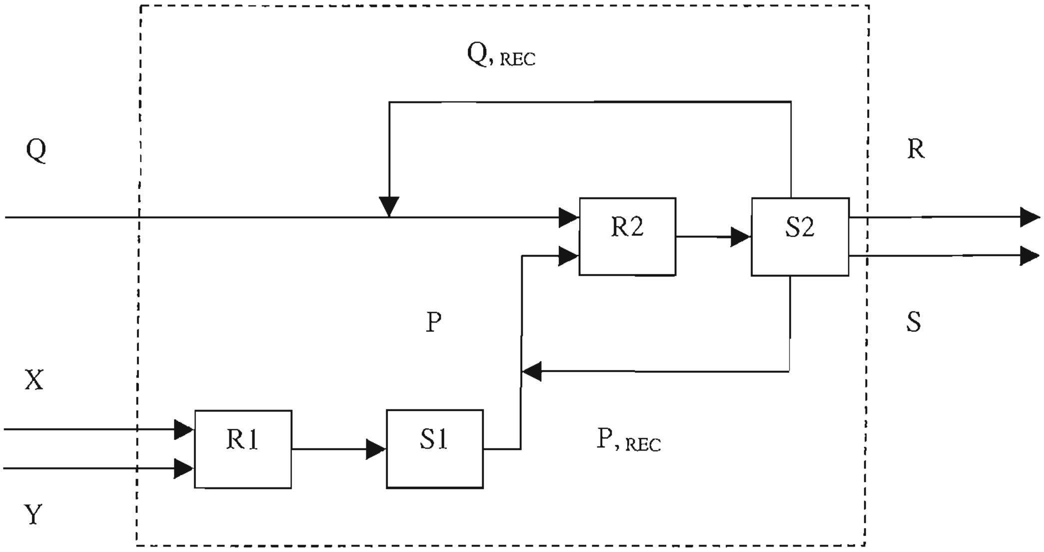


Figure 3.1: Total process block.

The economic optimisation involved the second reactor and separation units, where R and S are made from P and Q. Due to the lack of sufficient process information at the moment, some assumptions, which are given in the next section, should be made. Subsequently, the explanations for the choice of optimised inlet variables and the cost variables, and the derivation of cost function are presented.

3.2 The Assumptions in the Economic Optimisation

The assumptions in this economic optimisation are given as follows:

1. The cost of the second section, R2 and S2, builds the half of the total process cost.

2. No waste is formed in R2 and the raw materials; X, Y and Q are completely converted into the products, S and R.

3. Perfect separation of unconverted raw materials and products takes place in the separation unit S2. The unconverted raw materials are recycled to the second reactor. With this assumption, complete modelling of the separation unit, which is complicated by much of its information insufficiency in particularly physical properties, can then be neglected. It does not mean however that S2 is neglected from economic optimisation. The separation cost forms the most important process cost. A variable connecting the reactor performance to the separation cost is determined and explained in the next section.

4. The cost function to be minimised developed based on the profited cost evaluation for a reference process. This is the only economic information available at this moment and it does not give cost data in detail. Further economic evaluation by economic specialist is certainly required in the near future.

5. In order to develop the cost function later in this chapter, reference process conditions are required.

Further assumptions have to be made to complete the optimised model and they are presented along with the rest of explanations in this chapter in order to keep the context.

3.3 The Optimisation Tool, gOPT

gPROMS and its feature for process optimisation gOPT were utilised in the economic optimisation. For further information about the software, the readers are referred to gPROMS Advanced User's Guide. For the mathematical model of commercial adiabatic plug flow reactor is referred to Chapter 5.

3.4 Optimised Variables

The following are the optimised inlet variables and the cross sectional area of the reactor. In gOPT, these variables are denoted as time-invariant variables.

1. Molar feed ratio

   This variable is defined in chapter 5 as:

$$FR_{molar,in} = \frac{C_{Q,in}}{C_{P,in}} \quad (5.24)$$

   The inlet composition is denoted by the inlet molar ratio. It is essential to know under how much excess the process with equilibrium reactions should be operated in order to achieve the desirable production rate. In addition to that, recalling that the inlet stream to R2 is a mix of the fresh Q stream, outlet stream of S1 and the recycle stream, this feed ratio will give valuable information about how large the recycle streams should be.

2. Inlet temperature (T_{in})

   Assuming a simple configuration of adiabatic fixed beds in series, the reaction rate can also be manipulated by controlling the temperature at the inlet.

3. Liquid hourly space velocity (LHSV)

   Simplified as the ratio of liquid velocity and the reactor length (in unit m^3 feed/ m^3 cat/ h), this variable shows a measure of the performance of the reactor as a function of how much liquid fed into the reactor and the amount of the catalyst. As this variable has more important physical meaning rather than the liquid velocity and the reactor length individually, it is chosen as one of the optimised variables. This variable provides more information about how the reactor performs and leaves the reactor engineer with some freedom in scaling the fluid velocity and reactor length. Using this variable as an optimisation variable is allowed only when there is no change in the volumetric stream following pressure or composition changing. Until the model of volume as a function of composition changing is available, constant volumetric flow throughout the bed length is assumed.

Table 3.1. The optimised inlet variables

OPTIMISED INLET VARIABLES	DEFINITION
$FR_{molar,in}$	Inlet molar ratio of Q to P
T_{in}	Inlet temperature
$LHSV$	Liquid hourly space velocity

3.5 Variables in the Cost Function

Beside the fixed costs that are unaffected by the economic optimisation, the cost function is comprised of the reactor (R2) and the separation (S2) costs (see section 3.7), which are linearly varied by the following response variables:

1. The ratio of Q to S at the outlet, $\left(\frac{Q}{S}\right)_{out,mass}$

   This variable determines the separation cost, which forms the most important process cost. It says about the product distribution at the outlet stream of the reactor (R2) in terms of a ratio of the light component to the product. Unconverted Q and the main product S are the light and heavy components respectively. The mass ratio is used because all available economic values are expressed in per ton S produced.

   Higher ratio means more energy should be put in evaporation and this results in higher separation cost. A high ratio also means a low conversion, which usually results in a difficult and expensive product separation process. The optimiser strives to minimise this ratio. In addition to normalising the ratio change to per ton product, the advantage of having S at the denominator is that the optimiser is strongly forced to go the right optimum region, where minimum ratio is achieved not by ridiculously reducing Q in feed stream but by increasing the conversion to the optimum level, i.e. by increasing S production.

2. The reactor volume, $\frac{V_R}{S_{mass}}$

   The reactor volume can be calculated from in liquid hourly space velocity (LHSV, see Equation 4.9), which is the optimised inlet variable. Although within reason the actual size of the reactor plays a minor role in the overall cost, its effect is included in the cost function to add a little bit of cost overestimation. Furthermore, adding this variable into the optimised cost function safeguards the possibility that the reactor dimension resulted from LHSV optimisation is far from the realistic one. It gives an implicit control on LHSV optimisation, extreme and unrealistic value of LHSV will be punished by increase in total cost per ton product.

   In almost similar analogy for the reasoning at number 1, the presence of outlet S mass stream at the denominator gives an advantage in optimisation process. The relation between reactor volume and conversion is established by adding S term in the denominator. The increase in the reactor volume is accompanied by a proportional increase on the conversion until the optimum value is reached. Optimiser is guided towards a realistic local optimum region.

Table 3.2. The variables in the cost function

COST FUNCTION VARIABLES	DEFINITION
$\left(\frac{Q}{S}\right)_{out,mass}$	The mass ratio of Q to S at the outlet
$\frac{V_R}{S_{mass}}$	The reactor volume per ton S produced

3.6 The Operational Constraints

The optimisation is subjected to the following constraints:

1. The outlet temperature (T_{out})

   Because the reactor is operated adiabatically, the highest temperature is the outlet temperature and on this a constraint can be imposed. The optimised value of T_{in} is often influenced by this constraint. The reason for imposing the constraint on the temperature and not the other process variables is that often the operational capability of the equipment is strongly restricted by temperature. An example for that is the catalyst, which may not withstand a high operational temperature. Furthermore, optimisation of $FR_{molar,in}$ and $LHSV$ are already imposed by implicit constraints in the cost function variables, see section 3.5 for the explanations.

   This constraint is inequality endpoint constraint, it means that at the end of the optimisation T_{out} value may be lower or at the boundary value. When for example the outlet temperature may not exceed 500.15°K, it is mathematically defined as:

   $$T_{out} \leq 500.15 \tag{3.1}$$

   As a starting point, the constraint for T_{out} may be chosen within the current experimental temperature range. Afterwards, the boundary could be increased in order to see the trend outside the experimental range.

2. Mass production rate ($\Pr odRate$)

   If, for example, the second reactor has to achieve the demanded production rate of 1000 kt S/ ann, an equality endpoint constraint should be imposed and mathematically it is defined as:

   $$\Pr odRate = 1000 \tag{3.2}$$

   Imposing this constraint is not a compulsory for finding the optimum process condition. Optimisation of process conditions are unaffected by the scaling up the production rate. This is clear by looking to the definition of production rate implemented in gPROMS model:

$$ProdRate = \frac{C_{S,out} \times A \times v \times Mw_S}{8150h/ann} \quad (3.3)$$

Optimisation will influence $C_{S,out}$ and v value is related to the optimised LHSV (see formula 4.9). Increasing the production rate can be done independently by increasing the cross sectional area (A). If this production rate constraint would be imposed then the cross sectional area should be optimised. Again, the only purpose of co-optimising the area is for scaling up the production rate and not for finding the optimum process conditions. If this up scaling would be done, it is recommended to follow the following steps:

a. After finding the optimum process conditions, check what is the resulted production rate.

b. Define the cross sectional area as a variable in the gPROMS input file. Then increase or decrease its value accordingly until it results in a production rate that is approximately close to the required one.

c. Impose the production rate constant and use the area found in b as the initial guess in gOPT file. Then optimise the area.

Constraints are put in gOPT file and they are summarised in Table 3.3.

Table 3.3. The operational constraints

OPERATIONAL CONSTRAINTS	DEFINITION
$T_{out} \leq 500.15$	Temperature at the outlet
$ProdRate = 1000$	Production rate (carried out when necessary)

3.7 The Simplified Cost Function

The cost function is minimised by using gOPT optimisation tool of gPROMS. Expressed in fl/t S, the cost function looks as follows:

$$TotalCost = C_1 + C_2 \frac{(V_R / S_{mass})}{(V_{R,ref} / S_{mass,ref})} + C_3 \frac{(Q / S)_{mass}}{(Q / S)_{mass,ref}} \tag{3.4}$$

The first term on the right hand side of the equation represents the process cost unaffected by the economic optimisation on the second section (R2 and S2). The second term represents the effect of the change in the ratio of reactor volume and production rate with respect to the reference ratio. The third term represents the effect of the variation of product distribution on the separation cost, also with respect to the reference value.

Denominators are constants as well and the presentation of cost function can be further simplified to:

$$TotalCost = D_1 + D_2 (V_R / S_{mass}) + D_3 (Q / S)_{mass} \tag{3.5}$$

with

$$D_1 = C_1 \tag{3.6}$$

$$D_2 = \frac{C_2}{(V_{R,ref} / S_{mass,ref})} \tag{3.7}$$

$$D_3 = \frac{C_3}{(Q / S)_{mass,ref}} \tag{3.8}$$

The value of $(Q / S)_{mass,ref}$ was initially unknown and therefore several simulations based on the reference conditions and the current reactor and kinetic model were carried out for different inlet feed ratios (the reference value of $FR_{molar,in}$ is also unknown). The results were values of $(Q / S)_{mass,ref}$ between 4 and 6. For adding a little bit of overestimation into the economic consideration, 4 was taken as the reference value.

The derivations of the constants are presented next.

3.7.1 Fixed Cost

The first constant (C_1) is related to costs, which were assumed to be unaffected by the optimisation of R2 and S2.

$$C_1 = (\, NettoC_R + C_{U,P\,section} + Capex_{P\,section} + DirectFixedCost \,) \qquad (3.9)$$

C_1 comprises of the following cost elements:

a. The net raw material cost

$$NettoC_R = C_R - C_{BP} \qquad (3.10)$$

C_R is the raw material cost and C_{BP} is the value of the by-products from P section. The raw material cost is fixed as a complete conversion with no waste is assumed over the whole process block. The amount of by-products formed by P section is also assumed to be constant for the moment.

b. Utility cost of P section

Roughly approximated as one half of the total utility cost. The other half is assigned to S section, see number 3.

$$C_{U,P\,section} = 0.5 * C_{U,Total} \qquad (3.11)$$

c. Capital expenditure of P section

It is also roughly approximated as one half of the total capital expenditure.

$$Capex_{P\,section} = 0.5 * Capex_{Total} \qquad (3.12)$$

d. Direct fixed cost

It is comprised of operating cost, maintenance cost, taxes, insurance etc.

3.7.2 S Reactor Cost

The second constant (C_2) is related to S reactor cost, which is assumed to be linear to the reactor volume.

$$C_2 = Capex_R \qquad (3.13)$$

The capital expenditure for the reactor is estimated from the total capital expenditure as follows:

$$Capex_R = 0.2 * Capex_{S\,section} = 0.2 * (\, 0.5 * Capex_{Total} \,) \qquad (3.14)$$

It is assumed that S reactor costs only one fourth of the assigned capital expenditure for this section. The rest goes to S separation cost (see Equation 3.17).

3.7.3 S Separation Cost

The third constant (C_3) is related to the separation cost of S section, which is comprised of its utility cost and capital expenditure.

$$C_3 = (C_{U,S\,section} + Capex_S) \quad (3.15)$$

It consists of the following cost elements:

a. The utility cost of S section

One half of the total utility cost is assigned to this section:

$$C_{U,S\,section} = 0.5 * C_{U,Total} \quad (3.16)$$

b. The capital expenditure of S section

It is roughly approximated from the total capital expenditure as follows:

$$Capex_S = 0.8 * Capex_{S\,section} = 0.8 * (0.5 * Capex_{Total}) \quad (3.17)$$

Chapter 4

Mathematical Modelling of the Reactor

4.1 Key Modelling Assumptions

The assumptions in this modelling are given as follows:

1. Plug flow is assumed.
2. Negligible kinetic, potential energy and shaft work.
3. Negligible pressure effect on the rate of reaction. The concentration of the reactants in the liquid phase is a weak function of the pressure.
4. The liquid velocity is constant throughout the bed length.
5. Reactor bed is uniformly packed with the catalyst and the flow is evenly distributed over the bed cross section.
6. Kinetic model incorporate the internal and external mass transfer limitations.
7. Negligible catalyst deactivation.
8. The axial dispersion effects are negligible when the following criterion for the absence of both effects is met.

   $$\frac{L}{d_p} > 50 \tag{4.1}$$

   Both experimental and commercial reactors fulfil this criteria.
9. The lab-scale reactor is operated isothermally. The commercial-scale reactor is operated adiabatically.
10. Both reactors are operated at steady state.

4.2 Mass and Energy Balances

The general conservation relationship is:

Rate of Accumulation = Rate of Inflow – Rate of Outflow + Rate of Generation (4.2)

Consider an incremental section through the bed of cross-sectional area A and width ∂x :

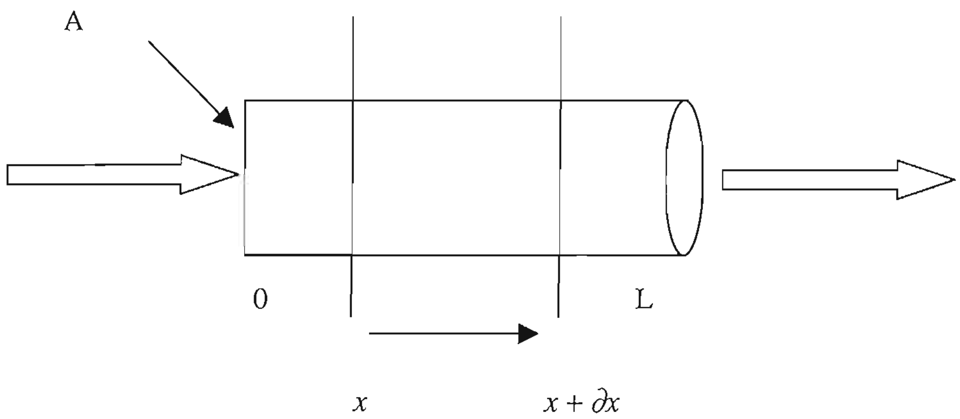


Figure 4.1 Flow of reactants through incremental section of a cross-section area A

4.2.1 Mass Balance of Component i

$$\frac{\partial (A\partial x \varepsilon C_i)}{\partial t} = vAC_i|_x - vAC_i|_x + A\partial x(1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} \upsilon_{ij} r_j \tag{4.3}$$

Dividing by $A\partial x$ and taking the limit as $\partial x \rightarrow 0$

$$\varepsilon \frac{\partial C_i}{\partial t} = -\frac{\partial (vC_i)}{\partial x} + (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} \upsilon_{ij} r_j \tag{4.4}$$

and at steady state, the accumulation terms becomes zero:

$$\frac{\partial (vC_i)}{\partial x} = (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} \upsilon_{ij} r_j \qquad , \forall i=1\ldots NC,\ \forall x \in (0,L] \tag{4.5}$$

Define a new variable:

$$z = \frac{x}{L} \quad ,0<z<1 \qquad (4.6)$$

which standardised the axial position into values between 0 and 1.

Taking the derivative of this new variable z and substituting it into the mass balance resulted in the following form of mass balance:

$$\frac{v}{L}\frac{\partial C_i}{\partial z} = (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} \upsilon_{ij} r_j \qquad ,\forall i=1\ldots NC,\ \forall z\in(0,1] \qquad (4.7)$$

The term $\frac{v}{L}$, which can be represented as a single quantity known as liquid hourly space velocity, has a physical meaning. The liquid hourly space velocity (LHSV) and the space time (τ) which are related to each other through the following relationship:

$$LHSV = \frac{1}{\tau} \qquad (4.8)$$

are the performance measures of the flow reactor. Under the assumption of constant density throughout the reactor length, the following expression of LHSV is valid:

$$LHSV = \frac{\phi v}{V_R} = \frac{v}{L} \qquad (4.9)$$

LHSV of 2 hr^{-1} means that two reactor volumes of feed at specified conditions are being fed into the reactor per hour. Inserting this term into the mass balance resulted in:

$$LHSV\frac{\partial C_i}{\partial z} = (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} \upsilon_{ij} r_j \qquad ,\forall i=1\ldots NC,\ \forall z\in(0,1] \qquad (4.10)$$

This final form of mass balance is implemented on isothermal lab scale reactor as well as adiabatic commercial scale reactor.

4.2.2 Energy Balance

Isothermal Lab Scale Reactor

Assuming that perfect isothermal situation holds at each point of the reactor:

$$T(z) = T_{in} \qquad ,\forall z[0,1] \qquad (4.11)$$

Adiabatic Commercial Scale Reactor

Assuming that kinetic energy, potential energy and work terms are negligible, the general conservation expression reduces to an enthalpy balance:

$$A\partial x\frac{\partial h_f}{\partial t} = AvH\,|_x - AvH\,|_{x+\partial x} + (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} r_j\left(-\Delta H_j\right)A\partial x + HeatS\partial x \qquad (4.12)$$

Again, dividing by $A\partial x$ and taking the limit as $\partial x \rightarrow 0$, the following expression is obtained:

$$\frac{\partial h_f}{\partial t} = -v\frac{\partial H}{\partial x} + (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} r_j\left(-\Delta H_j\right) + Heat\frac{S}{A} \qquad (4.13)$$

Neglecting the accumulation term at steady state and heat loss to the environment:

$$v\frac{\partial H}{\partial x} = (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} r_j\left(-\Delta H_j\right) \qquad ,\forall x \in (0, L] \qquad (4.14)$$

Substituting variable z (Equation 4.6) and LHSV (Equation 4.9) resulted in:

$$LHSV\frac{\partial H}{\partial z} = (1-\varepsilon)\rho_{cat}\sum_{j=1}^{NR} r_j\left(-\Delta H_j\right) \qquad , \forall z \in (0,1] \qquad (4.15)$$

Assuming an ideal mixture, the energy flow, H is given by:

$$H = \sum_{i=1}^{NC} C_i h_i \qquad , \forall i=1\ldots NC,\ \forall z \in (0,1] \qquad (4.16)$$

The molar liquid enthalpy of a pure component is a function of temperature and pressure in general

$$h_i = h_i(T, P) \qquad (4.17)$$

which upon differentiation yields

$$dh_i = \left.\frac{\partial h_i}{\partial T}\right|_P dT + \left.\frac{\partial h_i}{\partial P}\right|_T dP \qquad (4.18)$$

The final term is set to zero because the enthalpy of the component is assumed to be independence of pressure in liquid system.

Noting that

$$\left.\frac{\partial h_i}{\partial T}\right|_P dT = c_{p,i}(T)dT \qquad (4.19)$$

the following expression is found

$$dh_i = c_{p,i}(T)dT \qquad (4.20)$$

An expression for the liquid specific heat capacity is

$$c_{p,i}(T) = B1_i + B2_i T + B3_i T^2 \qquad (4.21)$$

Integrating *dhi* from the reference temperature (298.15K) and expression for h_i can be derived

$$h_i = \int_{Tref}^{T} c_{p,i}(T)dT \qquad ,\forall i=1...NC \qquad (4.22)$$

4.3 Boundary Conditions

4.3.1 Parameter Estimation

Isothermal lab scale reactor was utilised and the mass balance (4.10) is subjected to the following boundary condition:

$$C_i(0) = C_{i,in} \qquad ,\forall i=1...NC \qquad (4.22)$$

4.3.2 Experimental Design and Reactor Optimisation

At the reactor inlet (z=0), the same boundary condition holds:

$$C_i(0) = C_{i,in} \qquad ,\forall i=1...NC \qquad (4.23)$$

However, inlet concentrations cannot be assigned arbitrarily because their upper boundaries are dictated by thermodynamic model, which is unknown at the moment. Furthermore, in experimental design and reactor optimisation, the important measurable inlet variable is not concentration of reactants but their ratio. It gives formulated information on how excess of reactants will influence the reaction rates. A relationship between the inlet P and Q concentrations and their inlet molar ratio is described underneath.

The inlet molar feed ratio is defined as:

$$FR_{molar,in} = \frac{C_{Q,in}}{C_{P,in}} \qquad (4.24)$$

This molar ratio can be converted into the inlet volumetric feed ratio through the following expression:

$$FR_{vol,in} = FR_{molar,in} \frac{MW_Q}{MW_P} \frac{\rho_C}{\rho_Q} \tag{4.25}$$

The relationship between Q and P inlet concentrations and their ratio is established by the following expression:

$$C_{P,in} = \frac{1}{1 + FR_{vol,in}} \frac{\rho_P}{MW_P} \tag{4.26}$$

$$C_{Q,in} = \frac{FR_{vol,in}}{1 + FR_{vol,in}} \frac{\rho_Q}{MW_Q} \tag{4.27}$$

Substituting these expressions into Equation 4.24 and assuming that no products at the reactor inlet give the boundary condition for concentrations.

The energy balance of adiabatic commercial reactor is subjected to the following boundary condition:

$$T(0) = T_{in} \tag{4.28}$$

Chapter 5

RESULTS AND DISCUSSIONS

5.1 Parameter Estimation

Assuming that each measurement data is a result of random sampling and 5% relative error is valid for all concentrations, estimates of kinetic parameters were obtained. Appendix B shows how the predicted values fit the experimental data. Plots were generated by gPROMS model using the estimated kinetic parameters. The estimated model is rather poor in predicting the intermediate and product concentrations. The standard deviations in the activation energies and enthalpies are large and these estimates were therefore not accurate.

Correlation between parameters could indicate whether the parameter optimisation was hindered. High correlation imposes restrictions on the parameter optimisation process and may drive it off target. There are high correlations between Arrhenius constants estimated in this work, especially in the first reaction. When such high correlations exist between the estimates, very often the quality of the estimates is poor since highly correlated estimates are usually associated with high variances.

It is very unlikely that Arrhenius parameters were ill formulated cause such possibility has been reduced by applying parameter transformation. One possible explanation for this ill behaviour of kinetic parameters is a fairly small range of temperature over which the reaction rates were measured. Satterfield (1991) illustrated how such poor experimental design would subject the parameter values determined from Arrhenius plot or its equivalent to considerable error. Appendix E presents his argument. It is believed that at least 50°K temperature difference is needed to overcome this problem (personal comment from Prof. Grievink). The current experimental temperature range of 20°K (between low and middle temperature) and 40°K (between middle and high temperature) are obviously still too small. If there were enough data points at high temperature, larger temperature range of 60°K (between low and high temperature) could be applied. Unfortunately, the number of measurements at high temperature was not enough for allowing 9 parameters to be estimated. Therefore larger temperature range of 60°K (between low and high temperature) could not be applied and the data sets of middle temperature had to be included into the estimation.

Further assessment of the quality of the estimates was performed by looking to the joint confidence region of the estimates as given in Table 5.1. Desirable is to have a small confidence region as there is more information about the true values of parameters.

Table 5.1: Analysis of Variance

Confidence region	$SS(\bar{\theta})$	n	p	$\hat{\sigma}^2$	$(1-\alpha)100\%$	$F_\alpha(p, n-p)$	$SS(\overline{\theta_0}) \leq$
Expected	131	140	9	1	95	1.95	149
Obtained	1120	140	9	8.55	95	1.95	1265

The obtained confidence region is very large compare to the expected one indicating that the quality of the estimates is still very poor. Possible explanations are:

1. Model inadequacy

   Possibly, there are other significant aspects or mechanisms, which were not adequately modelled, such as:

   a. By-product formation.
      At the highest experimental temperature, a significant by-product formation was reported. Since the present number of recorded data was insufficient for allowing by-product parameter estimation, its kinetic model was excluded for the time being.

   b. Different reaction mechanism
      The kinetic modelling was started from a very general model and all main reactions involved were assigned the same importance. However, it was reported that the intermediate concentration stayed at a very low level during the course of the reaction. This fact may indicate that the first reaction is much faster than the second one and pseudo steady state might have happened. If pseudo steady state assumption would have been applied, different and more adequate kinetic model may appear. Different reaction mechanisms such as Langmuir Hinselwood, are also possible and should be investigated.

   c. Non-isotherm
      It was assumed that the reactor was in perfect isothermal condition. Any significant deviation from this assumption means that the reactor model applied on estimation process was wrong. Whether the reactor was indeed in isothermal condition should be checked.

   d. Non-ideal behaviour of the liquid mixture
      The liquid system under the research is highly non-ideal. As the thermodynamic model has not been made available yet, up to what extend this non-ideality influenced the reaction rate is still unknown should be investigated.

2. Inadequate error model

   The assumption that 5% relative error model for all concentrations could be inadequate. It is very likely that higher relative error should be assigned for low product concentrations, since their measurements are in general more difficult and less accurate. The following plot of residuals, where the relative residuals plotted against the observed concentrations, seems to confirm this suspicion.

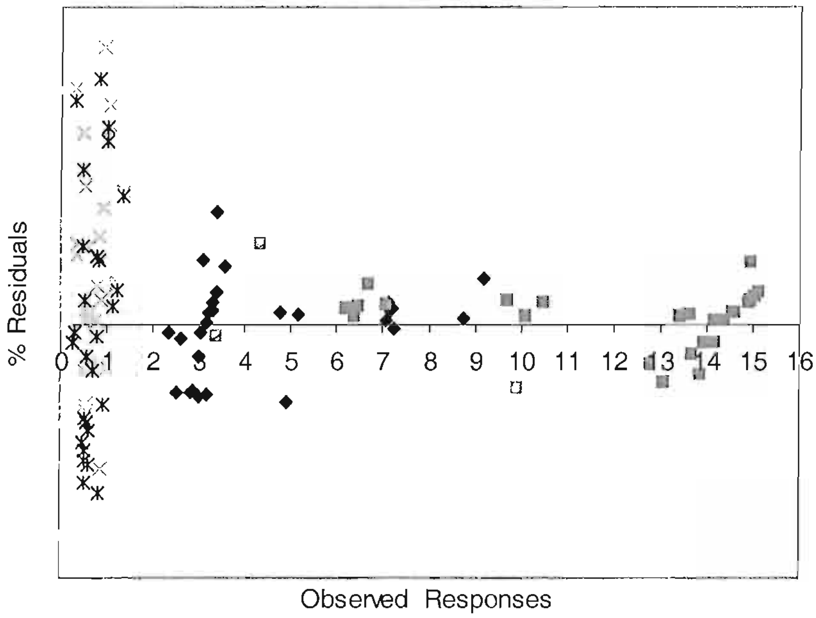


Figure 5.1: Residual plot of observed response with 5% variance model

The pattern shown opposed the preliminary assumption that the errors are uncorrelated random variables with mean zero and constant variance. The relative variance is increasing with the decrease in magnitude of observed responses (measured concentrations). Transformation of the response is often used to eliminate this problem. One variance stabilising transformations is taking the logarithmic values of the responses. However, changing the measurement apparatus with one that could stabilise the variance is really the last option. So firstly, in re-estimation of the parameters assign different CONSTANT RELATIVE VARIANCE (see gPROMS advance user's manual) for each of concentration type. Relatively high constant relative variance may be assigned to low product concentration. Experimentalist can give reliable estimates of the relative variance. Also it should be checked if there were any aspects left out from the first modelling, see number 1. Any significant aspects, which were not modelled, may generate systematic errors and show such residual pattern.

3. Poor experimental design

It has been mentioned earlier, a design with a small experimental temperature range, like in this case, might result in the persistence of high correlations between parameters, which subsequently caused large range of inaccuracies, see Appendix E for mathematical evidence. Another weakness in the previous experimental design is that the experimental regions were not fully explored, see Figure 5.2 to 5.5.

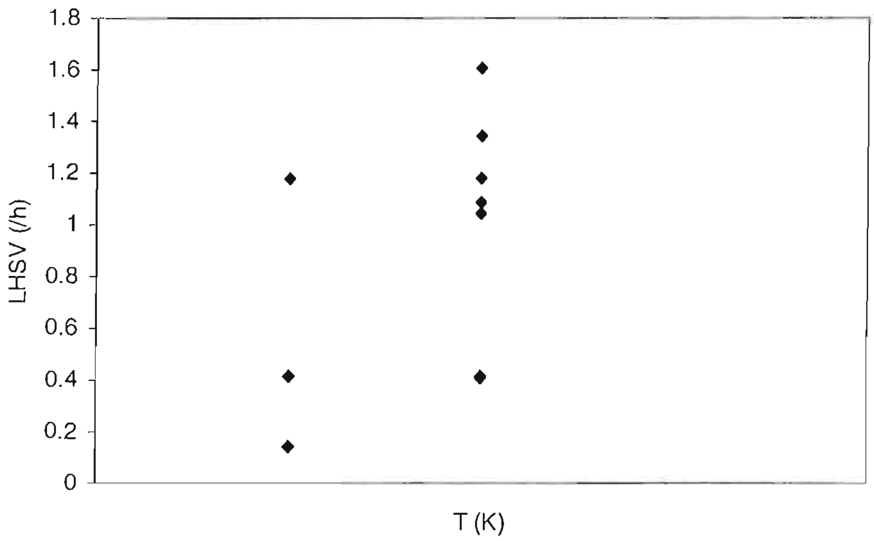


Figure 5.2: Experimental design for the highest feed ratio

There were 3 inlet variables varied in the experiments. Feed ratio was varied at four levels. Each plot represents one of feed ratios. Temperature was varied at three levels. The highest temperature is placed at the end of T-axis. The liquid hourly space velocity (LHSV) was varied over wide range.

If the kinetic model had to be validated over those inlet variable levels, measurements should be taken at all combinations of inlet variables. Shown in Figure 5.2 that there were no measurements taken at high temperature At the second feed ratio, see Figure 5.3, more measurements were needed at higher temperature levels. Many gaps of measurements also happened at other feed ratios, see Figure 5.4 and 5.5. The estimates became very inaccurate because the validity of the kinetic model on those places has not been determined yet.

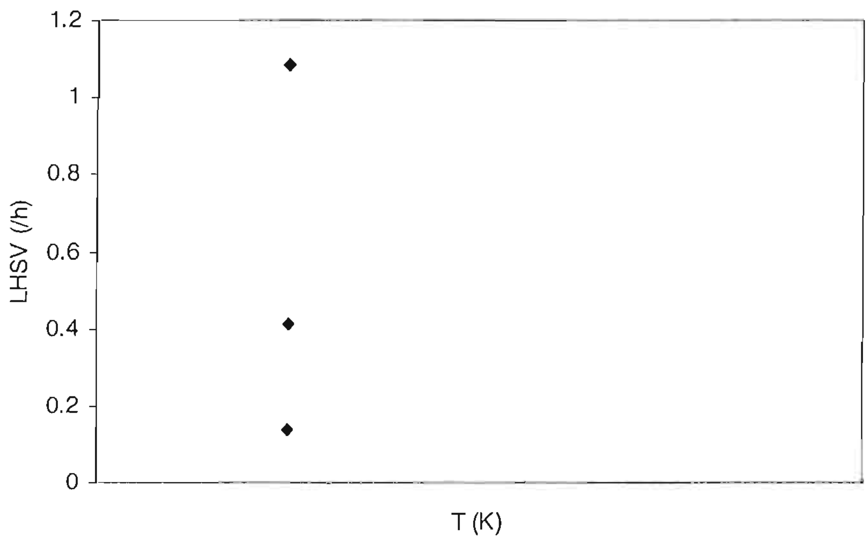


Figure 5.3: Experimental design for the second feed ratio.

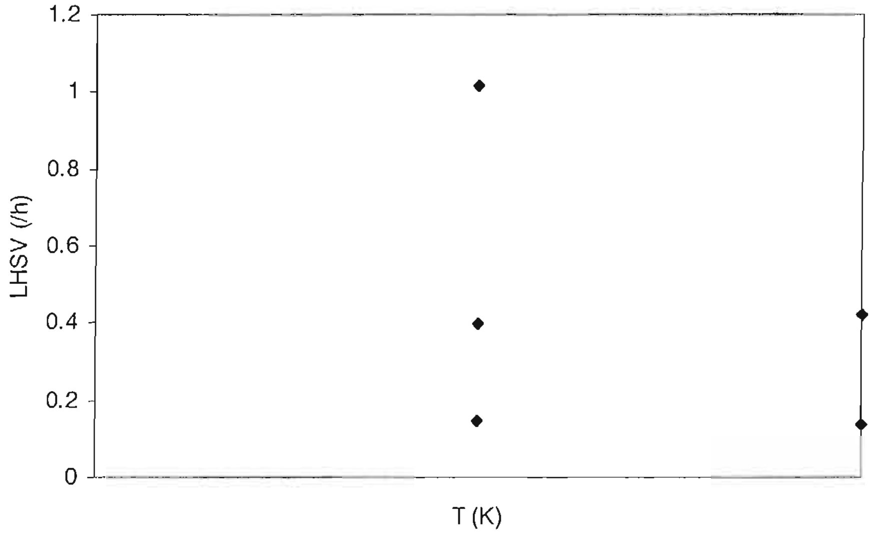


Figure 5.4: Experimental design for the third feed ratio.

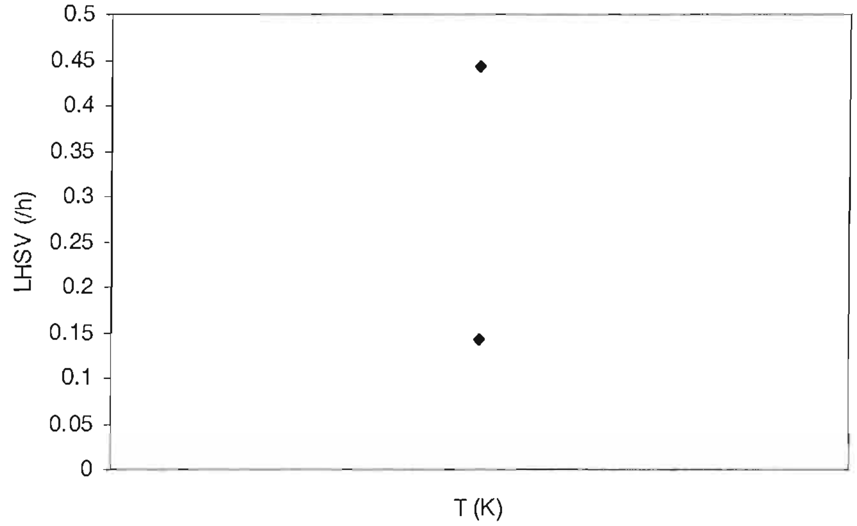


Figure 5.5: Experimental design for the lowest feed ratio.

5.2 Reactor Optimisation

Before moving on to the experimental design part, the optimisation of the reactor was carried out to find out the location of the economic optimum region. It is more interesting to design the experiments and validate the kinetic model on that optimum region. Using the cost function developed in Chapter 3, economic optimisation on the reactor was carried out. The result is that with the current estimated kinetic and reactor model, economic optimum is always found at the upper boundary of the temperature. The decrease in total cost per ton product continued when higher upper boundary of temperature was applied in the optimisation process, see Figure 5.6.

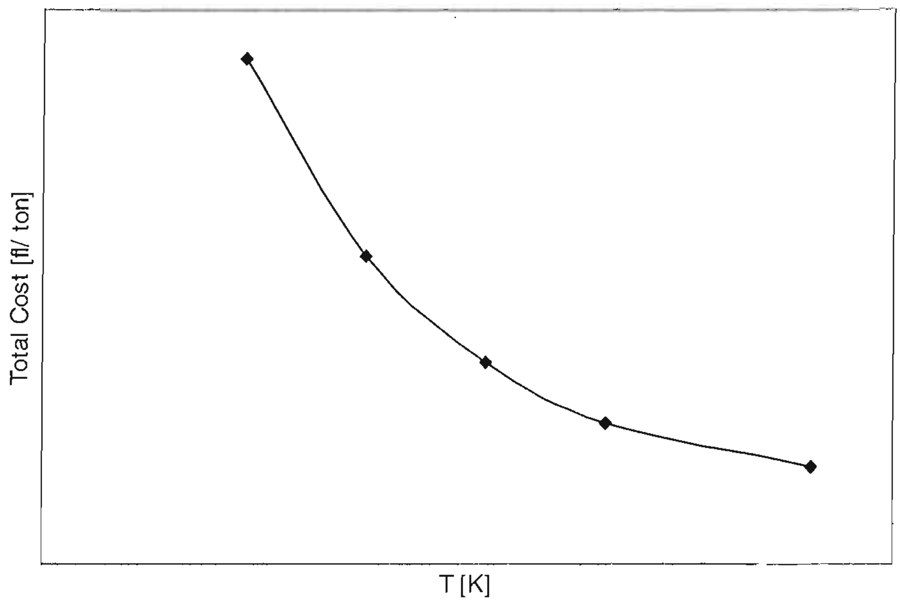


Figure 5.6: Total cost per ton product as a function of the highest opt. reactor temperature.

The total cost is expected to increase with the temperature, due to by-product formation. At the highest current experimental temperature, significant by-product formation was reported. Since the current kinetic model does not include by-product kinetic, it fails to predict the increase in the total cost due to increase in waste formation. Until the kinetic model is improved, the result of the optimisation cannot be considered as realistic.

The optimum values of other inlet variables were not at the boundaries and changed according to the applied temperature boundary. See figure 5.7 and 5.8. According to Figure 5.7, near stochiometric feed ratio was found to be more profitable for the reference reaction temperature. When the temperature was increased, lower feed ratio corresponding to excess in P was found to be more profitable.

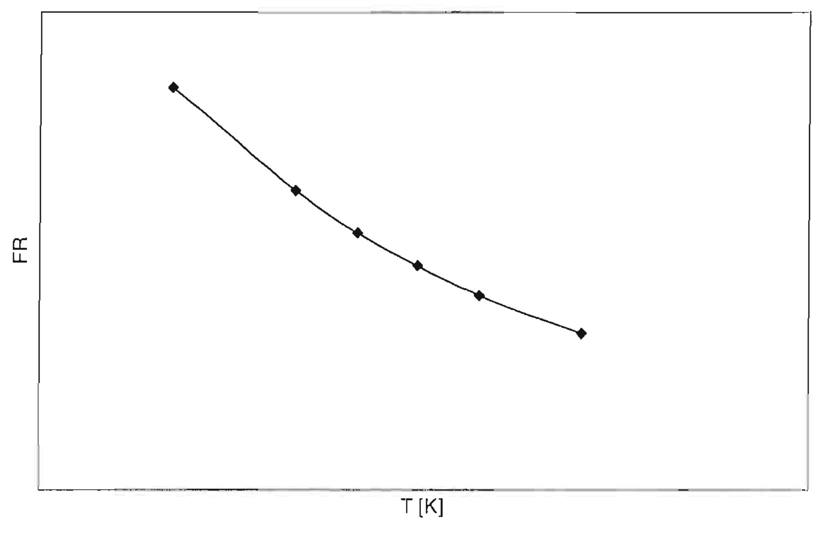


Figure 5.7: Optimum inlet molar ratio as a function of the highest opt. reaction temperature.

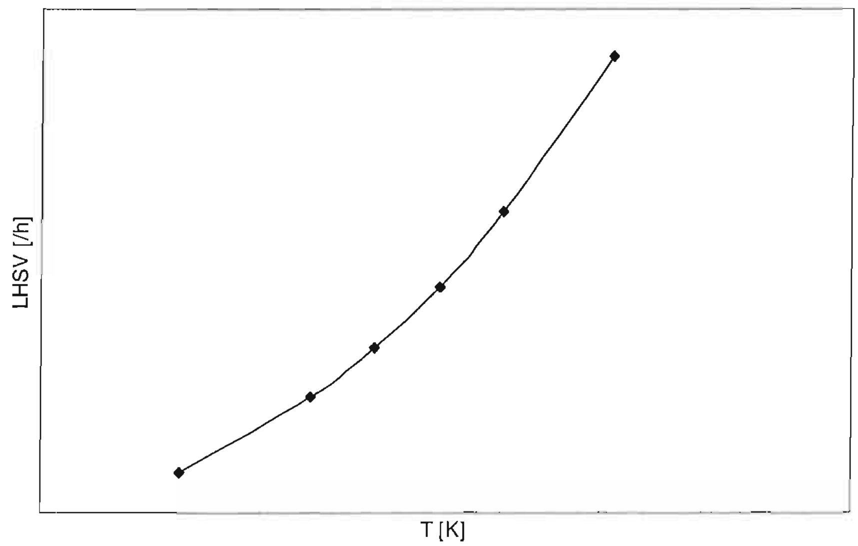


Figure 5.8: Liquid hourly space velocity as a function of the highest opt. reaction temperature.

Lower optimum reaction temperature seemed to be compensated with longer reaction time or small LHSV and as the result the reactor was larger at lower reaction temperature, see Figure 5.8 and 5.9.

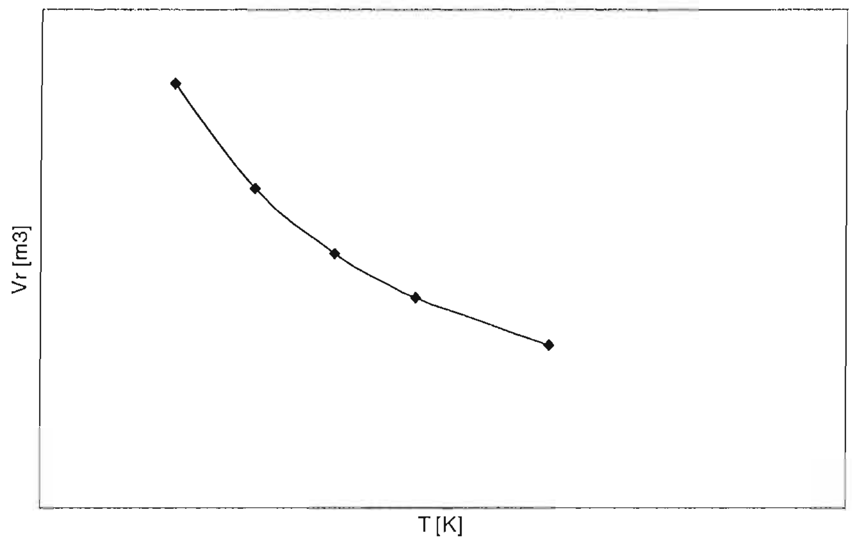


Figure 5.9: Optimum reactor volume as the function of the highest opt. reaction temperature.

A test of sensitivity of the optimised inlet variables to the variations in the constant values used in the cost function was also performed. See Appendix C for its graphical result. It has been found that the optimum temperature was very insensitive to the changes in the constants. If the total cost function is improved by the economic expert and some values of the constants are changed, the same kinetic and reactor model, unless they are improved by adding by-product kinetic, will still predict that higher optimum temperature is more profitable. Optimisation and sensitivity results add a stronger economic motivation for doing experiments at higher temperatures and kinetic modelling of the by-product formation.

5.3 Experimental Design

Several experimental designs using the method purpose in Chapter 2.3.3.3 were developed around the optimum conditions and their $|F^TWF|$ values were calculated. Unfortunately, all determinant values were found to be zero, which thus means no design based on the current kinetic model could improve the accuracy of the estimates. The columns in F-matrices corresponding to the model sensitivity to perturbations in enthalpies (ΔH_j) and activation energies ($E_{a,j}$) values were very close to zero, means that enthalpies and activation energies could not be determined. Principal component analysis conformed that enthalpies and activation energies for both reactions cannot be determined, see Appendix D. This statement is supported by large deviations found for both type of parameters, mentioned in Section 5.1. No improvement on the sensitivity of the response to those parameters could be done even after different experiments were added into the design.

Two possible sources of this problem are:

1. Incorrect Experimental Method

The kinetic experiments involving the reversible reactions are complicated by the interactions between forward and backward reactions. Suppose that the following kinetic model is the correct model and the reaction scheme is still the same:

$$\mathrm{P + Q \leftrightarrow I} \qquad (2.4)$$

$$\mathrm{I + Q \leftrightarrow R + S} \qquad (2.5)$$

$$r_1 = k_1(C_P C_Q - \frac{1}{Ke_1} C_I) \qquad (2.6)$$

$$r_2 = k_2(C_I C_Q - \frac{1}{Ke_2} C_R C_S) \qquad (2.7)$$

In these models, k_{-i} is calculated indirectly by calculating Ke_i. There are two experimental methods that work and each method tries to obtain pure information about each of the rate constants:

Method 1:

Each of the reversible reactions could be treated as two irreversible reactions. The first irreversible forward reaction provides data for the estimation of k_i. The reverse reaction, again irreversible, provides data for the estimation of k_{-i}. For this approach to provide useful parameter estimates, the concentration profile of the approximate irreversible reaction needs to be close to that of the true observed reversible reaction. This is aided by setting the initial concentration of one of the products equal to zero. Then the concentration profile over time of the approximating irreversible reaction will have the same gradient at $t \rightarrow 0$ as the reversible reaction. The approximation will clearly deteriorate as t increases and the reverse reaction becomes more important.

Method 2:

There is another experimental method that is less practical than treating the reversible reactions as two irreversible reactions. The method is based on the fact that the equilibrium, which is attained at infinite time, depends both on the initial values of concentrations and on the rate constants, see Appendix I for mathematical evidence. By having the concentration measurements at equilibrium and the initial values of concentrations the reverse rate constants can be approximated fairly accurate. The method thus suggests for measuring the concentrations at $t \to 0$ for estimating k_i and measuring the equilibrium compositions at $t \to \infty$, which is not practical, for estimating k_{-i}. The problem with this method is that the experiments cannot be performed infinitely and if one persists to use this method, then the measured compositions at the large reaction time is not the real equilibrium compositions and using this measurements for estimating k_{-i} may cause inaccuracies.

In order to gain more information about the true rate of each irreversible reaction component, both methods suggest to take the measurements when the interactions between forward and backward reactions are at their minimum. Although the second method suggests taking part of measurements at absolute equilibrium, it is for obtaining indirectly pure information for backward reaction. Applying correctly one of those methods may lead to accurate estimates.

To see which method that was applied on the previous experiments, the outlet concentration profiles should be checked. Presented in Figure 5.10 are the product concentration profiles at the lowest experimental temperature. Looking to the slope of the points nearest to t=0, the irreversible forward reaction (2.5) was approximated seemingly well. Although concentration change with time was still noticeable at the second and the third reaction times, there was no evidence that the reverse reaction was insignificant. If the reverse reaction takes place relatively significant, even though the change of concentration with time is still noticeable, the concentration profile does not approximate well the irreversible forward reaction. The experimental data does not contain information about k_i but the net rate, the result of interaction between k_i and k_{-i}. k_i can never be estimated from such data. Classifying this method into method 2 is also inappropriate. The measurements should have been taken at the extremes, when $t \to 0$ and when the equilibrium is reached. The equilibrium had not been reached in this case. Using these points for estimation may cause inaccuracies.

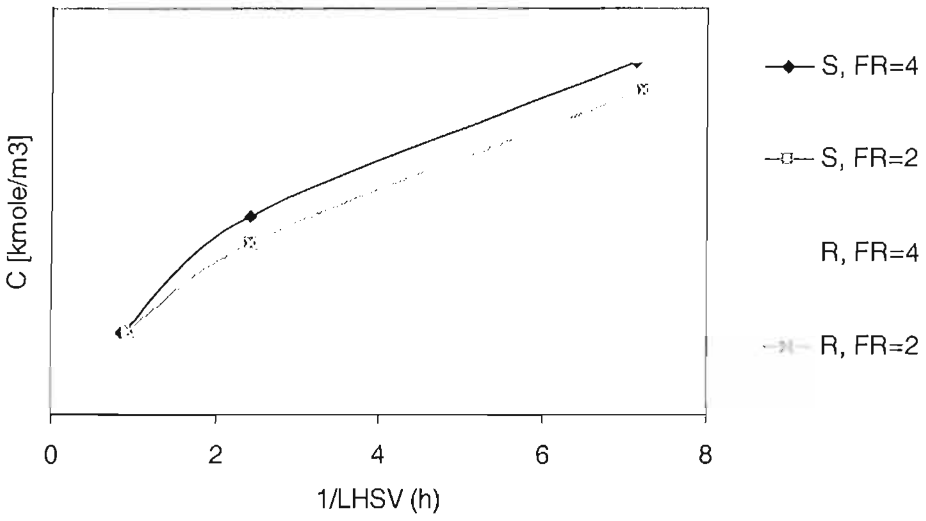


Figure 5.10: Product concentrations as a function of reaction time.

Figure 5.11 and 5.12 show the corresponding reactant concentration profiles. The concentration change with time was very small suggesting that the reactant concentrations already approached the equilibrium concentrations, although not in equilibrium yet. Reverse reaction had definitely played important role. Again, k_i and k_{-i} cannot be estimated from that data.

All measurements were taken in similar way in this study case. Pure information for each of rate constants was not obtained. Information obtained was the information about the net rate and not about each of the real forward and backward rates individually. Therefore, kinetic parameters corresponding to those rate constants could not be estimated accurately.

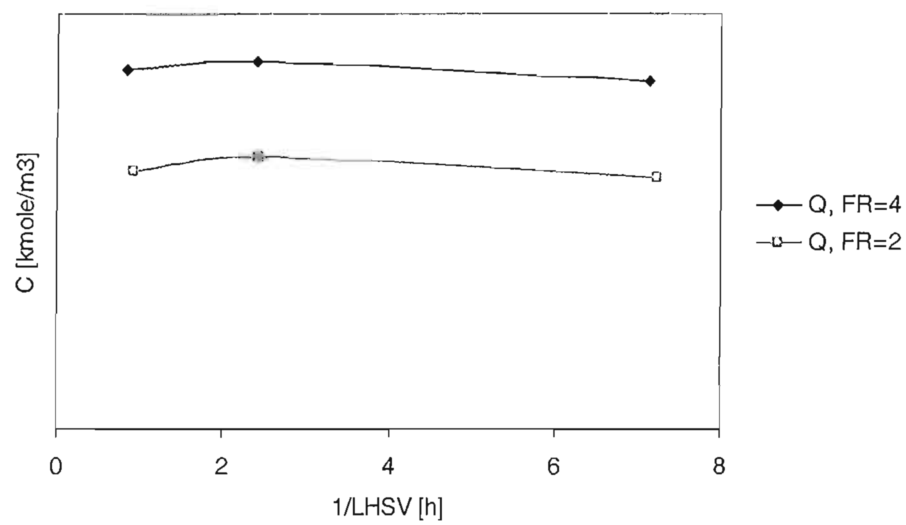


Figure 5.11: Q concentrations as function of reaction time.

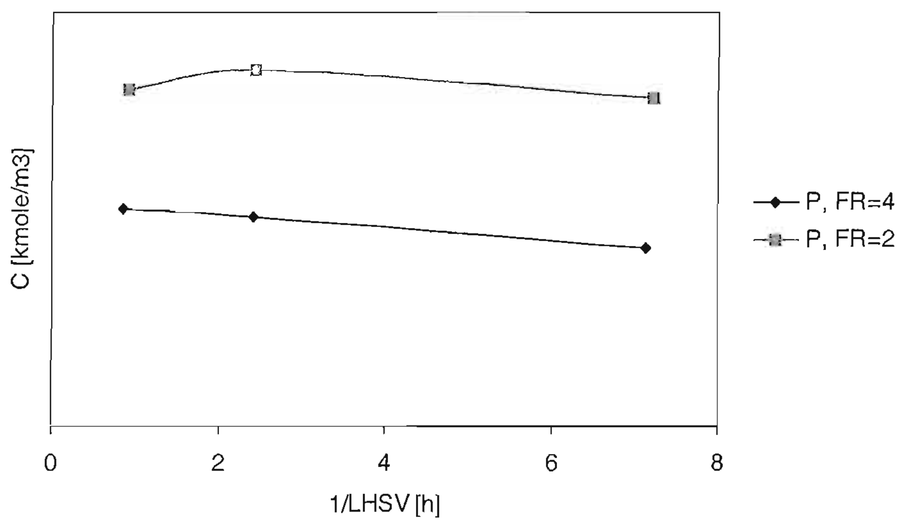


Figure 5.12: P concentrations as function of reaction time.

2. Hidden Parameter Dependencies.

The problem of hidden parameter dependencies has been illustrated in Section 2.4. It can be inherited from the reaction behaviour itself (like pseudo steady state). It was reported that the concentration of the intermediate was small and constant during the reaction course. So pseudo steady state assumption is very likely valid. Parameter dependency might have been revealed if this assumption would have been included into the previous kinetic modelling. Which parameters exactly depend to each other and in what kind of structure these parameters present in the models are still unknown.

Chapter 6

Conclusion and Recommendations

6.1 Conclusion

The main objective of the project is to optimise the economics of the commercial reactor. In order to achieve the objective, kinetic knowledge should be obtained first. Although the main objective of the project could not be achieved within the given time, the reproducible methods for parameter determination and reactor optimisation have been successfully developed. Their application in the near future will certainly help in optimising the design of the commercial reactor. Mathematical models for parameter determination and reactor optimisation have been built in gPROMS simulation software.

Due to high non-linearity of the kinetic models, a reproducible sequential procedure of kinetic parameter determination, which consists of parameter estimation and experimental design, have been developed and applied on the case. The first sequence of the sequential procedure have been carried out and the first set of estimates obtained. Statistical analysis shows that the current kinetic estimates are inaccurate. The poor quality of the prior experimental design is one of the sources of the inaccuracy. Firstly, on many places in the experimental region, the validity of the kinetic model has not been determined yet. Secondly, the experimental temperature range was too small resulting in the persistence of high correlation between Arrhenius parameters that causes large inaccuracies. Another source of the inaccuracy could be the inadequacy of the current kinetic, reactor or error model.

A principal component analysis on the kinetic model indicated that enthalpies and the activation energies could not be determined. The problem originated firstly from the hidden parameter dependency, which usually caused by the presence of the pseudo steady state in the reacting system. Prior experiments had indeed indicated the presence of pseudo steady state in the reacting system. The second source of the problem is the incorrect experimental method. It has been proven that the measured data does not contain sufficient information about the rate of irreversible components of the reacting system. Instead it contains the information about the net rate that is resulted from the interaction between forward and backward rates. Therefore, the quality of the parameter estimates corresponding to the rates of the irreversible reaction components becomes extremely poor. No designs based on the current data and model could be constructed by applying D-optimum approach for improving the accuracy of the kinetic estimates.

Reactor optimisation using the current inaccurate estimates suggested that many modelling aspects should be improved. First of all the total cost function, which describes how the economic of the plant is affected by the product distribution of the reactor, needs to be improved by the economic expert. Secondly, because the optimisation result has indicated a possibility that the economic optimum lays at a higher operational temperature, the unwanted by-product kinetic and the catalyst deactivation model should be incorporated.

6.2 Recommendations

It is recommended to apply the factorial design or central composite design approach. The approach would enable the experimentalist to explore the experimental region systematically and effectively. The recommended starting design is the square design, where two variables, temperature and the feed ratio, are varied in two levels, high and low. At least 50 degrees difference between the low and high levels should be allowed for the temperature, as smaller temperature range will result in high parameter inaccuracy, see Appendix E for the mathematical evidence.

It is advisable to obtain the parameters of the equilibrium constants, like the enthalpies and entropies with the help of a thermodynamic method. Then partially estimate only the parameters of the forward or backward rate constants. The first advantage is that usually thermodynamic method provides better estimates of enthalpies and entropies. Secondly, the number of parameter to be estimated is reduced and the model will more stable and close to linear. As it has been observed in the previous experiments, pseudo steady state occurs. Therefore, it is also highly recommended to apply pseudo steady state assumption on the next kinetic modelling. This may reveal which parameters cannot be estimated independently.

Furthermore, if possible, it is recommended to treat the reversible reaction as two irreversible reactions. For measuring the rate of forward irreversible reaction, set the initial concentration of the products equal to zero. Then for measuring the rate of backward irreversible reaction, the initial concentrations of the reactants are set as zero. At each combination of feed ratio and temperature in the factorial design, liquid hourly space velocity have to be varied as such that the measured concentration change is the initial concentration change of the irreversible reaction component.

Since the current optimisation predicts that higher temperature is more profitable, by-product formation and catalyst deactivation should also be modelled. Several assumptions applied on this estimation work such as the experimental reactor was isothermal and the reaction rate was unaffected by the non-ideal behaviour, have to be investigated. There is also a possibility that the kinetic model is not elementary, so another important task may be to discriminate between models of different reaction orders. When the complete and adequate kinetic model and improved total cost function are available, finding economic optimum design for the commercial reactor by applying the method developed in this work will be possible.

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APPENDICES

Appendix A

gEST for Steady State Experiments

A.1 Run File Structure

More than 20 experiments had been performed in isothermal steady state plug flow reactor. If the structure of RUN file proposed in gPROMS Advanced User Guide would have been applied, one RUN file had to be created for each experimental run. Another RUN file structure, which enabled us to combine data from different steady state experimental runs on one file, is shown in table A.1. This new structure can be employed as long as there is no $ sign in the associated gPROMS input file.

Table A.1: RUN file structure for Steady State experimental runs.

SPECIFICATION	COMMENTS
MEASURE {response variable name} {time}{value @ 1st run} {time}{value @ 2nd run} : {time}{value @ ith run}	Specify the measurement data. Full gPROMS pathname. For convenience, time of measurement is at the middle of associated interval duration (see INTERVAL).
INTERVAL {Number of experimental runs} {duration of 1st run} {duration of 2nd run} : {duration of ith run}	Specify the number of experimental runs. The duration of an experimental run. As there is no $ sign in gPROMS input file, arbitrary value can be assigned to the duration. For convenience, assign the same duration for all experimental runs.
PIECEWISE-CONSTANT {inlet variable name} {value @ 1st run} {value @ 2nd run} : {value @ ith run}	Specify the inlet variable. Full gPROMS pathname. Variable value in each run.

A.2 gEST Bugs

Bugs related to gEST were found in gPROMS version 1.8.2 for Window 95. The followings are their descriptions and temporary fixes:

1. Re-initialisation of gEST right after a failed initialisation, which happened when the given set of initial guesses are far from the local solution area, could not be carried out. The following message appeared:
   gEST error: Could not open for writing: code/(PROCESS name).chron.
   Re-initialisation could only be executed after gPROMS was disconnected and restarted.

2. The measured variable is the concentration at the outlet of the reactor, $C(i, L)$. gEST cannot recognise the notation of such distributed variable in RUN files. A new algebraic variable had to be introduced in gPROMS input files and used in RUN files.

   - Stated *Cout* in VARIABLE section and wrote it in EQUATION section of gPROMS input file as follows:
     $Cout(i) = C(i, L)$
   - Used *Cout* in MEASURE section of RUN file to specify the measurement data.

Appendix B

gEST vs. Simusolv

Two sets of estimates for kinetic parameters for the production of Q and P were obtained through two different paths: gEST and Simusolv. In this section, both results are visually compared to each other.

The concentrations are plotted against logarithmic values of the residence time (in hour), $\ln(\tau)$. Predicted data was generated by gPROMS. As can be observed, gEST model predictions fit experimental data better than ones of Simusolv. At very low concentration level, especially for intermediate and the products R and S, the model predictions by Simusolv become poorer. See Figure B.1, B.3 and B.5. Further statistical analysis of the results from Simusolv is recommended, so that both models can be compared to each other with more certainty.

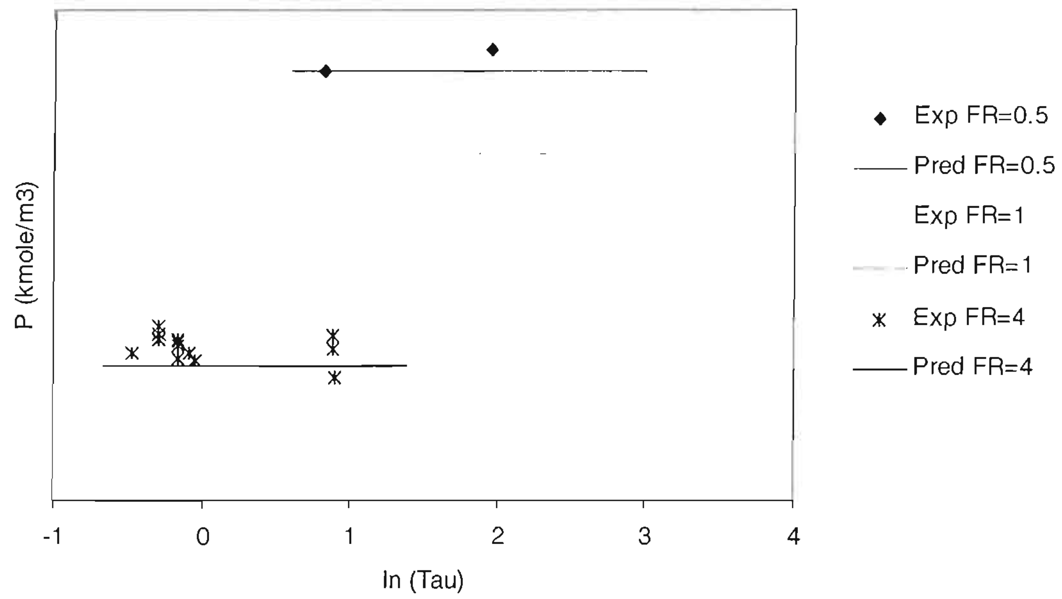

Figure B.1: Simusolv – P

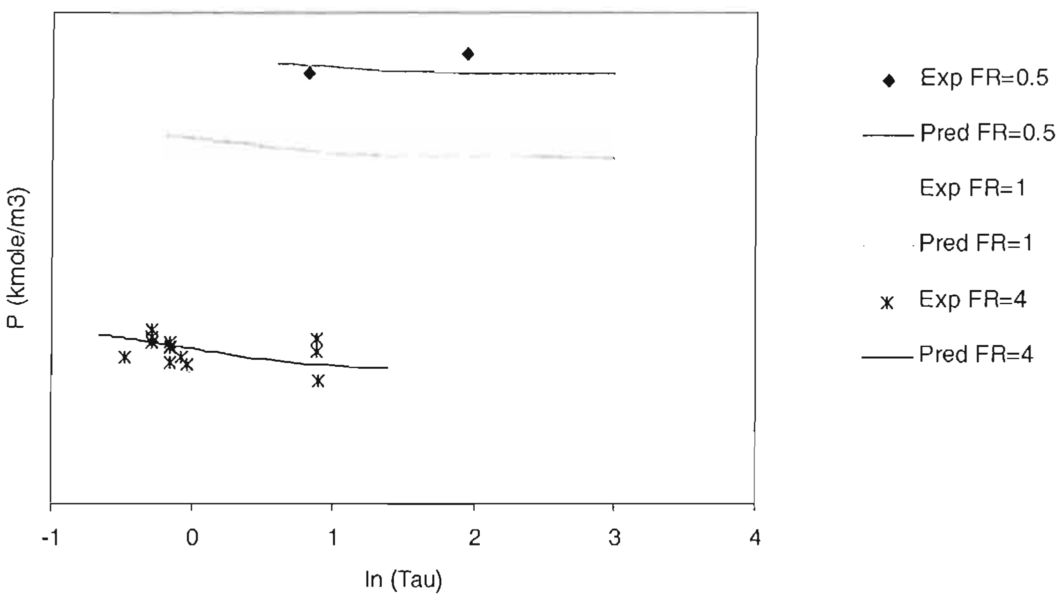

Figure B.2: gEST – P

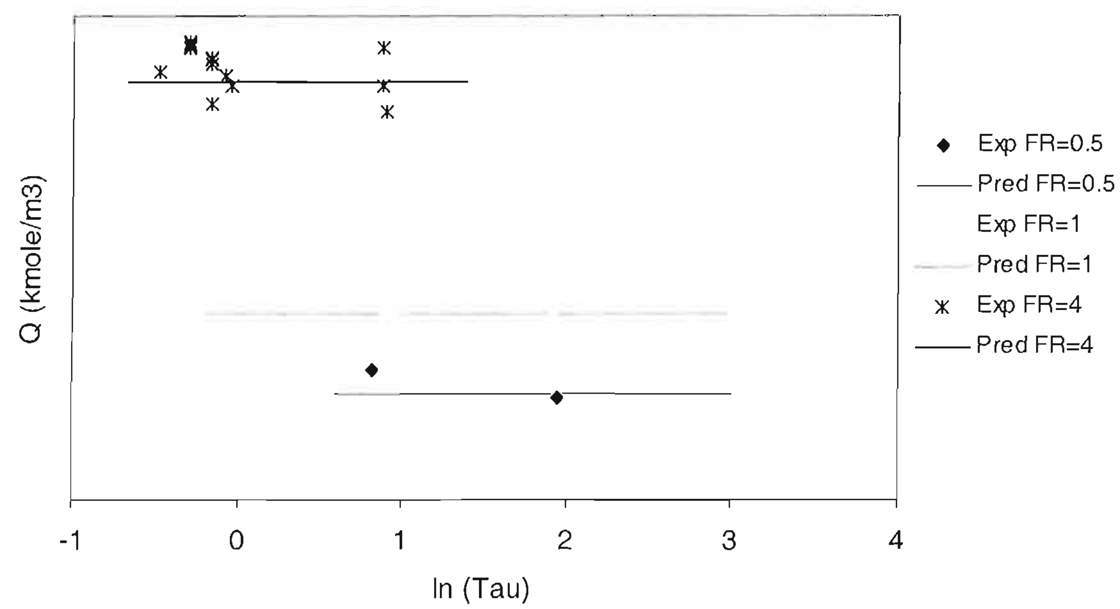

Figure B.3: Simusolv – Q

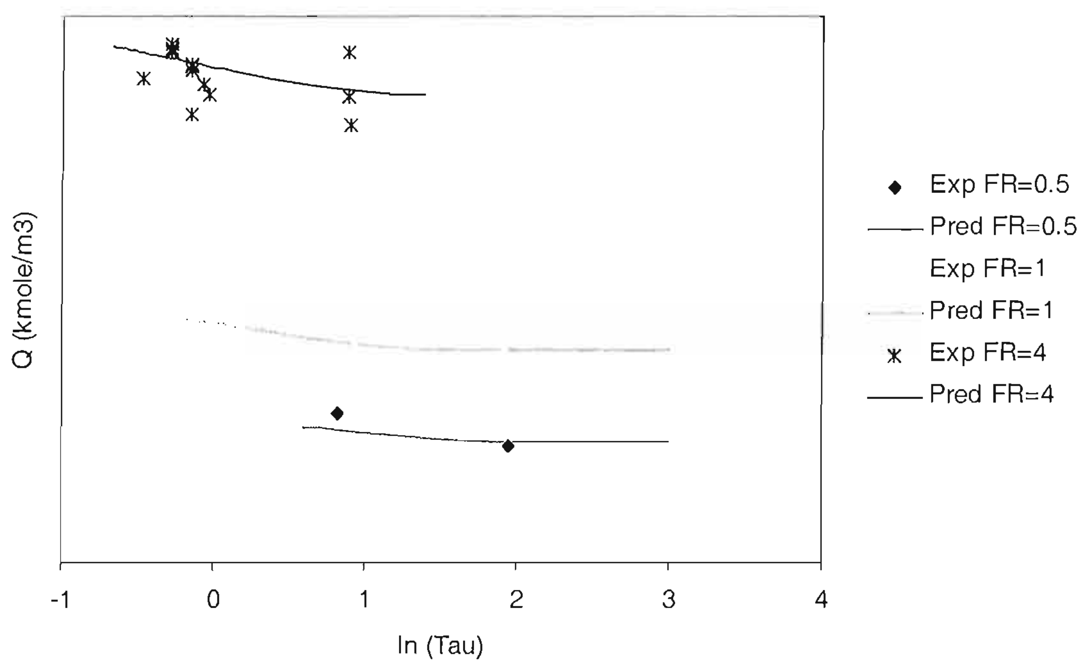

Figure B.4: gEST – Q

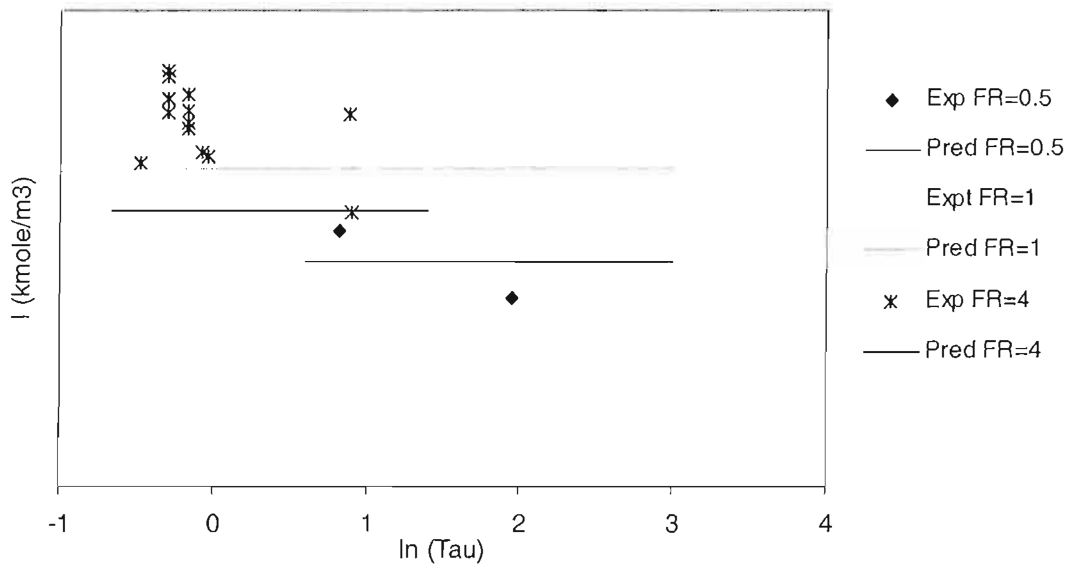

Figure B.5: Simusolv – I

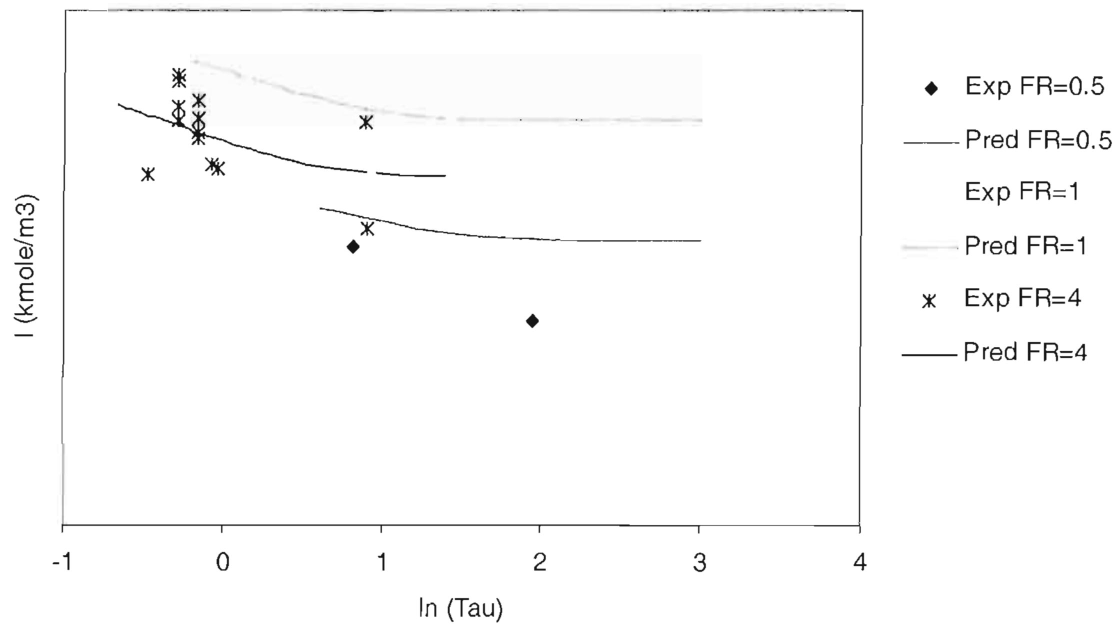

Figure B.6: gEST – I

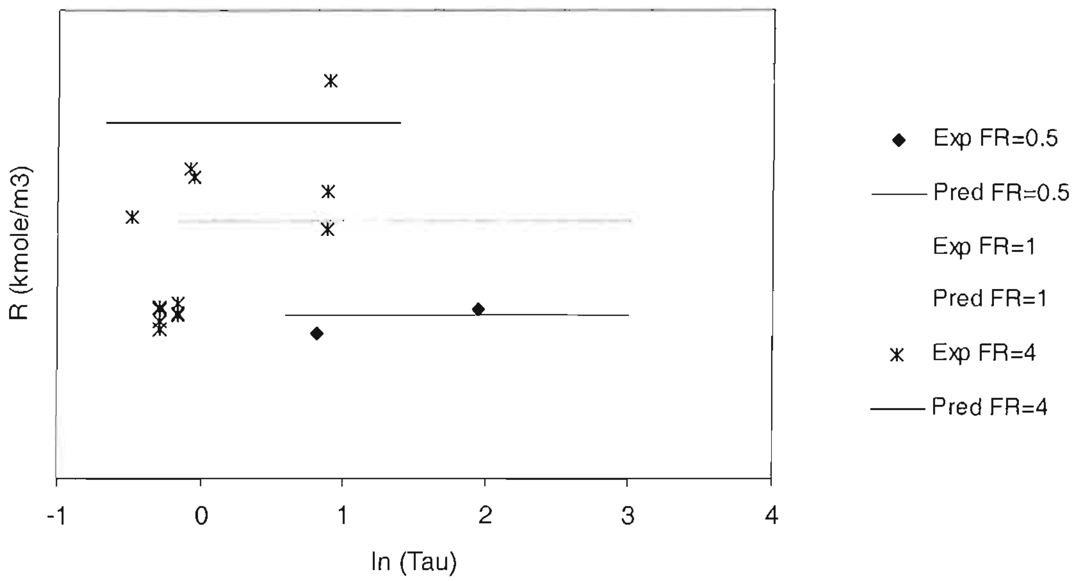

Figure B.7: Simusolv – R

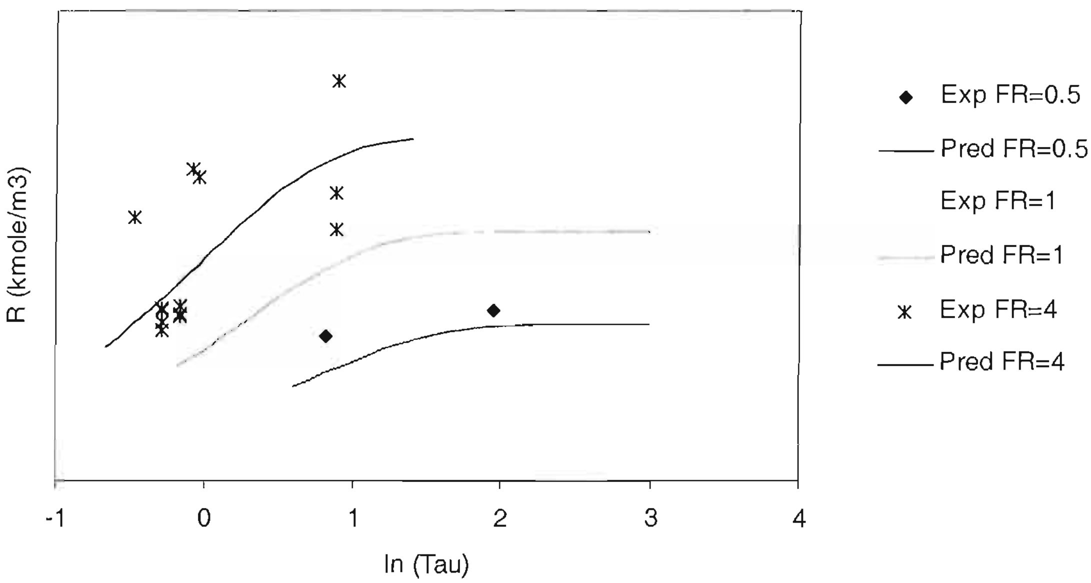

Figure B.8: gEST – R

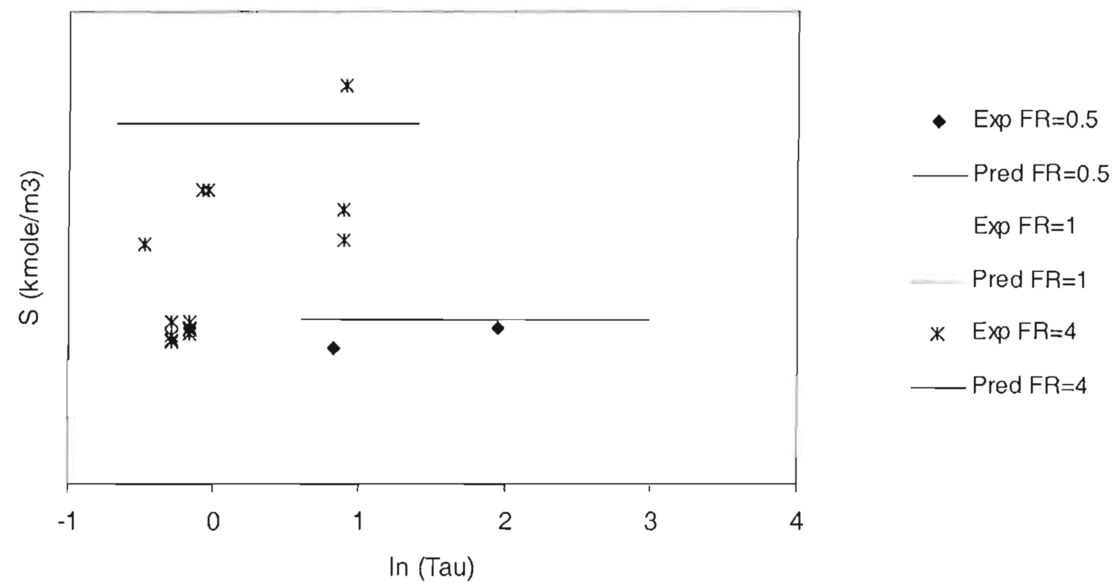

Figure B.9: Simusolv – S

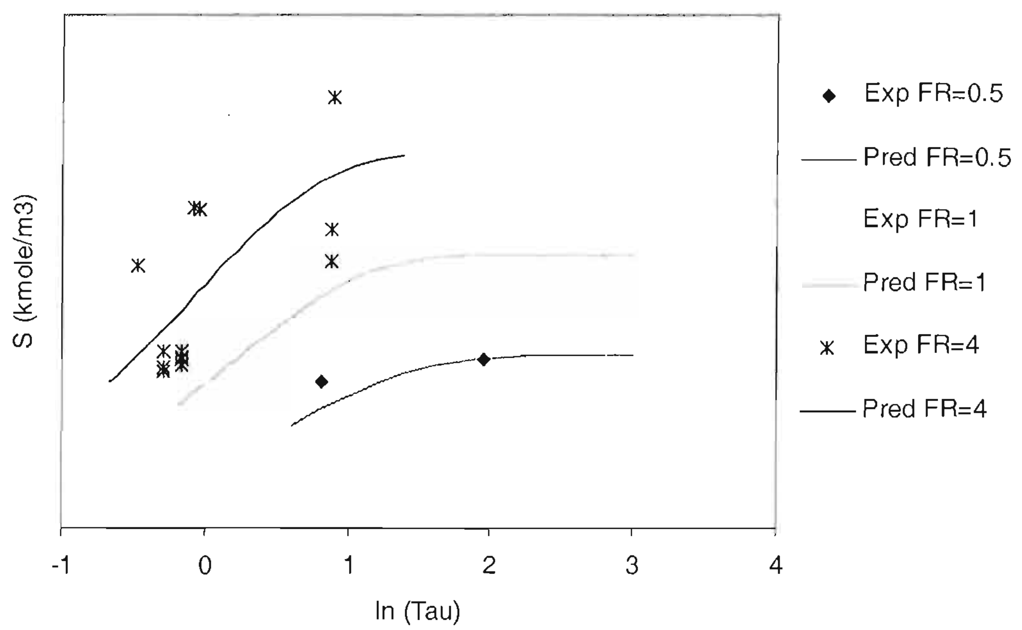

Figure B.10: gEST – S

Appendix C

Optimisation Sensitivity

The followings are the relative changes experienced by optimised variables and total cost if one of the constant in the total cost function is changed relatively to their reference values. It was found that the change in fixed cost constant (D1) did not affect the optimised variables but the total cost. It was changed by the same amount as the change in the constant. For further discussion is referred to Chapter 5.

C.1 The Sensitivity to Reactor Cost Constant (D2)

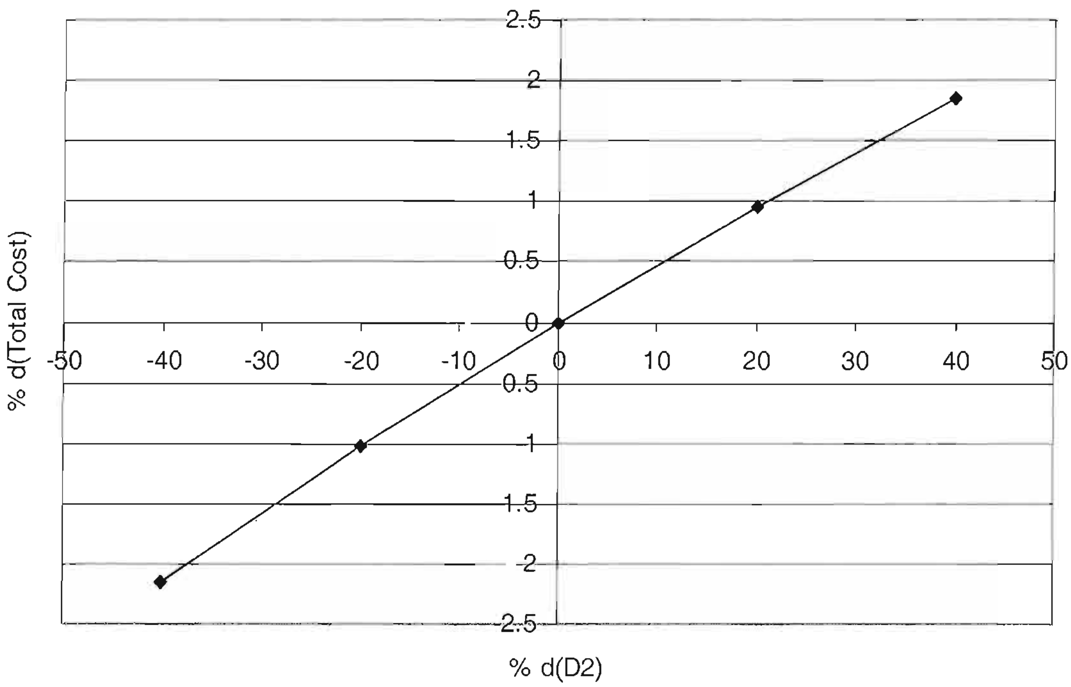

Figure C.1: Relative changes in the total cost when D2 was changed

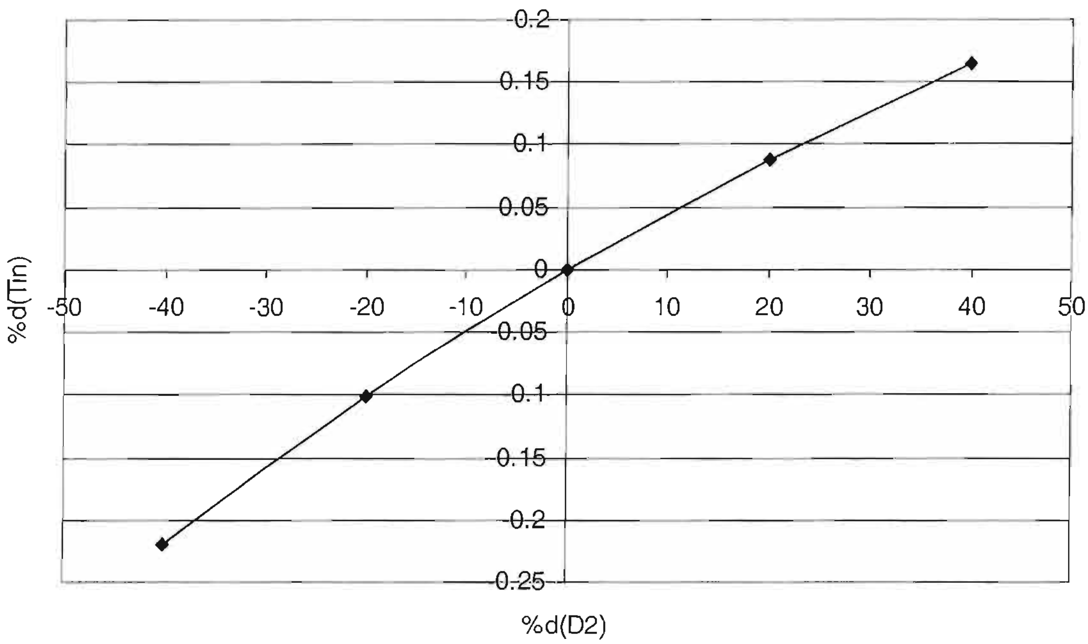

Figure C.2: Relative changes in optimised inlet temperature when D2 was changed

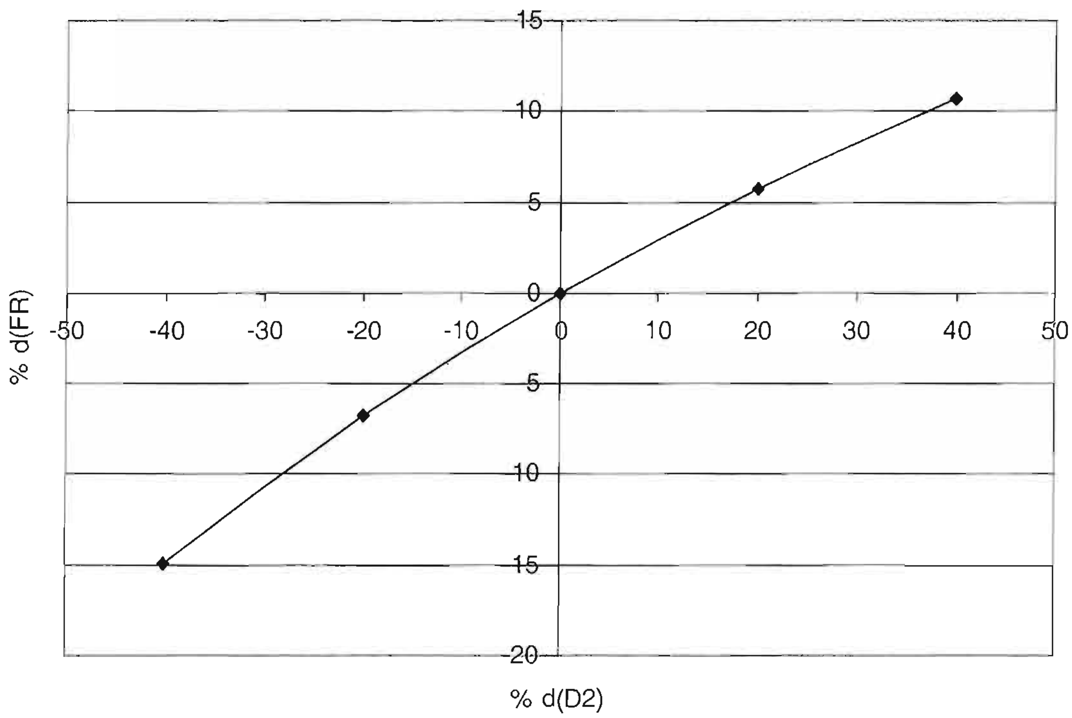

Figure C.3: Relative changes in the optimised molar feed ratio when D2 was changed

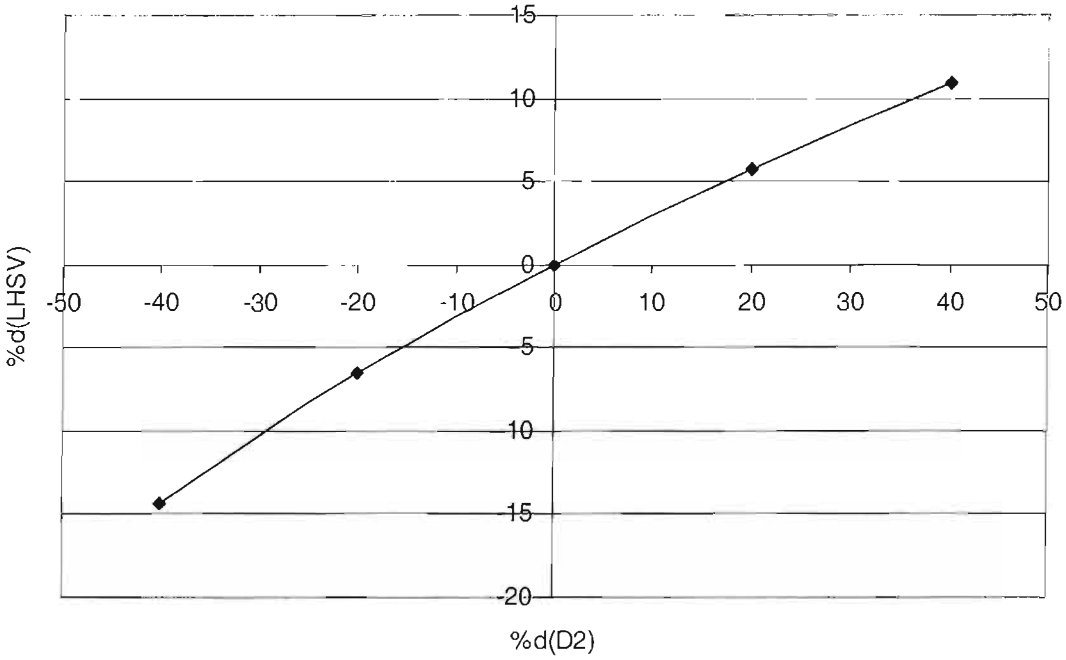

Figure C.4: Relative changes in the optimised liquid velocity when D2 was changed

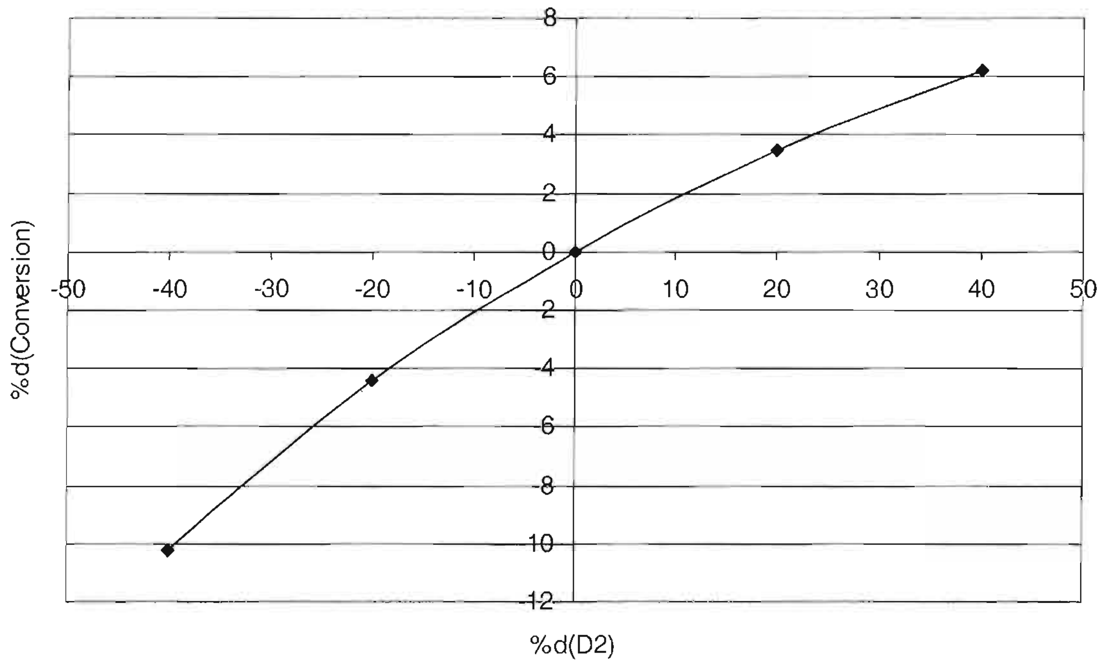

Figure C.5: Relative changes in the conversion when D2 was changed

C.2 The Sensitivity to Separation Cost Constant (D3)

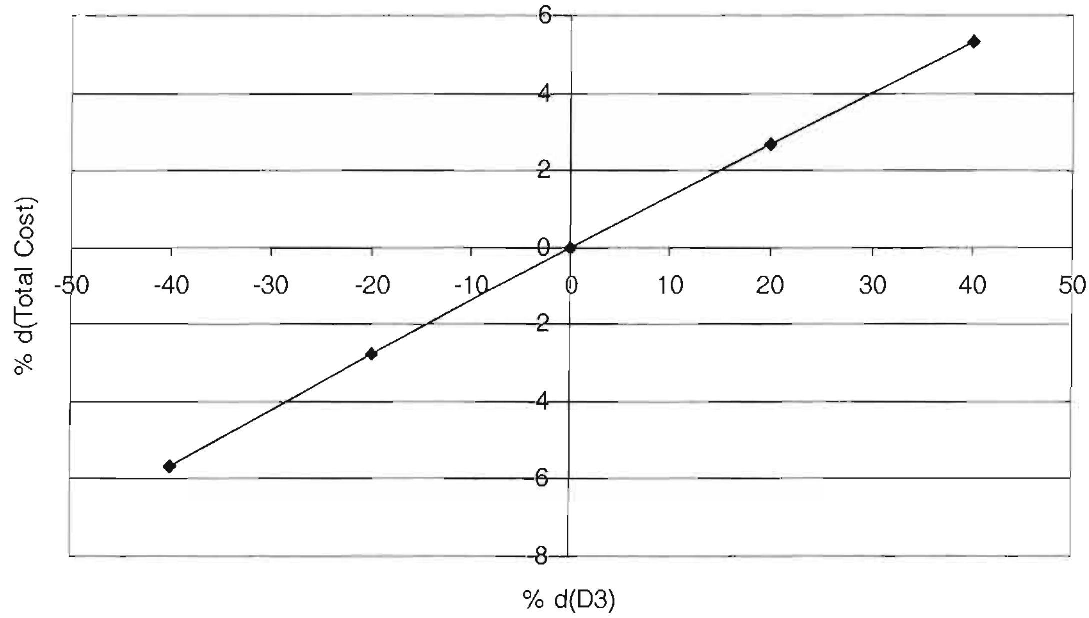

Figure C.6: Relative changes in the total cost when D3 was changed

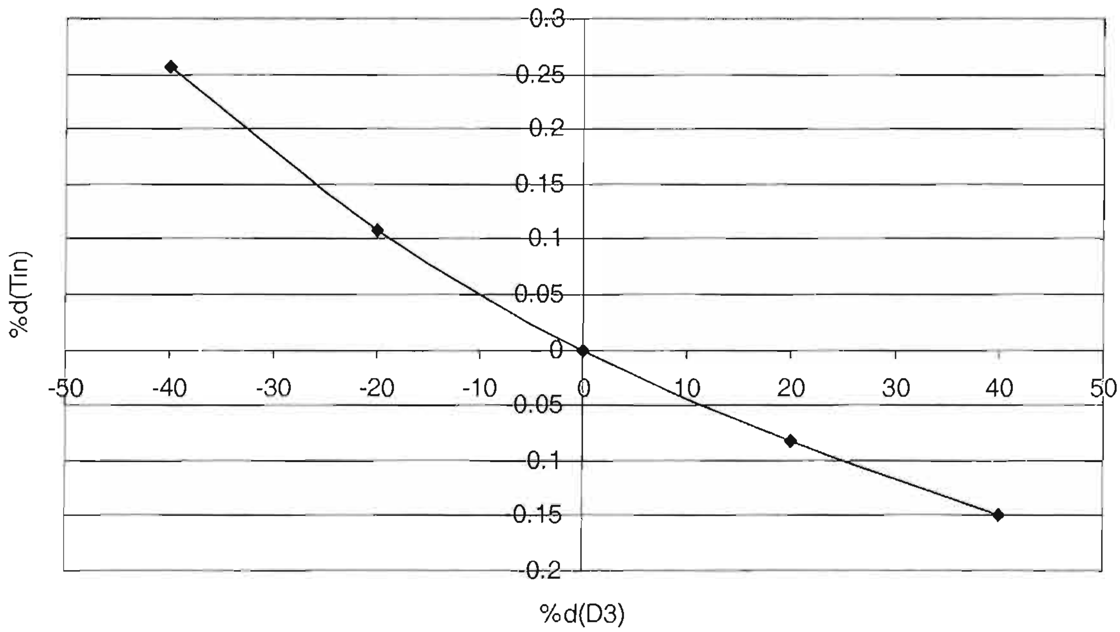

Figure C.7: Relative changes in optimised inlet temperature when D3 was changed

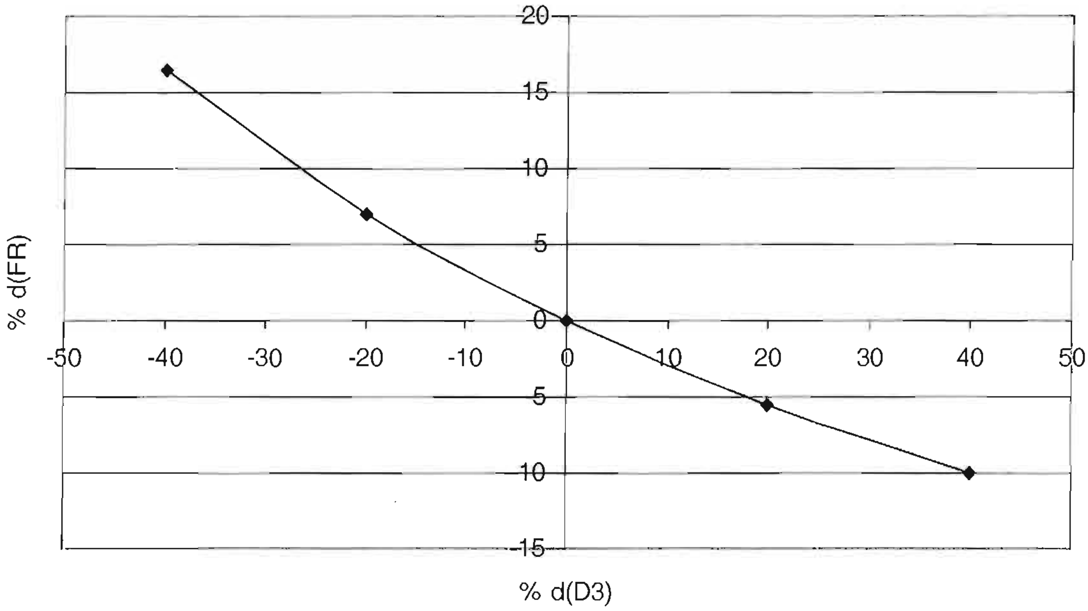

Figure C.8: Relative changes in the optimised inlet molar feed ratio when D3 was changed

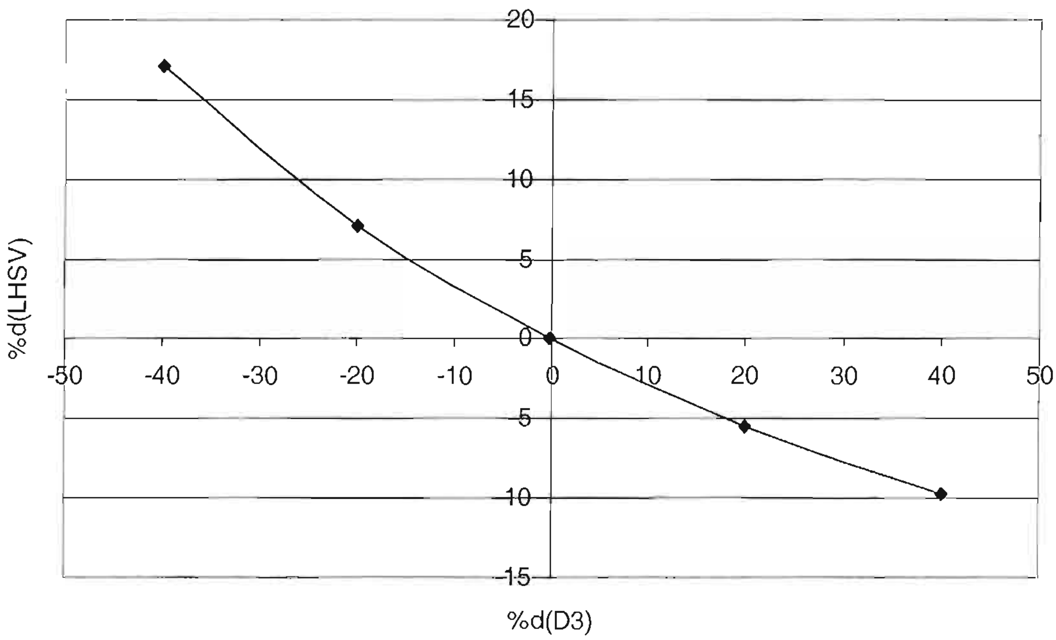

Figure C.9: Relative changes in the optimised liquid velocity when D3 was changed

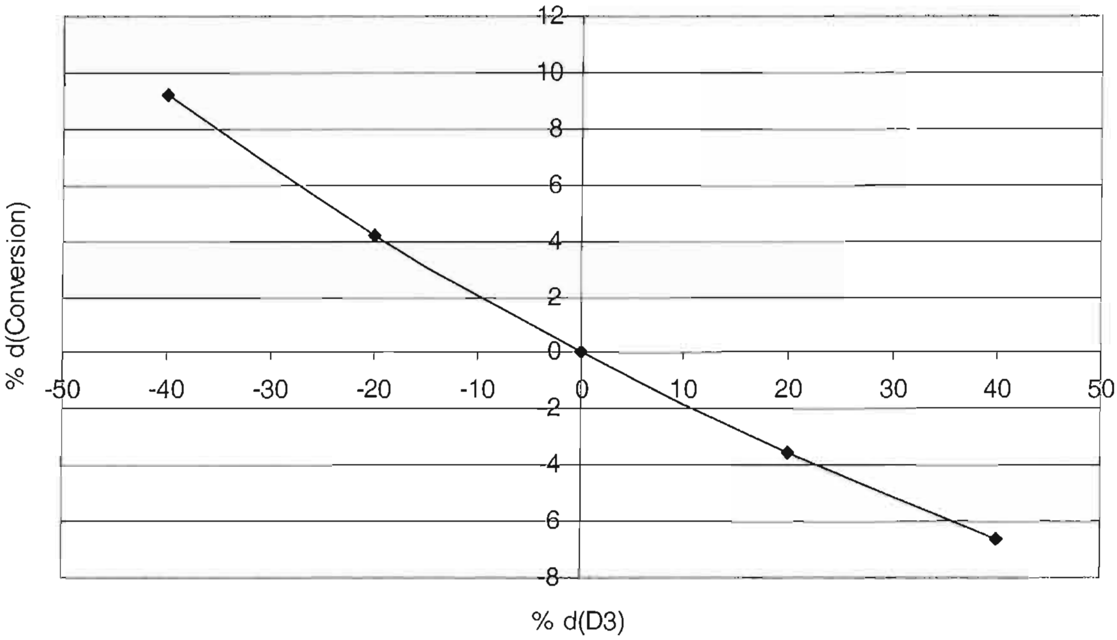

Figure C.10: Relative changes in the conversion when D3 was changed

Appendix D

Principal Component Analysis in Matlab

Matlab can be used for principal component analysis. F-matrices from different experiments can be combined in one m.file. Say that F^TWF matrix can be named as A-matrix.

Beck (1977) reported that parameters can be estimated if the sensitivity coefficients over the range of the observations are not linearly dependent. In order to find the estimate of the number of linearly independent rows or columns of matrix A ($=F^TWF$), the following Matlab function was applied:

$$R = rank(A) \tag{D.1}$$

If the rank of A matrix (the combined F-matrix) for this design was 8. All 8 parameters could probably be estimated.

The eigenvalues and eigenvectors of same matrix can be generated by applying the following Matlab function:

$$[v \quad d] = eig(A) \tag{D.2}$$

The eigenvectors were given in v-matrix and the eigenvalues were given in the diagonal matrix d.

Extremely small eigenvalues are assumed to be zero if the ratios of their values to the largest eigenvalues are below the tolerance value of 1.49E-08, which can be generated in Matlab in the following way:

$$Tolerance = sqrt(eps) \tag{D.3}$$

If there are 4 eigenvalues, which can be considered as zero, then the effective rank of A-matrix becomes 4 (= the number of the remaining eigenvalues). The dominant entries in the eigenvectors corresponding to those eigenvalues cannot be determined well from the design.

The eigenvalues can be represented graphically as in Figure D.1. The circles belong to the eigenvalues and the line belongs to the eigenvalues of a random matrix. If all parameters can be determined well, then the circles would have been above the random matrix line. The generated plots are semi-logarithmic plots of the eigenvalues generated by singular value decomposition of A-matrix and random matrix. Singular value decomposition is allowed when the matrix is nearly singular. The condition number of A-matrix, which is the ratio of the largest singular value of A-matrix to the smallest, can indicate the singularity of the matrix. The number can be obtained in Matlab in the following way:

$$c = cond(A) \tag{D.4}$$

If the number is large then the matrix is nearly singular, and singular value decomposition is allowed. The plots were generated by applying the following Matlab function (as applied on A-matrix):

$$semi\log y(svd(A),'o') \tag{D.5}$$

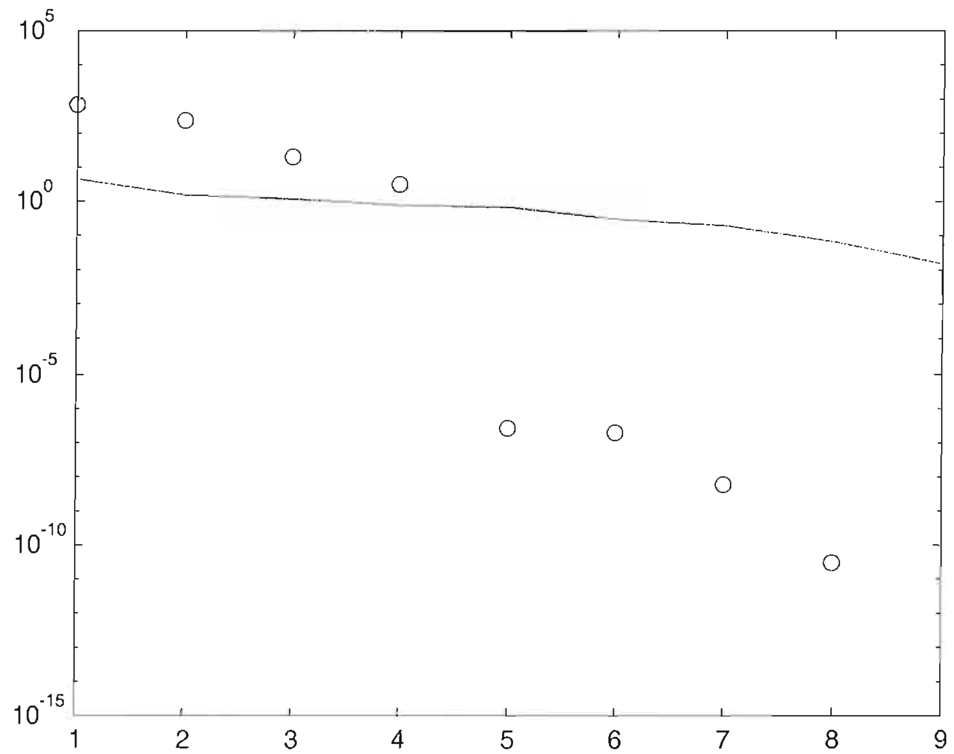

Figure D.1: An Example of a semi-logarithmic plot of the eigenvalues of A-matrix (o) and random matrix (-).

Appendix E

Ill Behaviour of Kinetic Parameters

Satterfield (1991) shows that if reaction rates are measured over only a fairly small range of temperature and the activation energy is determined from an Arrhenius plot or its equivalent, the value thus determined may be subjected to considerable error. Consider reaction at two temperatures T_1 and T_2 with corresponding measured reaction constants k_1 and k_2. Then

$$\ln\frac{k_2}{k_1} = \frac{-E_a}{R_g}\left(\frac{T_1 - T_2}{T_1 T_2}\right) \tag{E.1}$$

if $T_1 \approx T_2 \approx T$

$$\frac{dk_2}{k_2} - \frac{dk_1}{k_1} = \frac{\Delta T}{R_g T^2} dE \tag{E.2}$$

The maximum error in E occurs when $dk_2 = dk_1$. Hence

$$\partial E = \frac{2R_g T^2}{\Delta T}\frac{\partial k}{k} \tag{E.3}$$

He showed that if k is subjected to an error of ±20 percent, at T=673 K and for ΔT=30°C, the error in E_a may be as large as 50 kJ/mole. These strong correlations between k and E_a persist and can even hamper the optimisation steps during the parameter fitting process.

Appendix F

Estimating the Rate Constants From the Equilibrium Constants

It is mentioned in Section 5.3 that in the measurements at the equilibrium are informative. The statement can be explained better by considering the reaction in which A forms B and both forward and backward reactions are first order.

A↔B

The net rate of change of A is:

$$\frac{dC_A}{dt} = -kC_A + k'C_B \quad \text{(F.1)}$$

If there is no B present initially, at all times:

$$C_A + C_B = C_{A,0} \quad \text{(F.2)}$$

The solution of Equation I.1 is:

$$C_A = C_{A,0} \times \frac{k' + k\exp\{-(k+k')t\}}{k+k'} \quad \text{(F.3)}$$

At $t \rightarrow \infty$, the concentrations reach their equilibrium values, which are given by the equation as:

$$C_{A,\infty} = C_{A,0}\frac{k'}{k+k'} \quad \text{(F.4)}$$

$$C_{B,\infty} = C_{A,0} - C_A = C_{A,0}\frac{k}{k+k'} \quad \text{(F.5)}$$

It follows that the equilibrium constant of the reaction is:

$$K = \frac{C_{B,\infty}}{C_{A,\infty}} = \frac{k}{k'} \quad \text{(F.6)}$$

Equation F.6 relates the thermodynamic quantity, the equilibrium constant, to quantities relating to rates. The practical importance of Equation F.6 is that, if one of the rate constants can be measured, then the other may be obtained if the equilibrium constant is known. This is the method described in Section 5.3.