Modeling and Optimization of An Ammonia Reactor Using Multiple-Shooting Method

By

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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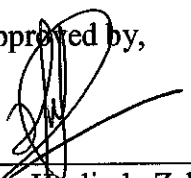
Approved by,



(Pn. Haslinda Zabiri)

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(Yong Chin Yew)

ABSTRACT

Optimization is concerned with selecting the best among the entire set by efficient quantitative methods. It is much very often required to solve dynamic optimization problems in the design and operation of complex chemical processes. The objective of this final year project is to model and find an optimal design for an ammonia reactor. For the past few years, ammonia has been widely used in the manufacturing of fertilizers, explosives and other chemical products. Hence modeling and optimizing ammonia synthesis has received a lot of attention among process industries. Apart from determining the optimal reactor length, the comparison of results obtained from different methods is presented.

The production of ammonia depends on temperature of feed gas at the top of the reactor (top temperature), the partial pressures of the reactants and the reactor length. The optimal design problem requires obtaining the optimal reactor length with maximum economic returns corresponding to various top temperatures.

This paper presents an alternative approach in solving the boundary value problem and at the same time determines the optimal solution. This method is called multiple-shooting. The software used for this modeling is MATLAB version 6.1. The ODE integration routine technique used is 'ode45' and the optimization routine of 'FMINCON' is selected. Apart from determining the optimal length of reactor, the comparison of results reported in earlier literature is analyzed and presented.

In this project, the values profiles of top temperature (T_f), reacting gas temperature (T_g) and mole flow rate of nitrogen per area catalyst (N_{N2}) at a top temperature of 694K were generated. From the results obtained, a top temperature of 694K yields an objective function value of \$5.0155 x 10^6 at an optimum reactor length of 6.6953m. These values agree with the latest literature work on the same case study that uses different method. By analyzing the results, multiple shooting method is found to be a robust, simple and fast computation technique for optimization problems in chemical processes.

ACKNOWLEGDEMENT

In order to complete the Final Year Research Project, many steps and procedures need to be taken and followed thoroughly. It would have been an intricate task to complete within the given time frame. It is the support and patience of the following individuals that made my project successful.

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NOMENCLATURE

z	Reactor length (m)
T_f	Feed gas temperature (K)
T_g	Reacting gas temperature (K)
N_{N2}	Mole flow rate of nitrogen per area catalyst (kgmol/m^2.h)
U	Overall heat transfer coefficient (kcal/m^2.h.K)
W	Total mass flow rate (kg/h)
C_{pf}	Heat capacity of feed gas (kcal/kg.K)
C_{pg}	Heat capacity of reacting gas (kcal/ kg.K)
S_1	Surface area of cooling tubes per unit length of reactor (m)
S_2	Cross sectional area of catalyst zone (m^2)
ΔH	Heat of reaction (kcal/ kg mole of N_2)
$-dN_{N2}/dx$	Reaction rate (kg moles of N_2/ h.m^3)
p_{N2}, p_{H2}, p_{NH3}	Partial pressure of N_2, H_2 and NH_3
k_1, k_2	Rate constants
f	Catalyst activity
F	Objective function ($/year)

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Ammonia is a major commodity chemical. Most of the world's ammonia production is used for fertilizers. It is also used in the manufacturing of explosives and other important chemicals and products. Therefore modeling and optimizing ammonia synthesis has received a lot of attention among the process industries. In modern ammonia plants, ammonia is produced from natural gas by the overall reaction below:

$$\text{Natural gas} + \text{water} + \text{air} \longrightarrow 3H_2 + N_2 + CO_2 \longrightarrow \text{ammonia } (NH_3) + CO_2$$

Ammonia is commercially manufactured by the Haber-Bosch process from natural gas using steam reforming process. There are several reaction stages and catalysts which are key to the economic operation of modern ammonia production plants.

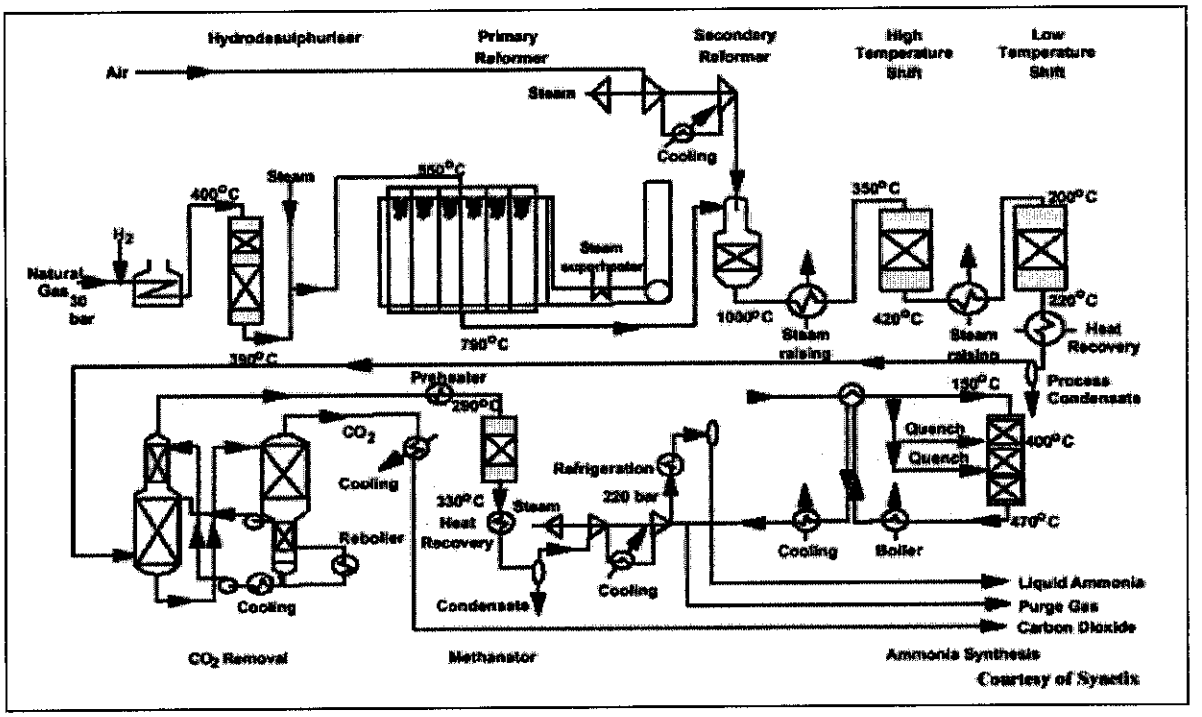


Figure 1.1: Overall Layout for Ammonia Synthesis [10]

The first stage is purification where impurities, mainly sulfur compounds, are removed from the gas stream. Steam reforming is performed in two stages. In the primary stage, the endothermic reactions take place at pressure around 30 bar and temperatures of about 750°C or higher. This is followed by an exothermic secondary reformer where air is added to the partially reformed gas stream. The carbon monoxide in the gas leaving the secondary reformer is converted to carbon dioxide in the shift reactors and then removed by scrubbing from the gas stream. Any residual carbon oxides are then converted back to methane by methanation before compression of the hydrogen and nitrogen to ammonia synthesis pressure. The final reaction stage is ammonia synthesis where the hydrogen and nitrogen combine to form ammonia. This reaction stage takes place at high pressure (100 ~ 350 bar) and is highly exothermic.

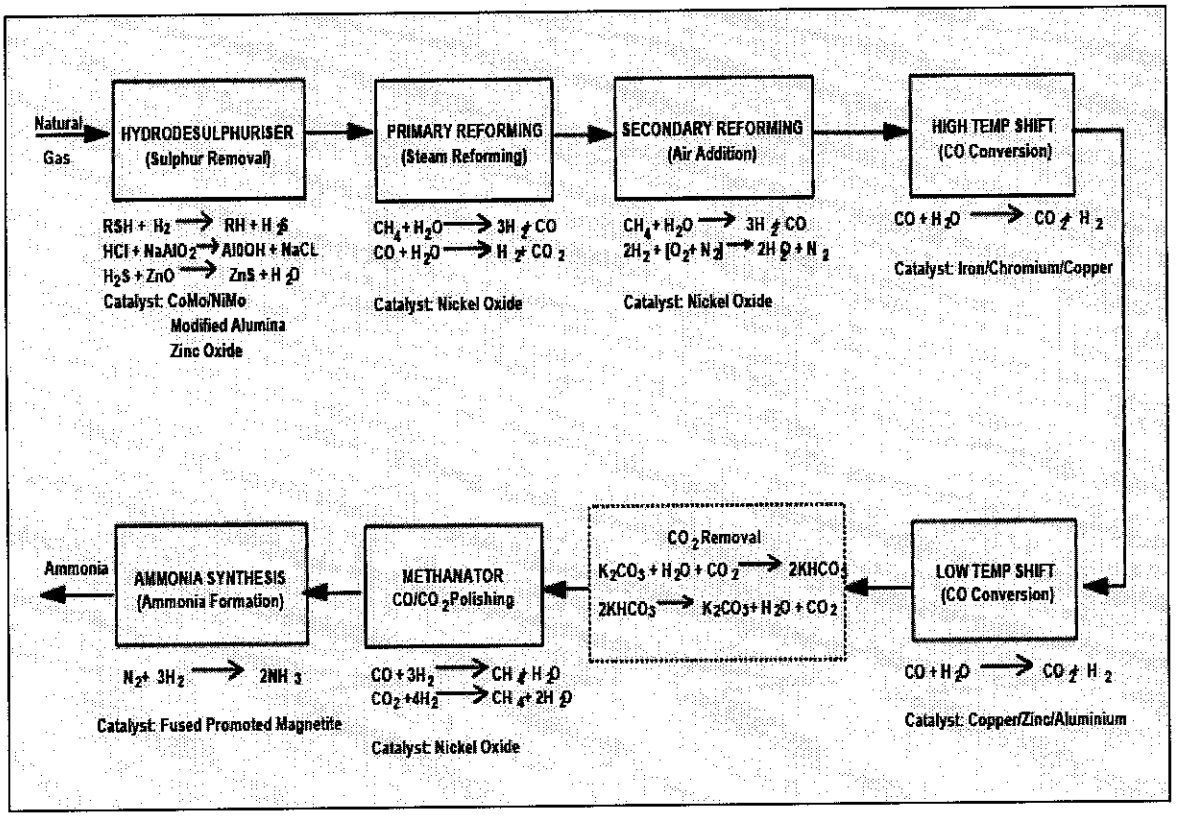


Figure 1.2: Chemistry of ammonia process [11]

1.2 Problem Statement

Ammonia synthesis using the Haber process is restricted by unfavourable position of the chemical equilibrium and by the relatively low activity of the promoted iron catalysts. Even at high pressure such as 30 MPa, not more than 20-25% of the synthesis gas is converted to ammonia per pass. The unreacted gas mixture is returned to the reactor. Since its development in 1913, industrial ammonia synthesis has always implemented a recycle process. Thus to produce 1 kg ammonia, 4-6 kg synthesis gas must be recycled through the reactor. To improve this, many studies were completed to find the optimal design of an ammonia reactor. According to *Babu, Angira and Nilekar (2004)*, the yield of ammonia depends on the temperature of the feed gas at the top of the reactor i.e. top temperature, the partial pressures of the reactants (nitrogen and hydrogen) and the reactor length. Thousands of combinations of feed gas temperature, nitrogen mass flow rate, reacting gas temperature and reactor length are possible. The optimal design problem requires obtaining the optimal reactor length with maximum economic returns corresponding to the various top temperatures.

1.3 Objectives and Scope of Study

The main objective of this final year project is to model and find an optimal design for an ammonia reactor and compare the results with previous studies so far. The basic scopes of study are modeling and optimization. From this project also, the profiles for T_f, T_g and N_{N2} at top temperature of 694K is determined. The results of the optimum temperature of the ammonia reactor, the reactor length and also the optimum objective function value will be compared to studies. The following assumptions were taken from *Edgar, Himmelblau and Lasdon* (2001) to simplify the development of ammonia reactor model:

- The rate expression is valid
- Longitudinal heat and mass transfer can be ignored
- The gas temperature in the catalytic zone is also the catalyst particle temperature
- The heat capacities of the reacting gas and feed gas remains constant
- The catalytic activity is uniform along the reactor and equal to unity
- The pressure drop across the reactor is negligible compared with the total pressure in the system.

In the optimization problem, there are four variables: the reactor length is independent variable whilst mass flow rate of nitrogen, temperature of feed gas and temperature of reaction gas are the dependent variables. There are three equality constraints and only one degree of freedom. The objective will be to maximize the economic return subject to the three equality constraints. Numerous works had been done in this field. The latest study in the optimal design was by *Babu, Angira and Nilekar (2004)* using a method called differential evolution and the result produced was more accurate. The final year project is to propose a new method in solving the design of the reactor which is multiple-shooting. The final findings will be compared to previous studies.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Haber Process

At the end of the 19th century, Chilean nitrates, were the major source of nitrates at the time for the Germans. It was clear, that this source would not be able to meet future demands. It was also realised that in the event of a war, any nation cut off from the Chilean supply, would not be able to make adequate amounts of munitions (military weapons). Germany (Haber's native country) was in particular dependent on this source of nitrogen compounds, to manufacture explosives. Following the allied block of the South American ports, this supply was well and truly cut off. An alternative method of producing nitrates was needed. Fritz Haber and Carl Bosch promptly developed this process in 1909 and had it patented in 1910. In World War 1, had Haber not invented the process, Germany would have been forced to surrender years earlier than it did. As a result the Haber-Bosch process indirectly, cost thousands of people their lives. Soon, the Germans adopted this process and started producing ammonia at industrial scale.

The production of ammonia is achieved by the direct combination of hydrogen and nitrogen, over an iron or aluminium catalyst. Hydrogen is obtained from the decomposition of methane by heating. Nitrogen is obtained from the distillation of liquefied air. It was the first chemical process to use high-pressure conditions. The reaction is shown below:

$$3\ H_2\ (g) + N2\ (g) \rightleftharpoons 2\ NH_3\ (g) \qquad \Delta H = -92\ KJ/mol \qquad \text{(Eq. 1)}$$

The process is highly exothermic with a ΔH value of 92.2 kJ per mole. As a result a compromise has to be made with regards to what temperature is used. A high temperature favours a higher rate of reaction and so equilibrium is reached more quickly; a high temperature however favours the backward reaction since the process is exothermic (Le-Chateliers principal states that any changes made to a reaction mixture will be

compensated for by the reaction). Therefore, since the process is exothermic, increasing the temperature promotes the backward reaction since this takes in heat from the surroundings, hence lowering the temperature. As a result, a compromise is made between the two. This compromised temperature is between 673 ~ 923 Kelvin.

The catalyst provides an alternative pathway for the reaction to occur, which has lower activation energy. This means that a lower temperature can be used without compensating the rate too much. Carl Bosch found that a mixture of Fe_2O_3 and Fe_3O_4 catalyses the reaction best over the temperature range 650 ~ 950 Kelvin.

Also due to Le-Chateliers principle a high pressure is used. The mol ratio of gases is 4:2, therefore if a high pressure is used the forward reaction is promoted, since at a higher pressure the products hold a smaller volume, hence decreasing the pressure. The pressure used is 200 - 400 atmospheres, which is quite high.

2.2 Process flow in Ammonia reactor

In this process, the inlet synthesis gas flows through an annular space and into an internally located heat exchanger that preheats the gas to synthesis temperatures. Quenching the bed effluents with cold synthesis gas controls inlet bed temperature. Most of conversion occurs in the first bed which has the highest driving force to the equilibrium. A bypass is provided around the intercooler for temperature control.

2.3 Ammonia Converter:

The ammonia converter (reactor) operates at high pressure ranges 100 - 300 bars. Its catalyst bed is divided into 3 layers. Quench gas is supplied in between beds and internal heat exchanger is provided to maintain the temperature at optimum level. The Synthesis Gas is fed to Converter at 150°C. The monitoring parameters are temperature profile and flow rate in ammonia converter.

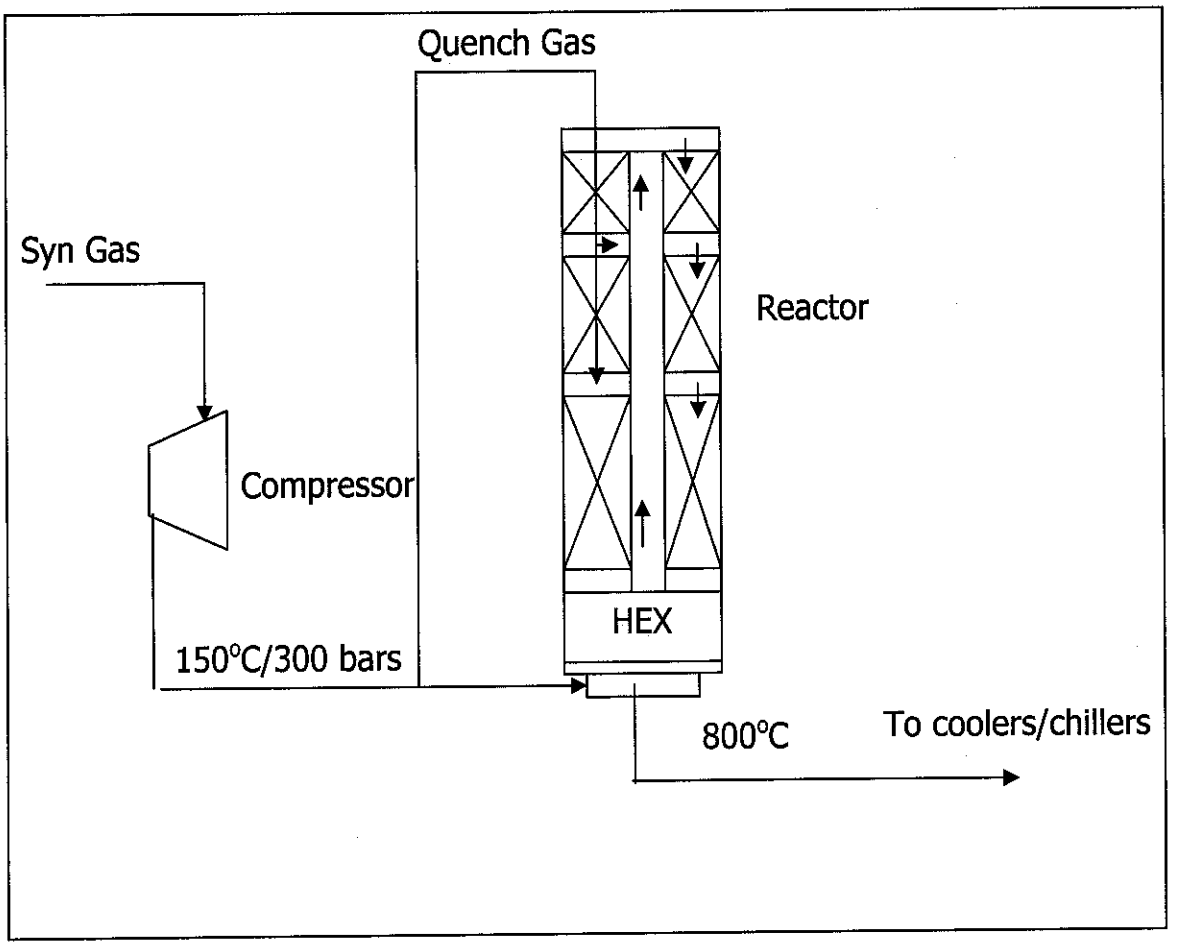


Figure 2.1: Process flow in Ammonia Converter

2.4 Previous Studies

In 1970, Murase et al. applied the Pontryagin's maximum principle to compute the optimum temperature trajectory along the reactor length. Although their formulation was correct, the stated objective function was wrong. This error was identified by Edgar and Himmelblau (2001) and used Lasdon's generalized reduced-gradient method to arrive at an optimal reactor length corresponding to a particular reactor top temperature of 694K. However a term mentioned in Murase's formulation was ignored, pertaining to te cost of ammonia already present in the feed gas, in the objective function. Also the expression of the partial pressure of nitrogen, hydrogen and ammonia used to simulate the temperature and flow rate profiles across the length of the reactor-were not correct. In 1990, Vasantharajan et al. obtained the optimal combination of the feed gas temperature at the top of the reactor and reactor length using a non-linear programming technique. Only a few internal points along the length of the reactor were selected for the simulation of the

reactor profiles. This does not appear to do justice to the not-so smooth reactor profiles and leaves behind an uncertainty of the globality of the obtained optimal solution.

A study done by *Upreti and Deb* (1996) used genetic algorithms (GA) to determine an optimal design for an ammonia reactor. This method is a search and optimization technique based on principles of natural genetics. Although there exist at least a couple of other studies on the optimal design of ammonia synthesis reactor, they have ignore some terms in the formulation of the objective function, for which the reported optimal solution does not match with the solution obtained using an enumerative search technique (*Upreti and Deb*, 1996). Using GA, the optimal reactor length was found to be at 5.33m and the typical economic return from the reactor operation with a top temperature of 694K comes out to be \$4.23 x 10^6 / year.

On another latter study, *Babu, Angira & Nilekar (2004)* published a paper which presents the application of two methods; i.e. Runge-Kutta variable step size and Gear's method in combination with Differential Evolution and verify the contradictory results reported using simple GA in the earlier literature. The results obtained indicate that the profiles of temperature and flow rate are smooth. At the top temperature of 694K, the reactor length was found to be 6.79m and gave the optimum objective function value of \$4.84 x 10^6/ year.

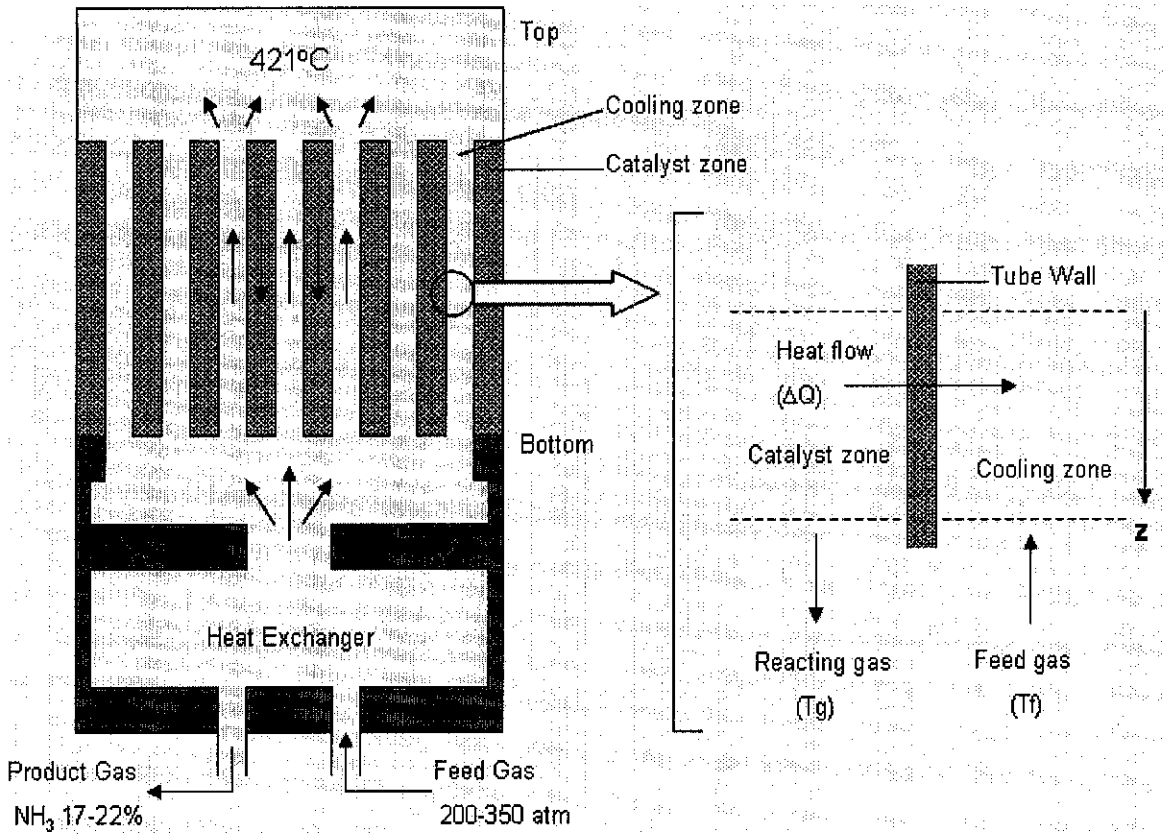


Figure 2.2: Ammonia synthesis reactor. The shaded blue coloured area contains the catalyst [Adapted from Murase et al., "Optimal Thermal Design of an Auto-thermal Ammonia Synthesis Reactor," Ind Eng Chem. Process Des Dev 9:504 (1970). Copyright, American Chemical Society.]

2.4 Problem Formulation

The yield of ammonia depends on the temperature of feed gas at the top of the reactor (top temperature), the partial pressure of the reactants and the reactor length. The optimal design problem is to obtain the optimal reactor length which yields the maximum economic returns from the reactor operation corresponding to various top temperatures.

Objective Function

$$F = f(z, N_{N2}, T_g, T_f) = 1.33563\times10^{7} - 1.70843\times10^{4} N_{N2} + 704.09(T_g - T_0) - 699.27(T_f - T_0) - [3.45663\times10^{7} + 1.98365\times10^{9} z]^{0.5} \quad \text{(Eq. 2)}$$

The objective function, F depends on four variables: the reactor length (z), mole flow rate of nitrogen per area catalyst (N_{N2}), the top temperature (T_g) and the feed gas temperature (T_f). From the system model, there are three differential equations and four variables, making the degree of freedom equal to one. By specifying the length of reactor, the remaining variable can be calculated using the system model and the pass these variables to the optimization routine as shown below;

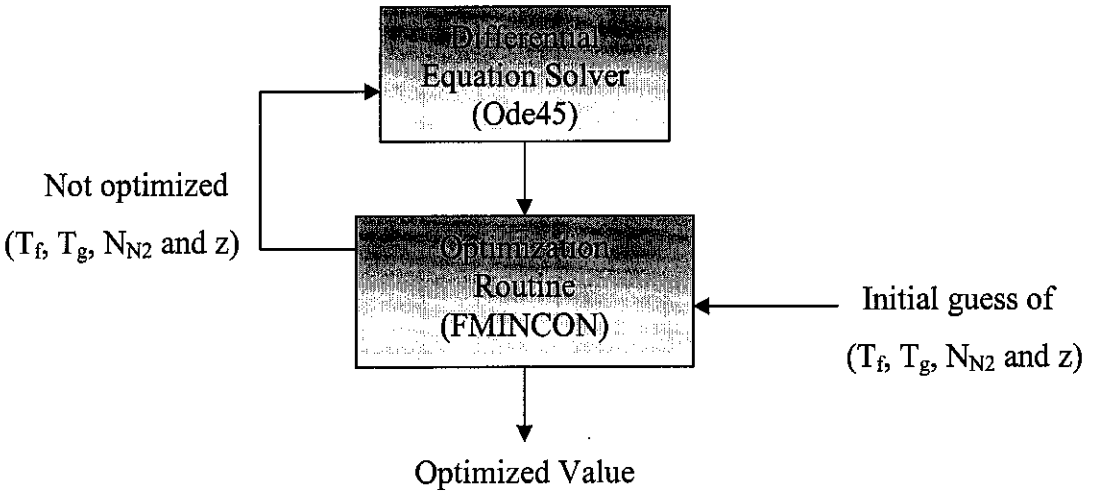


Figure 2.3: Computation procedure

Energy Balance Equations

There are three energy balances that need to be solved simultaneously to obtain the value of three variables: T_f, T_g and N_{N2}.

Energy Balance, Feed Gas

$$\frac{dT_f}{dz} = \frac{US_1}{WC_{pf}}(T_g - T_f) \qquad \text{(Eq. 3)}$$

Energy Balance, Reacting Gas

$$\frac{dT_g}{dz} = \frac{US_1}{WC_{pf}}(T_g - T_f) + \frac{(-\Delta H)S_2}{WC_{pg}}\left(\frac{-dN_{N2}}{dz}\right) \qquad \text{(Eq. 4)}$$

Mass Balance, N_2

$$\frac{dN_{N2}}{dz} = -f\left(k_1 \frac{p_{N2}p_{H1}^{1.5}}{p_{NH_3}} - k_2 \frac{p_{NH_3}}{p_{H_2}^{1.5}}\right) \qquad \text{(Eq. 5)}$$

where

$$k_1 = 1.78954 \times 10^4 \exp\left(\frac{-20800}{RT_g}\right)$$

$$k_2 = 2.5714 \times 10^{16} \exp\left(\frac{-47400}{RT_g}\right)$$

For the reaction, in terms of N_{N2}, the partial pressures are;

$$p_{N2} = \frac{286N_{N_2}}{2.598N_{N_2} + 2N_{N_2}}$$

$$p_{H_2} = 3p_{N_2} \qquad \text{(Eq. 6)}$$

$$p_{NH_3} = \frac{286(2.23N_{N_{20}} - 2N_{N_2})}{2.598N_{N_{20}} + 2N_{N_2}}$$

Boundary conditions

$$T_f(z=0) = T_0; \qquad T_g(z=0) = T_f; \qquad N_{N_2}(z=0) = 701.2\frac{kmol}{m^2 h}$$

Inequality constraints

The upper and lower bounds of the design variables are:

$$0 \le N_{N_2} \le 3220; \qquad 400 \le T_f \le 3220; \qquad z \ge 0$$

The reacting gas temperature (T_g) depends on the nitrogen mass flow rate (N_{N2}), feed gas temperature (T_f) and reactor length (z). Hence no implication on any boundaries of T_g required. All the initial guesses for all variables will be specified in the model and optimal solution is produced.

CHAPTER 3
METHODOLOGY

3.1 Procedure Identification

The project can be divided into two major parts: research and modeling. Preliminary research has been conducted to learn about ammonia synthesis used currently in the industry and also to find out what are the latest studies conducted so far on optimizing an ammonia reactor. The software used for modeling is MATLAB Version 6.1 and the method used to solve the objective function is Multiple-Shooting Method.

3.2 Tool – MATLAB

MATLAB is a high performance language for technical computing. It integrates computation, visualization and programming in a user-friendly environment where problems and solutions are expressed in familiar mathematical notation. Typical uses include:

a) Math and computation
b) Algorithm development
c) Modeling, simulation and prototyping
d) Data analysis, exploration and visualization
e) Research in numerical analysis and scientific computing.
f) Application development, including graphical user friendly interface building

MATLAB is an interactive system whose basic data element is an array that does not require dimensioning. Many technical computing problems can be solved using MATLAB, especially those with matrix and vector formulations in a fraction of the time. It would take a lot of time to write a program in a scalar non-interactive language such as C or FOTRAN compared to the simple language of MATLAB.

MATLAB which stands for matrix laboratory was originally written to provide easy access to matrix software developed by the LINPACK and EISPACK projects.

MATLAB has evolved over a period of years with input from many users. It has become a standard tool for students to use in introduction and advanced courses in mathematics, engineering and science. It is also the tool of choice for high-productivity research, development and analysis in many industries.

3.2.1 Ode Solver – Ode45

Ode45 is a function to solve initial value problems for ordinary differential equations (ODEs). This function is more suitable for non-stiff type of problem. It also has medium level of accuracy.

Syntax

[L, Y] = ode45 (*odefun*, *tspan*, y0, *options*)

where L is dependent variable and T is independent variable.

Arguments

i) *odefun* A function that evaluates the right-hand side of the differential equations. It solves systems of equations in the form y' = f(t,y) or problems that involve a mass matrix, M(t,y) y' = f(t,y).

ii) *tspan* A vector specifying the interval of integration, $[t_0,t_f]$.

iii) y0 Initial value of y.

iii) *options* Optional integration argument created using the odeset function.

Algorithm – Ode45 is based on an explicit Runge-Kutta formula. It is a one-step solver – In computing $y(t_n)$, it needs only the solution at the intermediately preceding time point, $y(t_{n-1})$.

3.2.2 Optimization Routine – FMINCON

FMINCON finds a constrained minimum of a scalar function of several variables starting at an initial estimate. This is generally referred to as constrained nonlinear optimization or nonlinear programming.

$$\min_{x} f(x) \quad \text{subjected to} \quad \begin{aligned} & c(x) \le 0 \\ & ceq(x) = 0 \\ & A.x \le b \\ & Aeq.x = beq \\ & lb \le x \le ub \end{aligned}$$

Where x, b, beq, lb and ub are vectors, A and Aeq are matrices, c(x) and ceq(x) are functions that return vectors, and f(x) is a function that returns a scalar. f(x), c(x) and ceq(x) can be nonlinear functions.

Syntax

x = fmincon (*fun*, x0, A, b, Aeq, beq, lb, ub, *cons*, options)

Arguments

i) *fun* The function to be minimized. It accepts a vector x and returns a scalar f, the objective function evaluated at x.

ii) *cons* The function that computes the nonlinear inequality constraints c(x) ≤0 and the nonlinear equality constraints ceq(x) = 0. This function accepts a vector x and returns two vectors c and ceq. The vector c contains the nonlinear inequalities evaluated at x, and ceq contains the nonlinear equalities evaluated at x.

iii) *options* Provide parameters which are only relevant when using large-scale algorithm or medium-scale algorithm.

Algorithm – fmincon uses a sequential quadratic programming (SQP) method. In this method, the function solves a quadratic programming (QP) sub-problem at each iteration. An estimate of the Hessian of the Lagrangian is updated at each iteration using the BFGS formula [7], [8].

3.3 Multiple-Shooting Method

In a sequential method, only the control variables are discretized; i.e. known as control variable parameterization methods. Given initial conditions and a set of control parameters, the process model is integrated with a Differential Algebraic Equation (DAE)

solver at each iteration. The control variables are represented as piecewise polynomials and optimization is performed with respect to the polynomial coefficients. The sequential approach is a feasible path method; in every iteration the DAE system is solved. However, this procedure is only robust when the system contains stable modes. Otherwise, finding a feasible solution for a given set of control parameters maybe difficult.

The simultaneous approach is based on complete discretization of the state and control variables leading to a large-scale non-linear programming (NLP) problem. This method directly couples the solution of the DAE system with the optimization problem; the DAE system is solved only once, at the optimal point, and therefore can avoid intermediate solutions that may not exist or may require excessive computational effort. They have advantages for problems with path constraints and with instabilities that occur for a range of inputs. On the other hand, disadvantages include the question of where to place the finite elements in order to maintain accuracy of the discretized DAE model and to determine the optimal breakpoint location in the optimal control profile, as well as the need to solve large NLP.

Multiple-shooting serves as a bridge between sequential approaches and simultaneous approaches. This technique has the same underlying approach as single shooting, but the integration is done over many intervals where in this case refers to the length of the ammonia reactor. The TWO main steps in carrying out this technique are;

i) control representation/ discretization

ii) state discretization by multiple-shooting

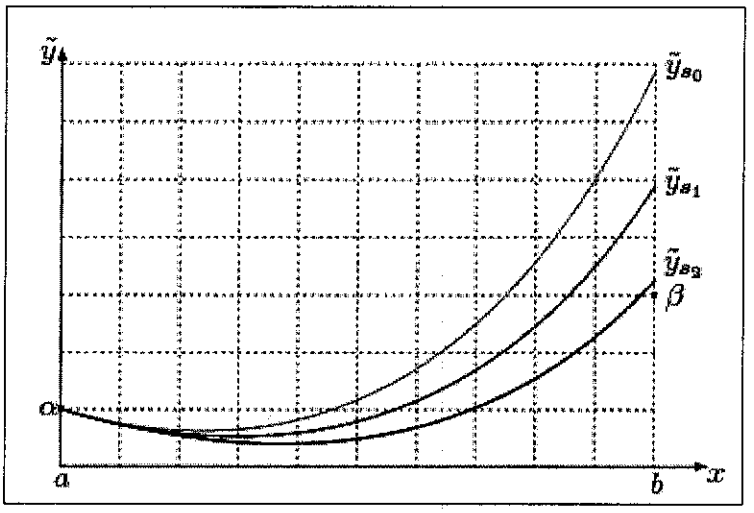


Figure 3.1: Illustration of Single Shooting Method

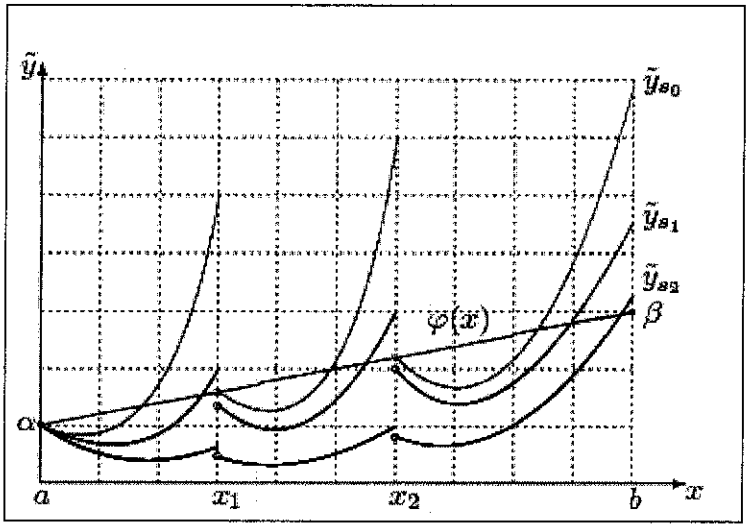


Figure 3.2: Illustration of Multiple-Shooting Method

Direct single shooting method represents a pure sequential approach whereas multiple shooting is considered as a hybrid approach because the model equations are solved "exactly" only on intervals during the solution iterations. Therefore direct single shooting method only requires two boundary initial value guesses (i.e. a and b) whereas multiple shooting approach requires initial guesses for all the node values (i.e. x_1, x_2, ...). The disadvantage of single shooting method is there can be serious problems with the

accuracy. The problems occur when making the correction to the calculated vector. This vector is usually corrected using a modified Newton's Method and in practice, the system must be linearized to use this method. If error is large, then convergence can be quite slow. This drawback can be fixed by implementing multiple shooting method.

For multiple-shooting, the length of the reactor is partitioned into smaller length elements and the DAE models are integrated separately in each element. Equality constraints are added to the nonlinear program in order to link the elements and ensure that the states are continuous across each element. Inequality constraints for states and controls can be imposed directly at the grid points.

Characteristics of Multiple Shooting;

i) Multiple shooting has been shown to be considerably more stable and efficient than single shooting for the solution of optimization boundary value problems
ii) The Nonlinear Programming problem to be solved is typically of smaller size than for simultaneous strategies based on collocation (this is true in case of stiff dynamic models)
iii) Initial guesses for the whole state trajectory are needed
iv) The initial value problem (IVP) solutions and derivatives computations are decoupled on different multiple shooting intervals
v) Continuity of the system trajectory is only fulfilled after successful termination of the sequential quadratic programming (SQP) solution procedure (up to solution tolerance). At the premature stops, both continuity conditions and state and end point constraints may be equally violated.

3.4 MATLAB Programming Codes

The three differential equations of material and energy balances need to be solved simultaneously in order to determine the parameters at each reactor length. For this project, four MATLAB files were developed to solve and optimize the three differential equations. The programs are for two intervals are shown as below;

a) ode3.m – To declare the variables, parameters and problems formulated in the optimization programs. This m-file need to be created first so that the subsequent m-files can run.

```
function dy = ode1(L,z)

y10 = 701.2;      % initial amount of N2
                                        % z (1) = NN2 (Nitrogen mass flow rate)
                                        % z (2) = Tf (Feed gas temp)
                                        % z (3) = Tg (Reacting gas temp)
deno = 2.598*y10 + 2*z(1);

% Equality constraints
p1 = 286*z(1)/deno;
p2 = 3*p1;
p3 = 286*(2.23*y10 - 2*z (1))/deno;

R = 1.987;                              % Gas constant in kcal/(kmol.K)
K1 = 1.78954e4*exp(-20.8e3/R/z(3));     % Specific reaction rate
K2 = 2.5714e16*exp(-47.4e3/R/z(3));     % Specific reaction rate

U = 500;                                %overall Heat Transfer coefficient in kcal/(h.m^2.K)
dH = -26e3;                             % heat of reaction in kcal/kmol N2
S1 = 10;                                % surface area of catalyst tubes / unit length of reactor in m
S2 = 0.78;                              % cross-sectional area of catalyst zone in m^2
W = 2.64e4;                             %total mass flow rate in kg/h
Cpg = 0.719;                            % heat capacity of reacting gas in kcal.(kg.K)
Cpf = 0.707;                            % heat capacity of feed gas in kcal/(kg.K)
f= 1;                                   %catalyst activity

sub = K1*p1*(p2^1.5)/p3 - K2*p3/(p2^1.5);

dy = ones(3,1);                         % a column vector

% Energy balance equation

dy(1) = -f*sub;
dy(2) = -U*S1/(W*Cpf)*(z(3)-z(2));
dy(3) = -U*S1/(W*Cpg)*(z(3)-z(2)) + (-dH)*S2/(W*Cpg)*(-dy(1));
```

b) Objfun.m – To define the objective function which is a function of T_f, T_g ,N_{N2} and length of reactor, z. The objective function value is equals to the profit margin.

```
function obj = objfun(y)

% f(z,NN2,Tf,Tg) = 1.33563 x 10^7 - 1.70843 x 10^4 NN2 + 704.09(Tg - T0) - 699.27(Tf-T0)
                   - [3.45663 x 10^7 + 1.98365 x 10^9z]^0.5


T0 = 694;          % initial T

obj = -(1.33563e7 - 1.70843e4*y(4) + 704.09*(y(12)- T0) - 699.27*(y(8)-T0) - sqrt(3.45663e7 + 1.98365e9*y(13)));
```

c) Constraints.m – To define all the equalities and inequalities constraints for the reactor. By running this program, profiles of T_f, T_g and N_{N2} at a specific length of reactor can be generated.

```
function [c,ceq] = mycon(y);

c=[];  % no inequalities

x10 = [ y(1) y(5) y(9) ];  % initial value of NN2, Tf, Tg
x20 = [ y(3) y(7) y(11) ];  % initial value of NN2, Tf, Tg

% Create or alter options structure for input ti ODE solvers
options = odeset('RelTol', 1e-8, 'AbsTol', [1e-8 1e-8 1e-8]);

% Solve initial value problems for ODE
[L,X1] = ode45(@ode3, [0 y(13)/2], x10, options);
[L,X2] = ode45(@ode3, [y(13)/2 y(13)], x20, options);

ceq(1) = X1(length(X1),1) - y(2);
ceq(2) = X1(length(X1),2) - y(6);
ceq(3) = X1(length(X1),3) - y(10);
ceq(4) = X2(length(X2),1) - y(4);
ceq(5) = X2(length(X2),2) - y(8);
ceq(6) = X2(length(X2),3) - y(12);
```

d) Universal.m – To clarify initial condition values, lower and upper boundaries, dimensioning the matrix, create or edit options parameter structure and call the optimization routine.

```
% initialize optimization variables: initial guess of the solution
%                NN2                          Tf                          Tg                    Length, z
%y =[xA1(1) xA1(2) xA2(1) xA2(2)  xB1(1) xB1(2) xB2(1) xB2(2)  xC1(1) xC1(2) xC2(1)  xC2(2)    z];
%y =[  y(1)    y(2)    y(3)    y(4)    y(5)    y(6)    y(7)    y(8)    y(9)   y(10)   y(11)   y(12)   y(13)];

% specify initial conditions (1st estimation)
y0 = [ 701.2  510  500  450      694  510  500  200      694   730   725  430  7];
% specify equality constraints
A = [ 0  1 -1  0  0  0  0  0  0  0  0  0  0
      0 -1  1  0  0  0  0  0  0  0  0  0  0
      0  0  0  0  0  1 -1  0  0  0  0  0  0
      0  0  0  0  0 -1  1  0  0  0  0  0  0
      0  0  0  0  0  0  0  0  0  1 -1  0  0
      0  0  0  0  0  0  0  0  0 -1  1  0  0];
  b = [1e-5; 1e-5; 1e-5; 1e-5; 1e-5; 1e-5];
Aeq = [ 1 0 0 0 0 0 0 0 0 0 0 0 0
        0 0 0 0 1 0 0 0 0 0 0 0 0
        0 0 0 0 0 0 0 0 1 0 0 0 0];
beq = [ 701.2; 694; 694 ];
% lower bounds
lb = [ 701.2   0       0     0     694 400 400 400   694 400 400 400 0];
% upper bounds
ub = [ 701.2 3220 3220 3220   694 800 800 800   800 800 800 800 10];

% create or edit OPTIONS parameter structure
options = optimset('LargeScale', 'off', 'Display', 'iter', 'MaxfunEvals', 100000);
% Parameter1 = LargeScale, Value = off (fsolve)
% Parameter2 = Display, Value = 'iter' (displays output at each iteration)
% Parameter3 = MaxfunEvals (maximum number of function evaluations allowed)
% call the optimization routine
% fmincon (to find a minimum of a constrained nonlinear multivariable function)
[y, fval, exitflag, output] = fmincon(@objfun, y0, A, b, Aeq, beq, lb, ub, @constraints,options);
```

3.5 Project Process Flow

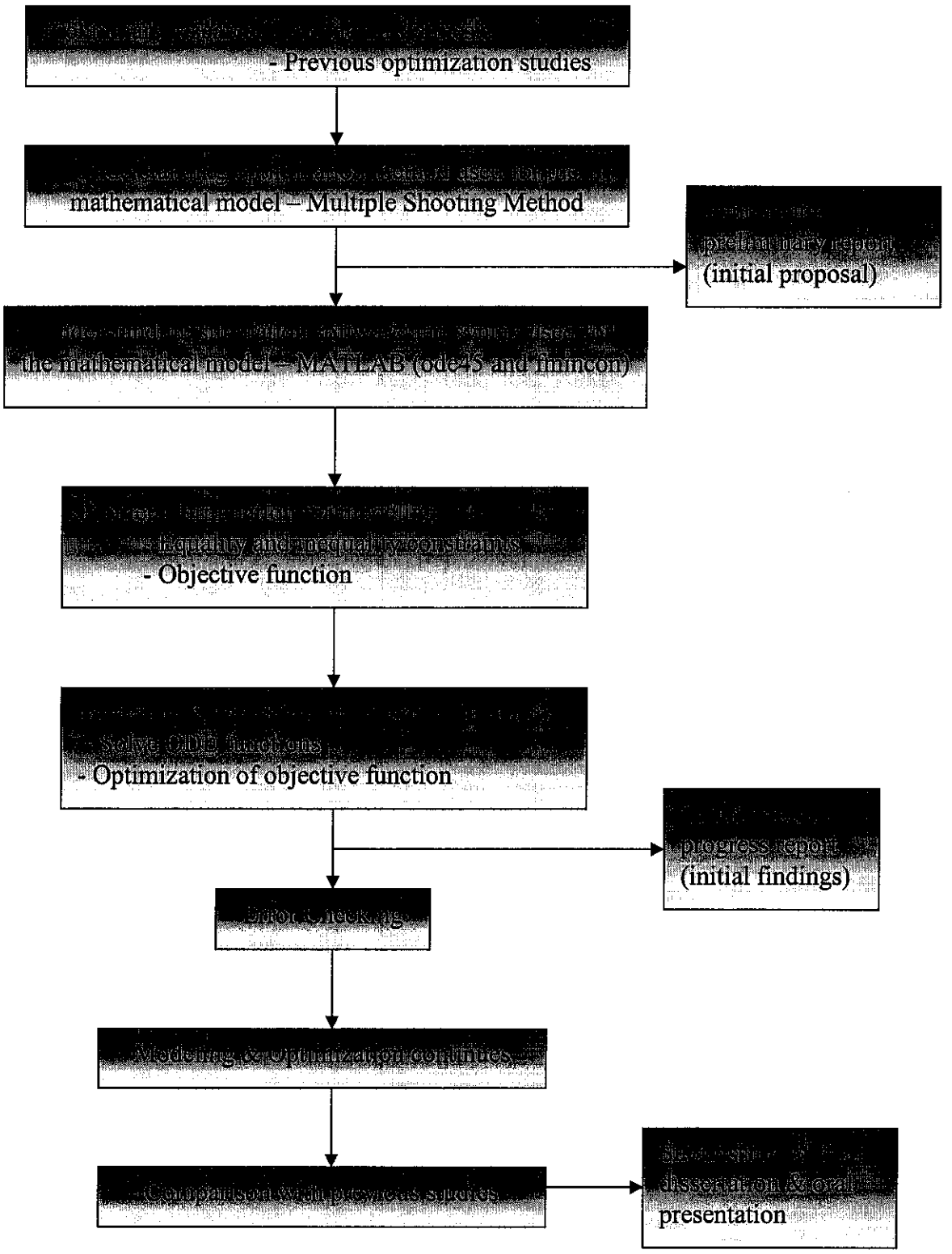


Figure 3.3: Project work flow diagram

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Result from Optimization

Number of intervals	Number of iterations	Time taken for optimizer to terminate successfully (s)	Objective function, f(x) (Profit Margin, $/yr)	Optimal Reactor Length (m)
2	4	2.172	5.0155×10^6	6.6953
4	5	5.828	5.0155×10^6	6.6953
8	5	19.000	5.0155×10^6	6.6953

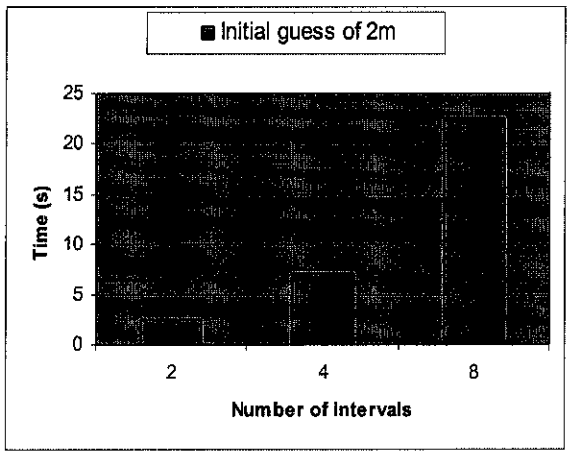
Table 4.1: Summary of number of intervals, time taken, profit and optimal reactor length for initial guess of 7m.

From the results obtained, it is clear that irrespective of the number of interval, the same optimized values for objective function ($5.0155 x 10^6/year) and reactor length (6.6953m). This consistency authenticates the robustness of the multiple shooting method regardless the number of intervals.

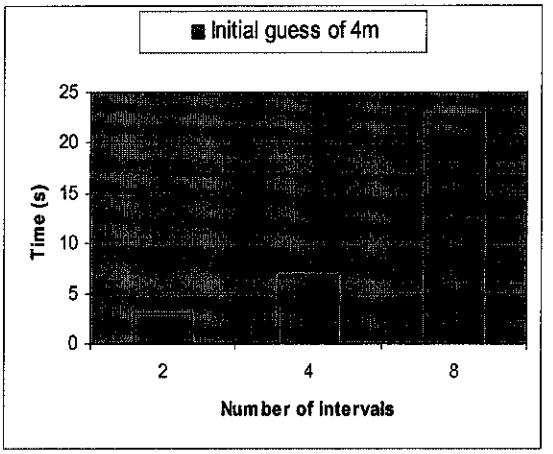
Initial guess of reactor length (m)	2 intervals		4 intervals		8 intervals	
	Iteration	Time (s)	Iteration	Time (s)	Iteration	Time (s)
2	6	2.453	6	7.016	6	22.515
4	7	2.922	6	6.954	6	22.953
5	5	2.515	5	5.953	6	22.828
7	4	2.172	5	5.828	5	19.000
10	5	2.656	6	7.484	5	20.297
15	6	3.172	6	7.578	5	20.282

Table 4.2: Summary of initial guess of reactor length, intervals, time taken for optimization terminated successfully and number of iterations

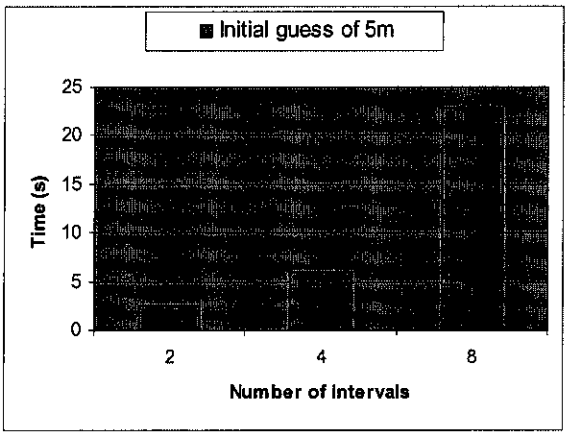
From Table 4-1, an initial reactor length of 7m is the nearest to the optimal value which is 6.6953m. The least time taken is 2.172s for two intervals, followed by four intervals which give a reading of 5.828s and finally 19s for eight intervals. This proves that as the number of intervals increases, the more iteration is required to optimize the objective function and as a result of that, the time taken increases. Also the closer the initial guesses to the optimal value, the lesser the time taken for the convergence.



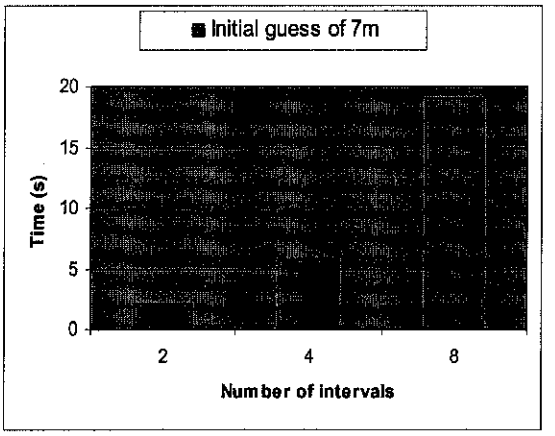
(a) Initial reactor length guess of 2m



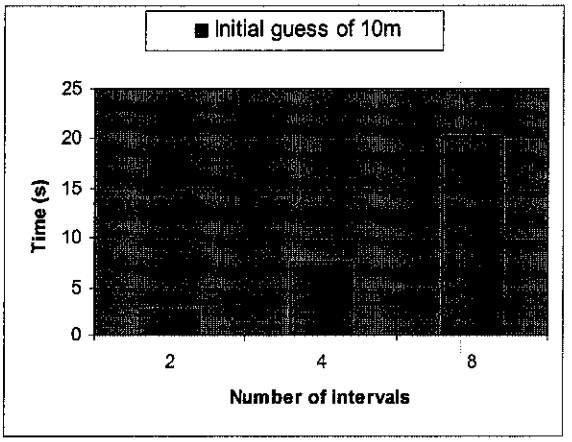
(b) Initial reactor length guess of 4m



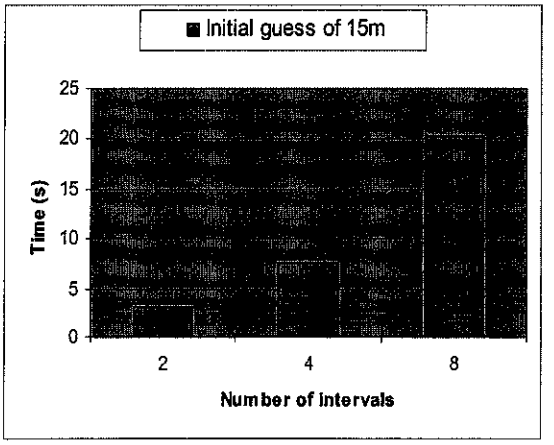
(c) Initial reactor length guess of 5m



(d) Initial reactor length guess of 7m



(e) Initial reactor length guess of 10m



(f) Initial reactor length guess of 15m

Figure 4.1: Convergence time comparison for 2, 4 and 8-intervals for varying initial guessed values of the reactor length

Initial guess of reactor length (m)	Objective function, F (Profit Margin, $/yr)	Optimal reactor length, (m)
2	4.45973×10^6	3.5667
4	4.45973×10^6	3.5667
5	5.0155×10^6	6.6953
7	5.0155×10^6	6.6953
10	5.0155×10^6	6.6953
15	5.0155×10^6	6.6953

Table 4.3: Summary of initial guess of reactor length, objective function and optimal reactor length for two intervals

Initial guess of reactor length (m)	Objective function, F (Profit Margin, $/yr)	Optimal reactor length, (m)
2	5.0155×10^6	6.6953
4	5.0155×10^6	6.6953
5	5.0155×10^6	6.6953
7	5.0155×10^6	6.6953
10	5.0155×10^6	6.6953
15	5.0155×10^6	6.6953

Table 4.4: Summary of initial guess of reactor length, objective function and optimal reactor length for four intervals

Initial guess of reactor length (m)	Objective function, F (Profit Margin, $/yr)	Optimal reactor length, (m)
2	5.0155×10^6	6.6953
4	5.0155×10^6	6.6953
5	5.0155×10^6	6.6953
7	5.0155×10^6	6.6953
10	5.0155×10^6	6.6953
15	5.0155×10^6	6.6953

Table 4.5: Summary of initial guess of reactor length, objective function and optimal reactor length for eight intervals

Based on Table 4-3, Table 4-4 and Table 4-5, the objective function and optimal length reactor show consistent values of \$5.0155 x 10^6 per year and 6.6953m respectively. However, as shown in Table-2, two intervals failed to converge to the correct values when subjected to poor initial guesses of 2m and 4m. When these two values were used, the objective function was only \$ 4.45973 x 10^6 per year with corresponding reactor

length of 3.5667m only. This is because for multiple-shooting, one of the requirements is that the need to supply the initial guesses for all the nodes values. The more intervals used in the system, the more node values can be initialized and clearly if the state trajectory is known, this can dampen the effect of bad initial guesses for the inputs. The 4 and 8-intervals system has more node and input values that can be specified compared to 2-intervals systems. These node values for the states and the intermediate reactor initial guesses dampen the effect of the initial reactor length guesses of 2m and 4m, and the solution converges. Overall, these results show that the higher the number of intervals used, the more robust the multiple-shooting method to bad initial guesses.

4.2 Results on profiles of top temperature at 694K

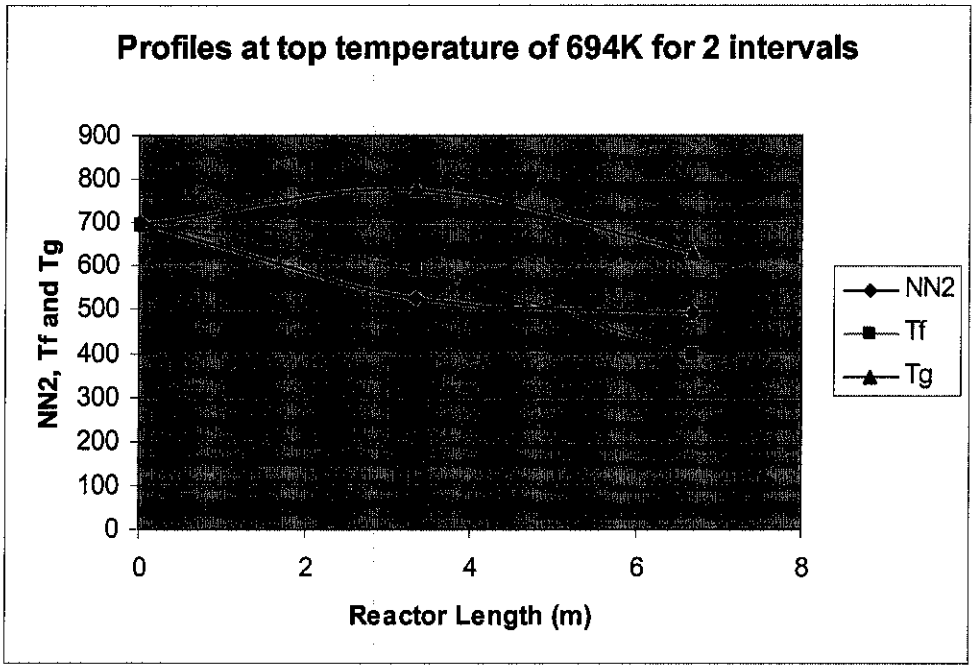


Figure 4.2: Profiles for 2-intervals

Reactor Length, z (m)	N_{N2} (kgmol/m^{2}h)	T_f(K)	T_g(K)
0	701.2	694	694
3.34765	528.14	592.39	778.97
6.6953	490.84	400	629.65

Table 4.6: Results obtained from optimization for two intervals

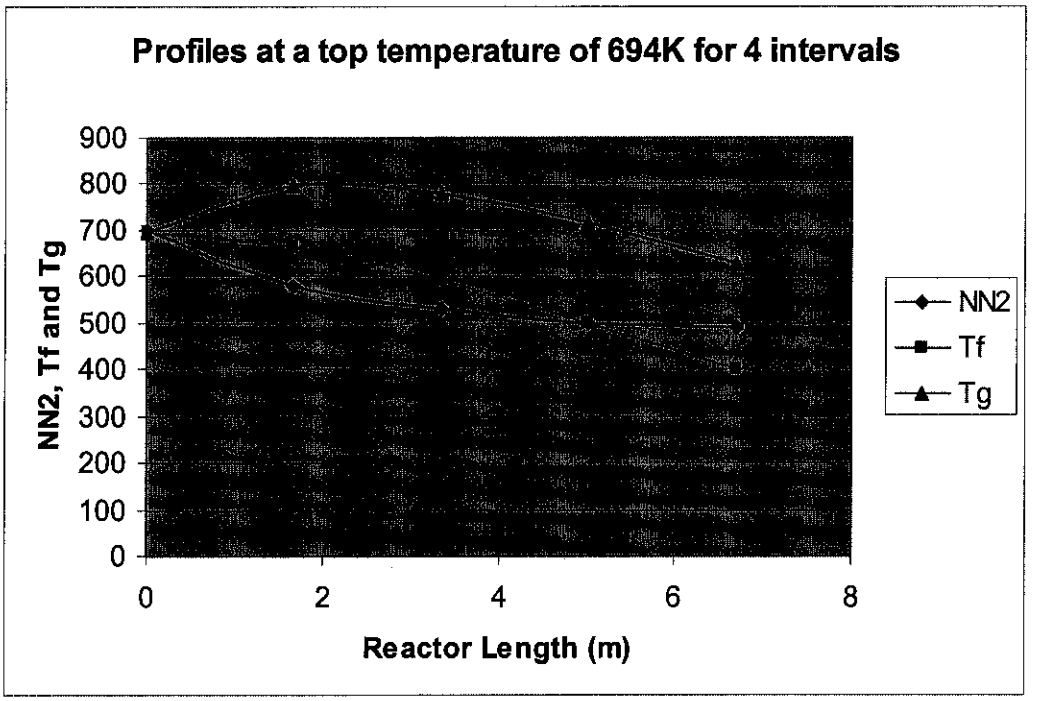


Figure 4.3: Profiles for 4-intervals

Reactor Length, z (m)	N_{N2} (kgmol/m^{2}h)	T_f (K)	T_g (K)
0	701.2	694	694
1.673825	578.79	665.89	797.14
3.34765	528.14	592.39	778.97
5.021475	500.09	501.2	719.1
6.6953	490.84	400	629.65

Table 4.7: Results obtained from optimization for four intervals

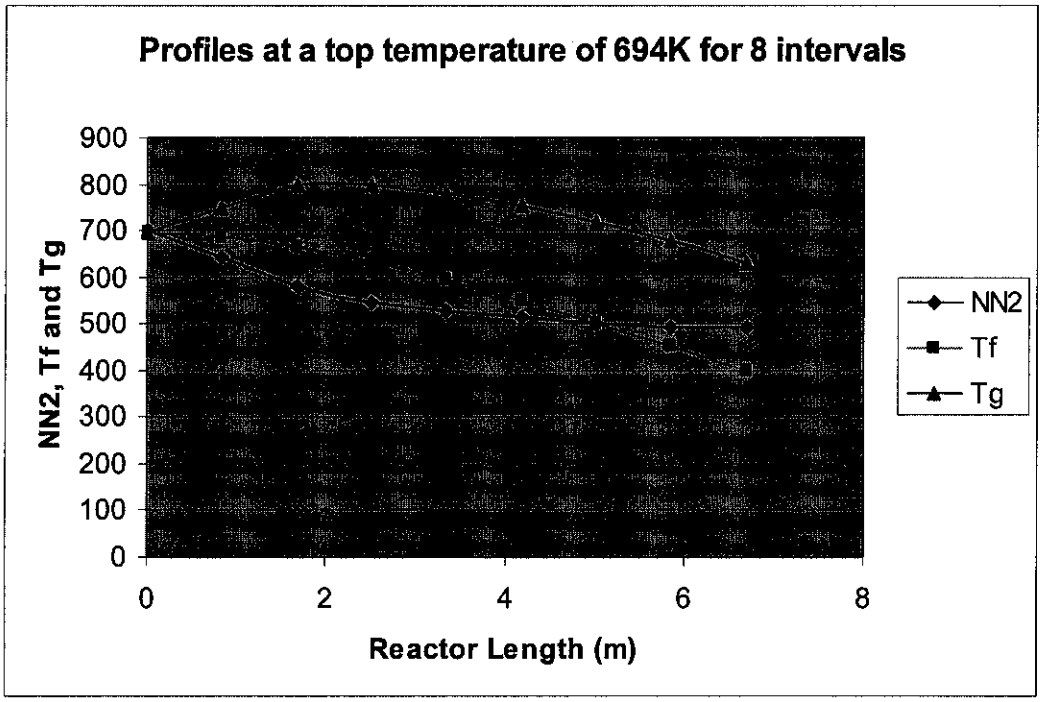


Figure 4.4: Profiles for 8-intervals

Reactor Length, z (m)	N_{N2} (kgmol/m^{2}h)	T_f (K)	T_g (K)
0	701.2	694	694
0.836913	644.81	687.65	748
1.673825	578.79	665.89	797.14
2.510738	546.83	631.97	797.93
3.34765	528.14	592.39	778.97
4.184563	512.08	548.49	752.98
5.021475	500.09	501.02	719.1
5.858388	493.45	451.14	677.15
6.6953	490.84	400	629.65

Table 4.8: Results obtained from optimization for eight intervals

4.3 Comparison with previous studies

A top temperature of 694K is the top temperature of interest in previous optimization studies. Hence, this temperature is the benchmark for initial condition for the multiple-shooting method. By comparing the result with previous studies, the profile of the graphs shows a similarity with previous studies done by *Babu, Angira & Nilekar (2004)* using Runge-Kutta Variable Step (RKVS) size method with Differential Evolution (DE) and Gear's method (GEAR) with DE. Almost similar profiles are obtained. Comparison to RKVS and GEAR method were presented in the Table 4-9 on the next page.

Parameters	RVKS with DE	GEAR with DE	Multiple Shooting
z	5.156	4.900	5.021
N_{N2}, T_f	511.75	511.55	500.00

Table 4.9: Reactor length at which variables N_{N2} and T_f intersect

From the Table 4-9, the difference in prediction of intersections is less than 5.0% between multiple-shooting method and RKVS & GEAR method. Hence this indicates that multiple-shooting method gives accurate results and suitable to be used as an alternative method for solving the three coupled differential algebraic equation.

Methods used	Optimal Reactor Length (m)	Objective function value ($/yr)
PMP [1]	5.180	Not reported
LGRG [2]	2.580	1.290×10^6
GA [3]	5.330	4.230×10^6
RKVS with DE [4]	7.160	4.848×10^6
GEAR with DE [4]	6.790	4.848×10^6
Single Shooting [5]	7.820	5.150×10^6
Multiple Shooting	6.695	5.015×10^6

Table 4.10: Optimum reactor length and objective function using various numerical methods

The table above shows the results obtained from different methods and its comparison with those obtained in [1, 2, 3, 4, 5] using Pontryagin's Maximum Principle (PMP), Lasdon's Generalized Reduced-Gradient method (LGRG), Genetic Algorithm (GA),

Runge-Kutta Variable Size (RKVS) with Differential Evolution (DE), Gear's Method (GEAR) with DE and Single Shooting Method respectively. From Table 4-10, the optimum reactor length of 2.58m is reported in [2] and 5.18m in [1], both of which are wrong due to the errors in their problem formulations as pointed out in [3]. An optimum reactor length of 5.33m and the corresponding objective function value is \$4.23 x 10^6/ year, reported in [3] are also not correct as found [4]. Among other methods, GEAR and RKVS have the same objective function value though the optimum reactor length is slightly different in each case. The correct optimum reactor length can be considered as 6.79m with an objective function value of \$4.84 x 10^6/ year as reported in [4]. The result given by multiple-shooting strategy as found in this study agrees considerably well with these values as reported by [4].

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

In this study, an alternative approach of solving an optimal design problem for an ammonia reactor to give maximum economic has been presented. The method, namely multiple-shooting, has been demonstrated to be able to give accurate results of reactor length 6.6953m with corresponding profit of \$5.0155 x 10^6/year. These values agree considerably well with those obtained by recent study of *Babu, Angira & Nilekar (2004)* using different approach. According to *Upreti and Deb* (1996), the optimal results obtained with the revised formulation are found to agree with industrial practice as documented by Eymery (1964). It has also been found that the increasing number of intervals, the robustness of multiple-shooting strategy increases especially to poor initial guesses. The convergence time also increases with respect to the number of intervals. This successful application of multiple-shooting method for the optimal design of ammonia synthesis reactor indicates that this method has great potential and can be applied to advantage in all the highly non-linear and complex engineering problems.

For future projects, the ammonia reactor in the modeling can be changed from a packed bed reactor to a different type of reactor. The optimization process could be different and could be more profitable. This can be studied in detailed in the future.

CHAPTER 6

REFERENCES

[1] A. Murase, H. L. Roberts, and A. O. Converse, "Optimal Thermal Design of an Autothermal Ammonia Synthesis Reactor", Industrial & Engineering Chemistry Research, 9, 503-513, 1970.

[2] T. F. Edgar & D. M. Himmelblau, Optimization of Chemical Processes. Singapore, Mc-Graw-Hill, Inc., Page Nos. 534-539, 2001.

[3] S.R. Upreti, & K. Deb, "Optimal Design of an Ammonia Synthesis Reactor using Genetic Algorithms", Computers & Chemical Engineering, 21, 87-92, 1997.

[4] B. V. Babu, Rakesh Angkira & Anand Nilekar, "Optimal Design of an Auto-thermal Ammonia Synthesis Reactor using Differential Evolution", The Eight World Multi-Conference on Systematic, Cybernatics and Informatic SCI 2004, Orlando, Florida, USA, 18-21 July, 2004, pp 132-137.

[5] Shahirah Bt. Ansary, "Modeling and Optimization of an Ammonia Reactor using MATLAB", Final Year Research Project, Universiti Teknologi PETRONAS, July, 2005

[6] Zabiri, H. (2005) "Multiple-shooting strategy for Optimal Control System Design of Differential-Algebraic equations systems", Accepted for publication in the Proceedings of International Conference of Chemical & Bio-process Engineering, Sabah.

[7] Fletcher, R. and M.J.D. Powell, "A Rapidly Convergent Descent Method for Minimization," Computer Journal, Vol. 6, pp. 163-168, 1963.

[8] Goldfarb, D., "A Family of Variable Metric Updates Derived by Variational Means," Mathematics of Computing, Vol. 24, pp. 23-26, 1970.

[9] Eymery J., Dynamic behavior of an ammonia synthesis reactor. (D.Sc. thesis). MIT (1964).

[10] http://www.cheresources.com/ammonia.shtml

[11] http://www.jmcatalysts.com/pct/marketshome.asp?marketid=2&id=45