Dynamic Studies of Steam Methane Reformer (SMR) in Ammonia Plant

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.

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Tronoh, Perak

JANUARY 2009

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.

NORZULIANA BT MOHAMMAD NAZIR

ABSTRACT

Mathematical modeling and simulation of Steam Methane Reformer (SMR) over sulfide nickel catalyst on alumina support has been studied. It is consists of primary and secondary reformers which is play an important role in the production of ammonia. This study consists of chemical reaction kinetics; chemical reaction equation and rate constants for a given catalyst; to develop a mathematical model for a steam reformer incorporating the reaction kinetics; to study the behavior of the reactor for changes in different variables such as feed rate, feed composition, temperature, etc.

ACKNOWLEDGEMENT

I would like to take this opportunity to acknowledge and thank everyone that has given me all the supports and guidance throughout the whole period of completing the final year project. Firstly, many thanks to the university and the Final Year Project coordinators that have coordinated and made the necessary arrangements.

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Finally, many thanks to my fellow colleagues for their help and ideas throughout the completion of this study. Thank you all.

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ABBREVIATIONS AND NOMENCLATURES

N_j = moles

F_j = Molar flow rates

r_j = net rates of formation

V = volume (m^3)

W = weight (kg)

k = specific reaction rate

C_j = concentrations

T = temperature (K)

P = pressure (Pa)

R = 8.314 m^3.Pa/mol.K

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Journals, patents, info from PETRONAS Ammonia Sdn. Bhd, and techniques belong to KTI, Kellogg, Topsoe, ICI, Selas and TEC companies have been study closely for this project. The products from Ammonia/Syngas plant are:

- Carbon monoxide (CO), gas
- Oxogas (mixture of H_2 and CO)
- Ammonia

The CO and oxogas are produced from natural gas and steam. Ammonia is produced from a mixture of hydrogen and nitrogen in the ratio of H_2 to N_2 at 3:1. The fuel for the reformer furnace is by product off-gases (primary fuel) and natural gas (secondary fuel). The reactions by which this ratio is achieved are given as follows:

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ Methane reforming reaction (Reaction 1)

$CO + H_2O \leftrightarrow CO_2 + H_2$ Water gas shift reaction (Reaction 2)

$CH_4 + 3/2\ O_2 \leftrightarrow 2H_2O + CO$ Combustion reaction (Reaction 3)

Reaction 1, the steam reforming reaction, and reaction 2, the water gas shift reaction, are endothermic and occur in the primary reformer. Reaction 3, the combustion reaction, is exothermic and occurs along with reactions 1 and 2 in the secondary reformer. Optimization of the reforming process involves the manipulation of parameter to achieve high process yield while maintaining low operating and installed costs.

The parameters which are monitored in this design include temperature, pressure, steam to carbon ratio, and percent oxygen in the air feed. The steam reforming process has the following reactions:

Reaction (1) describes the mechanism of reforming all hydrocarbons.

1. $C_nH_m + nH_2O \leftrightarrow n\,CO + (n + m/2)\,H_2$ - heat
   [$CH_4 + H_2O \leftrightarrow CO + 3H_2$] Methane reforming reaction

Reaction (2) provides an overall summary of how CO_2 is formed but is actually formed from CO as indicated in reaction (3)

2. $C_nH_m + 2nH_2O \leftrightarrow n\,CO_2 + (2n + m/2)\,H_2$ – heat
3. $CO + H_2O \leftrightarrow CO_2 + H_2$ + heat [Water gas shift reaction]

1.2 Problem Statement

The focus on this project is basically on mathematical modeling and simulation of the primary reformers. In the study of steam reformation in a real system, reactor geometry, steam-to-carbon-ratio, temperature and pressure of the reaction, flow pattern inside the reactor and other parameters are all factors that affect a reformer's performance.

Accurate individual analysis of each limiting mechanism (heat transfer, mass transfer and chemical kinetics) is perhaps the preferred method for quantifying reactor performance, but the interactions between the mechanisms often make such combined analysis difficult, if not impossible.

1.3 Objectives and Scope of Study

The objective of this project is:

- To develop mathematical modeling and simulation studies of Steam Methane Reformer (SMR) in Ammonia Plant using Polymath.

The scopes of this study include complex interaction of heat transfer and coupled chemical reactions. The furnace in the present system is a side-wall fired type in which the burner energy is transferred by radiation and convection to the reformer tubes, passes through the tube walls by conduction and is transferred to the catalyst bed by a combined mechanism.

In order to perform a complete analysis of the reformer, the behavior under transient conditions, such as start-up, shutdown, change of operating conditions and feed disturbances in addition to steady state should be investigated.

CHAPTER 2

LITERATURE REVIEW

2.1 Steam Methane Reformer (SMR)

A methane reformer is a device used in chemical engineering, which can produce pure hydrogen gas from natural gas using a catalyst. SMR uses an external source of hot gas to heat tubes in which catalytic reaction takes place that converts steam and lighter hydrocarbons such as natural gas (methane) or refinery feedstock into hydrogen and carbon monoxide (syngas). The SMR furnace is a process furnace that is used to maintain the reactants at a temperature that favors the production of hydrogen. Steam reforming is achieved by reaction over a catalyst at high temperature. In addition to the energy required to provide the steam, the overall reaction is endothermic, so energy must be added to drive it.

Below is diagram for Production of 1,000 Metric Tons per day of ammonia (Nitrogen and Hydrogen in a 3:1 stoichiometric ratio)

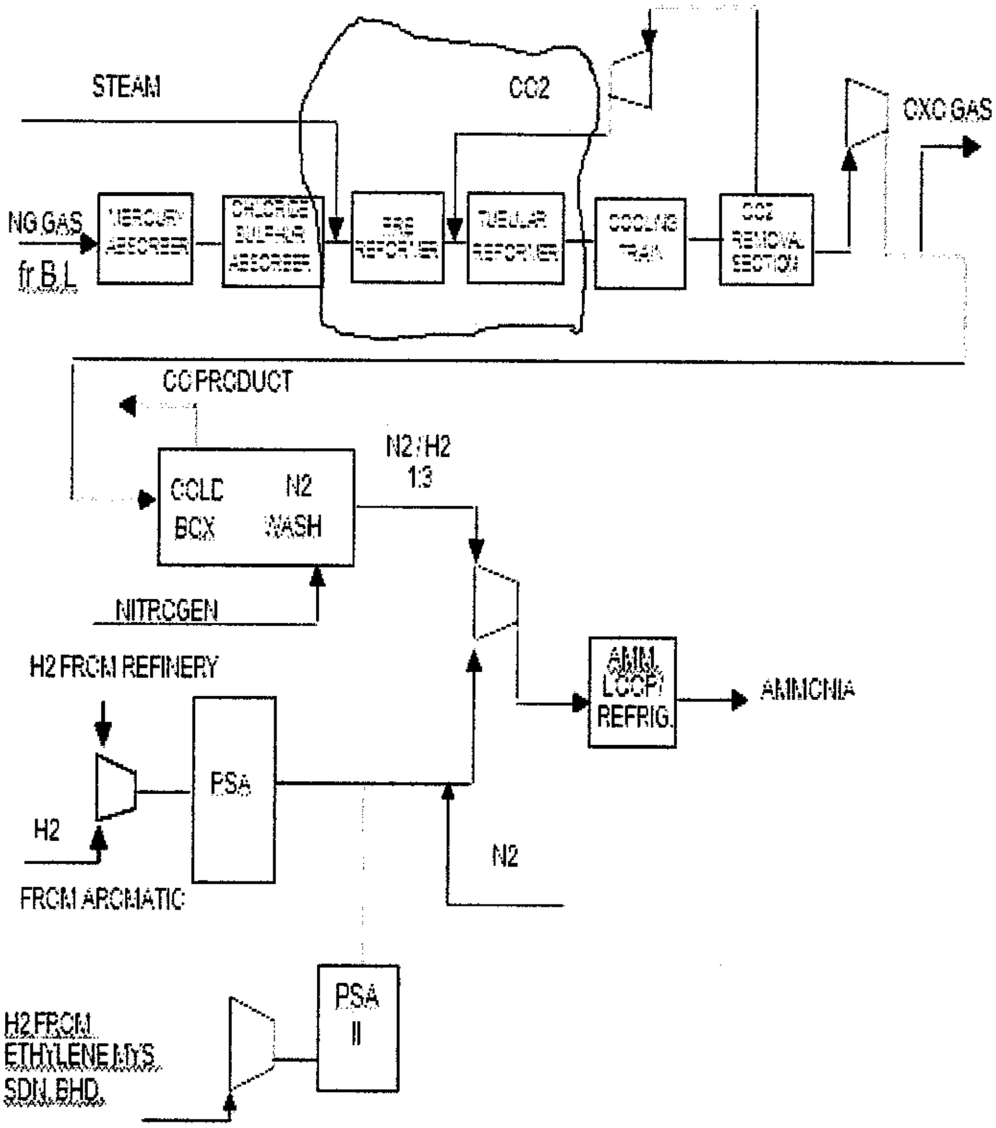


Figure 2.1: Process step to produce Ammonia (PASB)

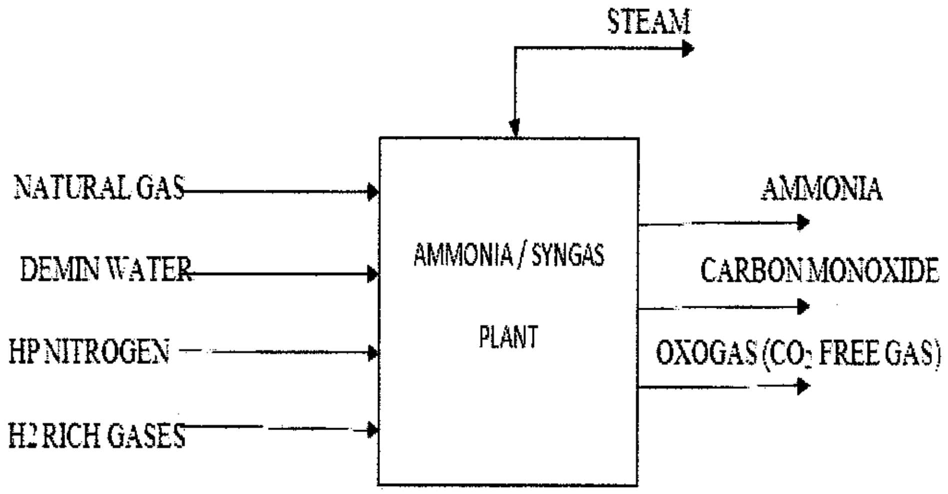
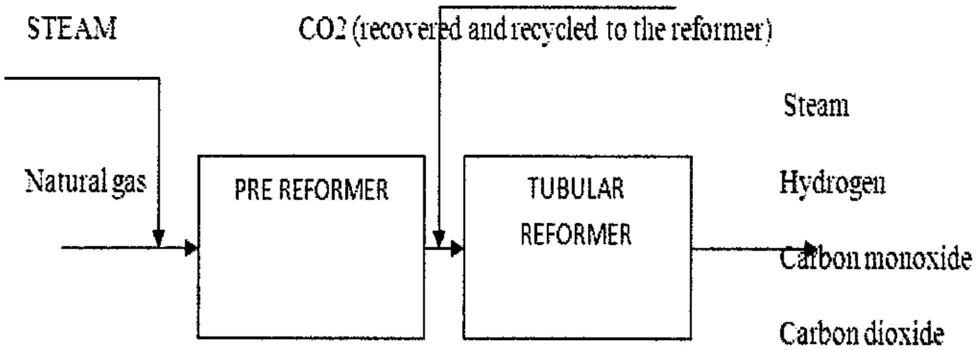


Figure 2.2: Diagram (PASB)



*Based on the assumption that all downstream processes are ideal, all the carbon monoxide found in the secondary reformer outlet stream will be converted to hydrogen. Therefore, the addition of the hydrogen and carbon monoxide should be in at least a 3:1 ratio with Nitrogen upon exiting the secondary reformer.

Figure 2.3: Reformer section (PASB)

2.2 Process Description of Reformer in Ammonia Plant

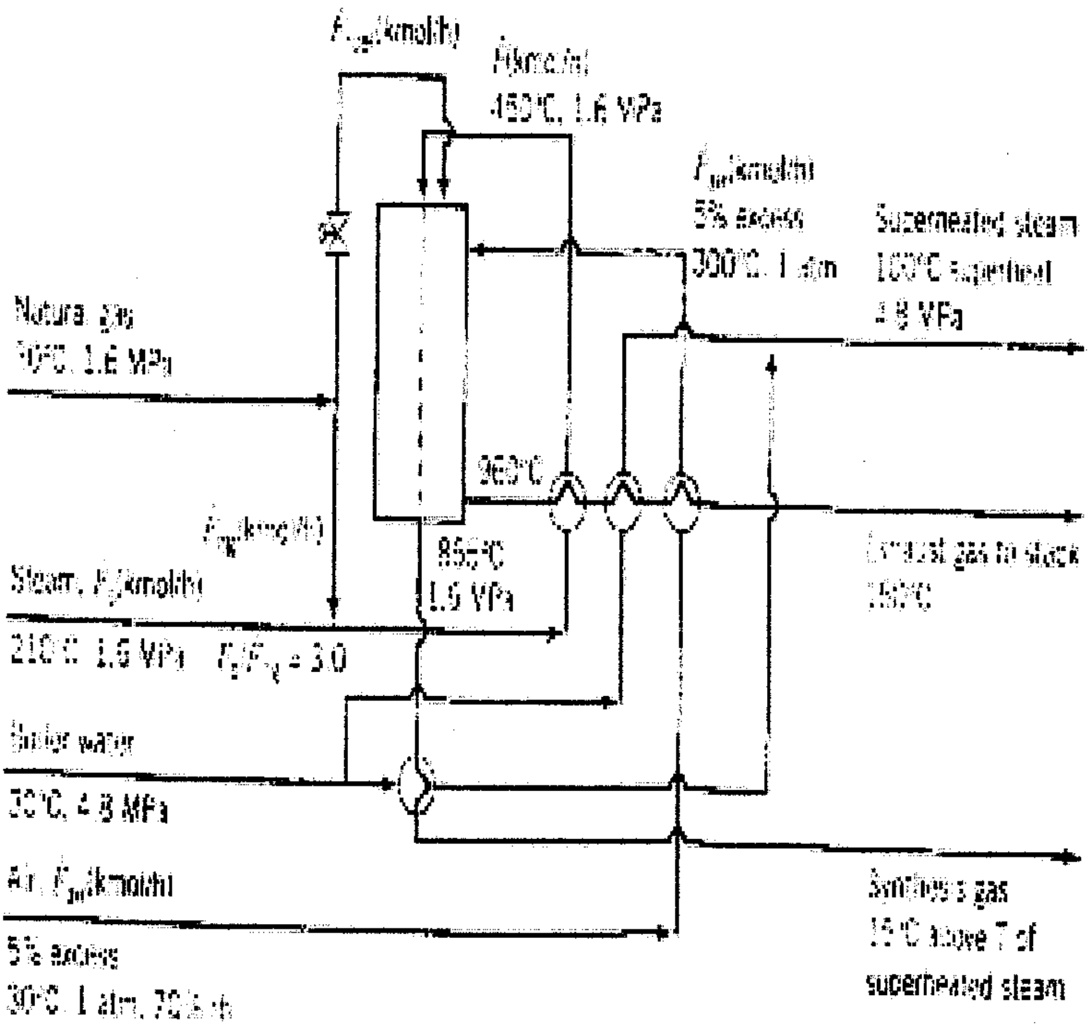


Figure 2.4: Detailed schematic diagram of reformer (Elementary Principles of Chemical Process Textbook by Richard M.Felder, Ronald W.Rousseau)

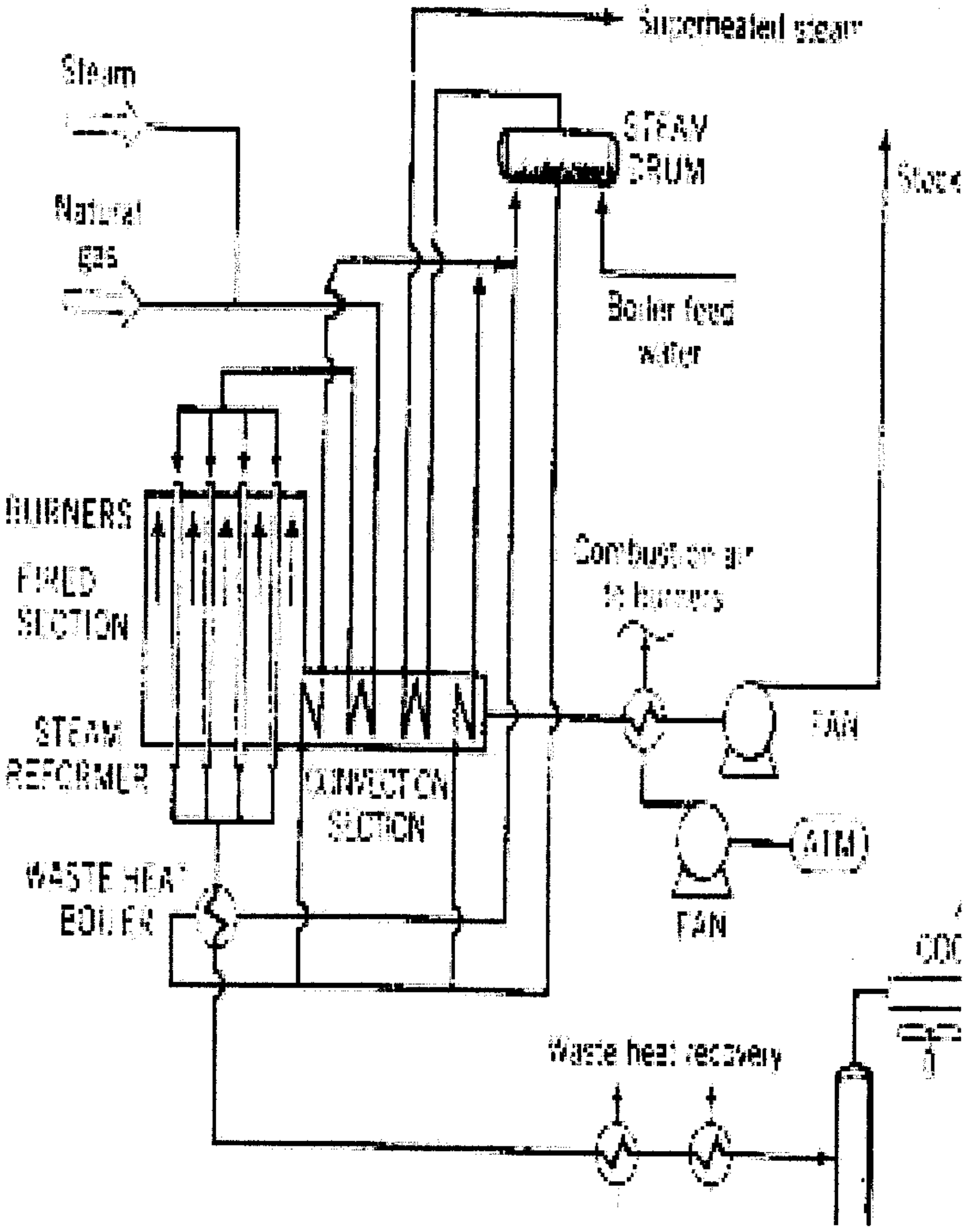


Figure 2.5: Reformer (Elementary Principles of Chemical Process Textbook by Richard M.Felder, Ronald W.Rousseau)

A mixture of carbon monoxide, hydrogen, and carbon dioxide is produced by steam reforming, a process in which natural gas and steam are mixed and reacted in a reformer operated at 1.6 MPa. Natural gas may be assumed to consist entirely of methane (CH_4), although other compounds may be present in small concentrations. In the present process, steam and natural gas are fed to the reformer in a ratio of 3.0 moles of steam per mole of methane. The reformer consists of an arrangement of vertical tubes filled with nickel-impregnated ceramic catalyst. Rows of these tubes are located inside an insulated firebox, where they are heated by the combustion of natural gas.

The natural gas and steam that are blended to become the reformer feed enter the process at 30°C and 210°C, respectively. The mixture is preheated to 450°C by exhaust gas from the firebox/ chamber, and it is introduced to the reformer through a header that distributes the mixture evenly among the parallel reformer tubes. Two key reactions occur: the steam-reforming reaction itself,

$CH_4 + H_2O\,(g) \leftrightarrow CO + 3H_2$

and the water-gas shift reaction,

$CO + H_2O \leftrightarrow CO_2 + H_2$

The product gas leaves the reformer at 855°C and 1.6MPa.

Energy efficiency in steam reforming is improved by recovering heat from the burner exhaust gas, which leaves the firebox at 960°C. The exhaust gas is cooled in a series of heat-exchange operations that preheat the reformer feed streams to 450°C, produce superheated steam at 4.8MPa and 100°C superheat from boiler feed water at 30°C, and preheat the combustion air to 300°C. The superheated steam is used to drive turbines elsewhere in the process or it can be exported, for example to generate electricity. The burner exhaust gas leaves the heat-recovery units and enters a stack at 150°C for release to the atmosphere.

2.3 Functions for each Reformer

2.3.1 Pre-reformer

The pre-reformer converts all the heavier hydrocarbons to CH_4, H_2 etc. The natural gas and hydrogen mix from the desulphurization section has steam added and is heated with the hot flue gas from the reformer waste heat convection section. From here, the reaction mixture goes to the pre-reformer loaded with high activity nickel catalyst. Higher hydrocarbons are not present in the gas leaving pre-reformer that consist of steam, carbon oxides and methane that can be heated to higher temperature (>600°C) without any thermal cracking.

Note:

- If the steam to carbon ratio drops to very low levels, and especially if the steam flow stops completely, even for few seconds, a heavy carbon lay down must be expected.

- On the other hand, if the catalyst is exposed to steam alone, it will be oxidised.

The minimum operating temperature must be observed. If the catalyst contains magnesia, under certain conditions it may react with steam to form Magnesium hydroxide.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

The conditions at which the reaction may take place depend on the steam partial pressure and temperature. In case of extensive oxidation of the catalyst, it has to be replaced. If the catalyst is slightly oxidized it will be reduced during start-up, but the activity will decreased to some extent.

2.3.2 Tubular reformer

Heat flux limited, thus based on a calculated reformer heat duty of 50MMkcal/hr, the reformer:

Sized to contain = 230 catalyst tubes
Inner diameter tube = 4 inches

Length tube = 35 feet

Maximum heat flux through tube walls, f = 5,921.176 kcal/ft^2hr

Total needed surface area of reformer tubes, d/f = a = 8457.28ft^2

t = a/36.7ft^2 per tube = 230 tubes needed.

Catalyst volume was calculated from tube number and tube volume. The primary reformer contains a total of 690ft^3 of catalyst.

Diameter = 12 ft, Long = 20 ft

10 feet of reactor length are left void of catalyst so that combustion may occur away from the catalyst.

2.3.2.1 Heat Input

The heat released in the tubular reformer is supplied by the firing of the two fuels. The primary fuel consists of off-gases from the PSA unit, the cold box unit and the Nitrogen wash unit. The hydrogen stream from the cold box unit may be utilized as fuel if it is off spec or the ammonia plant is down. The secondary fuel consists of natural gas. The fuels are supplied through one common fuel line. The reformer is fired by using all primary fuel available and supplemented by natural gas. The duty controller controls the total heat input to the radiant section. The setting of the duty controller should be adjusted by the operator to keep the desired temperature at the reformer outlet.

Note: The higher the temperature, the lower unconverted methane.

If there is a loss of one of the fuel streams then flow controller will compensate by increasing the natural gas flow. The flow of natural gas to the fuel header is controlled by the duty controller during normal operation. The setting of duty controller represents the total fuel heat input to the tubular reformer as measured by the individual flow meters on each gas stream that feeds the reformer burner.

2.4 Methane Content in the Reformer

The methane content in the process gas at the outlet of the reformer is determined by the following parameters:

- Operating pressure
- Reforming temperature
- Steam/carbon ratio
- Approach to the theoretical equilibrium which depends on the capacity and the catalyst activity.

An increase in the reforming temperature or the steam/ carbon ratio will lower the methane content, while an increase in operating pressure will increase the methane context exit the reformer. Minimum methane content is required for maintaining the methane balance in the cold box unit. As the catalyst ages, the approach to equilibrium of the effluent gas will tend to increase, causing an increase in methane leakage.

2.5 Carbon Monoxide Content in the Reformer's Outlet

The carbon monoxide content outlet the tubular reformer is determined by the same parameters as the methane content. An increase in operating pressure or steam/carbon ratio will lower the carbon monoxide content, while an increase in reforming temperature will increase the carbon monoxide content exit the reformer. Maximum carbon monoxide production is obtained by maximum recycle of CO_2 from the CO_2 removal section.

2.6 Catalyst properties

Table 2.1: Table of Catalyst Properties

Catalyst density (g_{cat}/m^3)	2355.2
Nickel content (wt.%)	9.8
S content (wt.%)	4.9
Alumina content (wt.%)	Balance
Surface area (m^2/g)	155
Total pore volume (ml/g)	0.9
Size of the sphere (mm)	1.75
Average crush strength (N)	25

2.7 Mathematical model

2.7.1 Mathematical modeling of dynamic systems

A simplified mathematical model of the physical system can determine the overall complex behavior of the dynamic system. The analysis of a physical system steps:

(a) Mathematical modeling of a Physical System.

All components of the physical system are linear. The resulting mathematical model may be linear or non-linear, depending on the given physical system. Accurate mathematical modeling of any physical system will lead to non-linear differential equations have either no solution or difficult to find a solution. Assumptions are made to linerise a system, which permits quick solutions for practical purposes.

(b) Formulation of Governing Equations

Once the mathematical model is developed, we can apply the basic laws of nature and the principles of dynamics and obtain the differential equations that govern the behavior of the system. The resulting of mathematical model may be linear or non-linear, depending upon the behavior of the elements or components of the dynamic system.

(c) Mathematical solution of the governing equations

There are many technique available for finding the solution, namely, the standard methods for the solution of ordinary differential equations, Laplace transformation methods, matrix methods, and numerical methods.

(d) Physical Interpretation of the results

The solution of the governing equations of motion for the physical system generally gives the performance.

2.7.2 Control system configurations

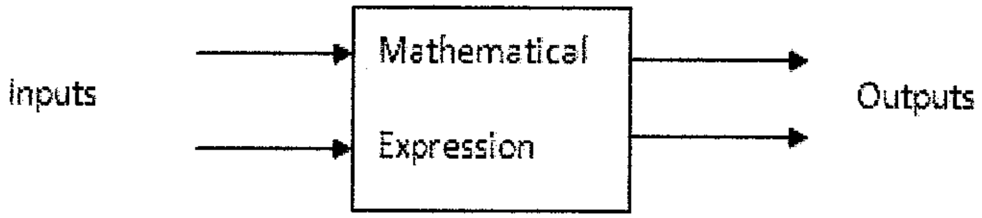


Figure 2.6: Block representation

2.8 Polymath Software

For this project, polymath software has been used to solve all the differential equations simultaneously. POLYMATH 6.X is a proven computational system, which has been specifically created for educational or professional use. The various POLYMATH programs allow the user to apply effective numerical analysis techniques during interactive problem solving on personal computers. Results are presented graphically for easy understanding and for incorporation into papers and reports. Students, engineers, mathematicians, scientists, or anyone with a need to solve problems will appreciate the efficiency and speed of problem solution.

The Polymath has 4 major programs:

(a) LEQ Linear Equations

(b) NLE Nonlinear Equations

(c) DEQ Differential Equations

(d) REG Regression

For this study, DEQ Differential Equations has been used. The purpose of this program is to provide a solution for a system of simultaneous first-order ordinary differential equations and explicit algebraic equations.

There are five numerical integration algorithms available within Polymath. RKF45 has been used to solve the ordinary differential equations.

The Runge-Kutta-Fehlberg (RKF45) is the default algorithm that is highly recommended for most problems.This algorithm monitors the estimate of the integration error, and reduces or increases the step size of the integration in order to keep the error below a specified threshold. The accuracy requested is that both the relative and absolute (maximal) errors be less than the truncation error tolerance. The default value of this tolerance is 1.0E-6. (All the tolerances can be changed in "Settings"). If the integration progresses very slowly the reason for that may be that the system of equations is stiff. Stiff systems of equations contain variables that change (decay) in widely varying time scales. For such systems, the RKF algorithm may require a very small step size for integration and one of the available still algorithms, STIFF or STIFFBS, should be used.

2.9 Summary of Properties

2.9.1 Catalyst

- Type of catalyst: Sulfide nickel catalyst on a gamma support (Ni-0309S)
- Cheap and popularly used.
- Catalyst properties:

Catalyst density (g_{cat}/m^3)	2355.2
Nickel content (wt.%)	9.8
S content (wt.%)	4.9
Alumina content (wt.%)	Balance
Surface area (m^2/g)	155
Total pore volume (ml/g)	0.9
Size of the sphere (mm)	1.75
Average crush strength (N)	25

Source: Journal Kinetic and modelling study of methane steam reforming over sulfide nickel catalyst on a gamma alumina support by D.L. Hoang*., S.H. Chan, O.L.Ding

2.9.2 Tubes in the primary reformer

Sized to contain	230 catalyst tubes
Inner diameter tube	4 inches
Length tube	35 feet
Maximum heat flux through tube walls, f	5,921.176 kcal/ft^{2}hr
Total needed surface area of reformer tubes, A	8457.28ft$^{2\backslash}$
Total Catalyst	690ft^3

Source: http://www.owlnet.rice.edu/chbe403/nh3ref97.html

2.9.3 Operating conditions for 1,000 metric tons per day of Ammonia

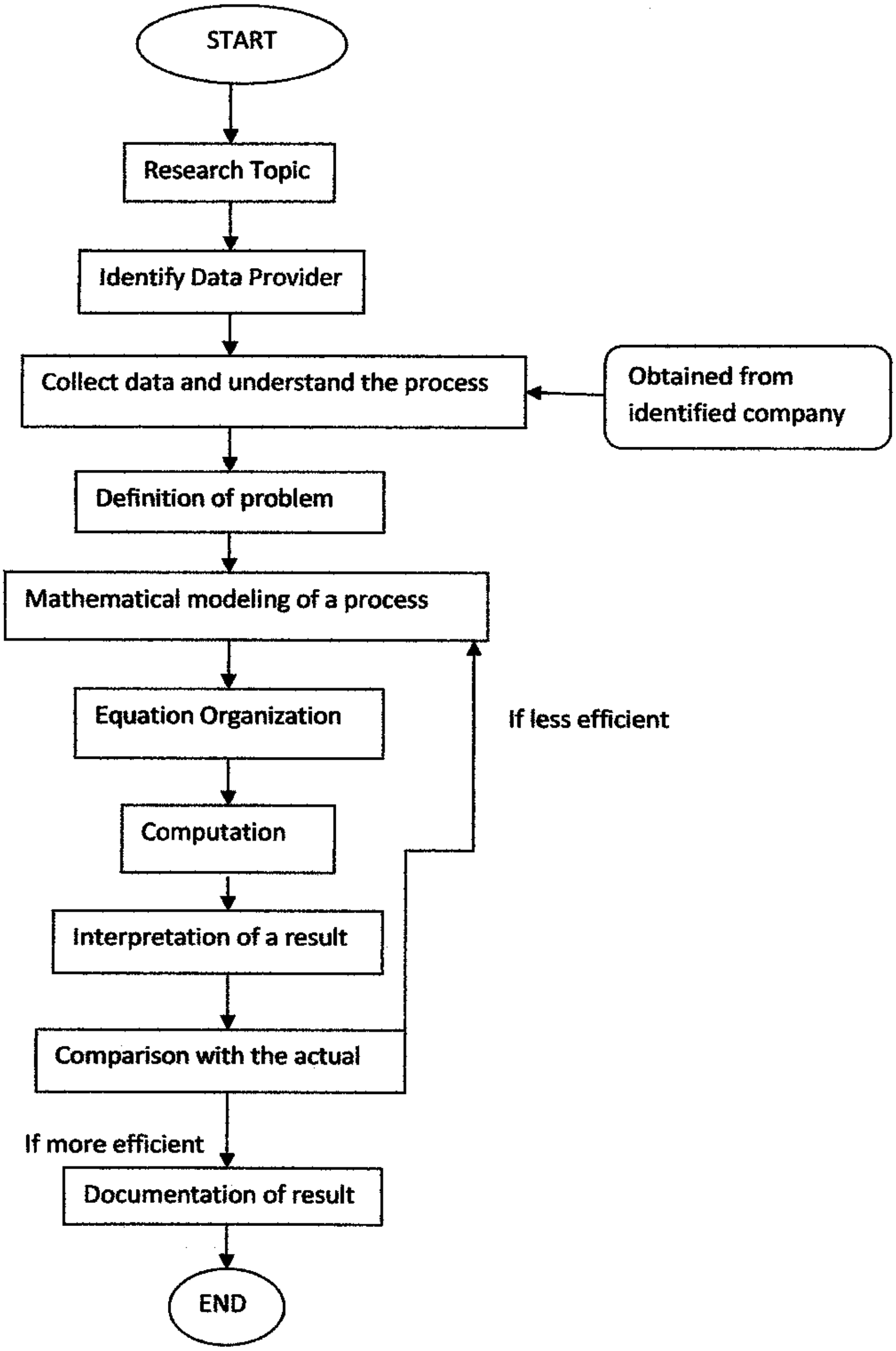
Temperature (°C)	600
Pressure (bar)	39,220
Vapor Fraction	1.00
Mole Flow (kmol/hr)	5004.443
Mass Flow (kg/hr)	87,783.203
Volume Flow (Cum/hr)	9,150.887
Enthalpy (MMKCal/Hr)	-212.141
Mole Flow (KMol/Hr)	
CH_4	1250
H_2O	3750
H_2	Too small
CO	Too small
CO_2	3.00
N_2	1.443
O_2	Too small
AR	Too small

Source: http://www.owlnet.rice.edu/chbe403/nh3ref97.html

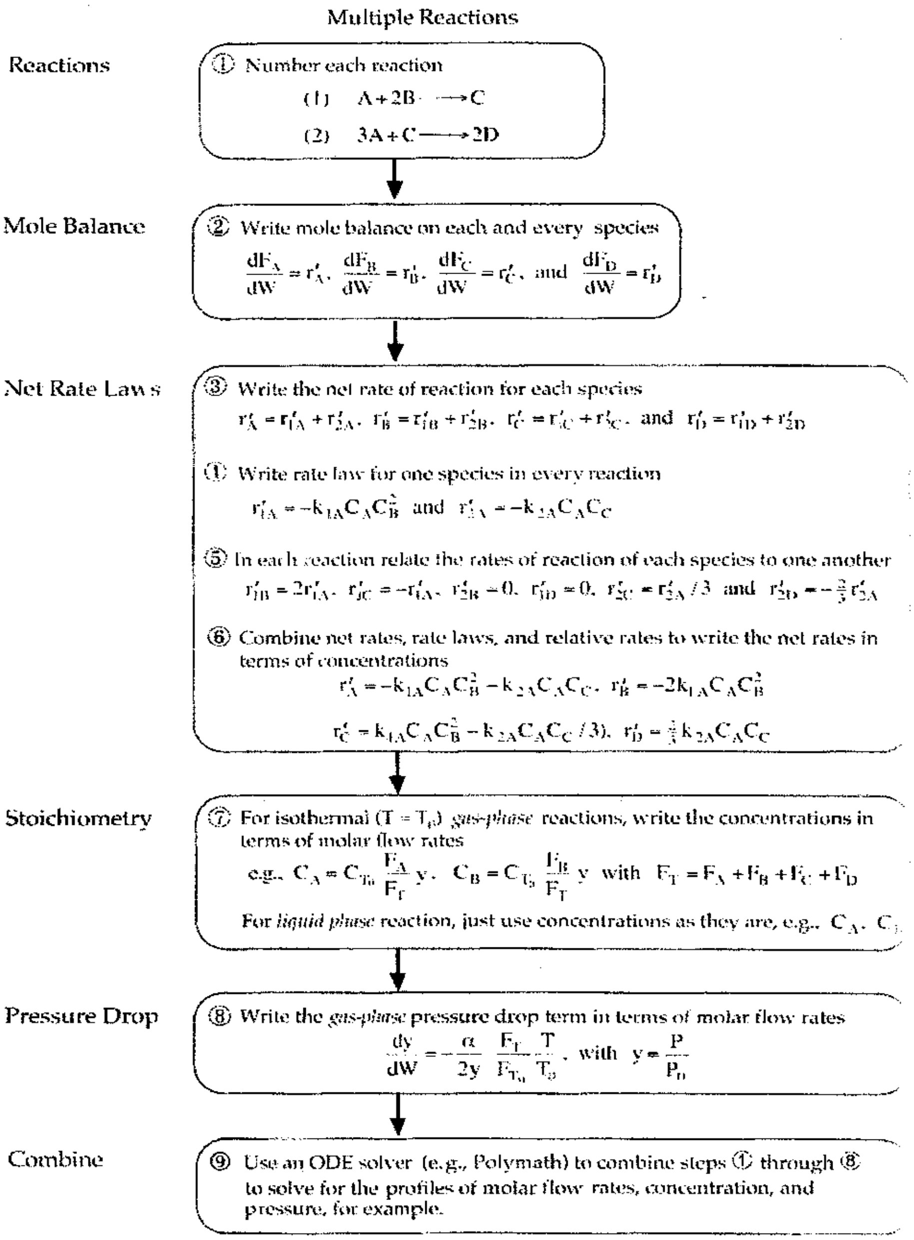
CHAPTER 3

METHODOLOGY

3.1 Overall methodology


START
Research Topic
Identify Data Provider
Collect data and understand the process
Obtained from identified company
Definition of problem
Mathematical modeling of a process
If less efficient
Equation Organization
Computation
Interpretation of a result
Comparison with the actual
If more efficient
Documentation of result
END

3.2 Algorithm for Solution of Complex Reaction



Multiple Reactions

Reactions

① Number each reaction

(1) $A+2B\longrightarrow C$

(2) $3A+C\longrightarrow 2D$

Mole Balance

② Write mole balance on each and every species

$$\frac{dF_A}{dW}=r'_A,\ \frac{dF_B}{dW}=r'_B,\ \frac{dF_C}{dW}=r'_C,\ \text{and}\ \frac{dF_D}{dW}=r'_D$$

Net Rate Laws

③ Write the net rate of reaction for each species

$$r'_A=r'_{1A}+r'_{2A},\ r'_B=r'_{1B}+r'_{2B},\ r'_C=r'_{1C}+r'_{2C},\ \text{and}\ r'_D=r'_{1D}+r'_{2D}$$

④ Write rate law for one species in every reaction

$$r'_{1A}=-k_{1A}C_AC_B^2\ \text{and}\ r'_{2A}=-k_{2A}C_AC_C$$

⑤ In each reaction relate the rates of reaction of each species to one another

$$r'_{1B}=2r'_{1A},\ r'_{1C}=-r'_{1A},\ r'_{2B}=0,\ r'_{1D}=0,\ r'_{2C}=r'_{2A}/3\ \text{and}\ r'_{2D}=-\tfrac{2}{3}r'_{2A}$$

⑥ Combine net rates, rate laws, and relative rates to write the net rates in terms of concentrations

$$r'_A=-k_{1A}C_AC_B^2-k_{2A}C_AC_C,\ r'_B=-2k_{1A}C_AC_B^2$$

$$r'_C=k_{1A}C_AC_B^2-k_{2A}C_AC_C/3),\ r'_D=\tfrac{2}{3}k_{2A}C_AC_C$$

Stoichiometry

⑦ For isothermal ($T=T_0$) *gas-phase* reactions, write the concentrations in terms of molar flow rates

$$\text{e.g., } C_A=C_{T_0}\frac{F_A}{F_T}y,\ C_B=C_{T_0}\frac{F_B}{F_T}y\ \text{ with }\ F_T=F_A+F_B+F_C+F_D$$

For *liquid phase* reaction, just use concentrations as they are, e.g., C_A, C

Pressure Drop

⑧ Write the *gas-phase* pressure drop term in terms of molar flow rates

$$\frac{dy}{dW}=-\frac{\alpha}{2y}\frac{F_T}{F_{T_0}}\frac{T}{T_0},\ \text{with}\ y=\frac{P}{P_0}$$

Combine

⑨ Use an ODE solver (e.g., Polymath) to combine steps ① through ⑧ to solve for the profiles of molar flow rates, concentration, and pressure, for example.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Discussion

The operation behavior of natural gas reformer closely relates to:

- Structure parameters
- Operation conditions.

Structure parameters: Furnace tube diameter, length, wall thickness, heat conduction property, blackness, tube pitch (or pitch between two rows of tubes if multiple rows); burner pattern and arrangement; chamber structure size; and flue gas tunnel arrangement and so on.

Operations conditions: Natural gas components, water carbon ratio, inlet temperature and pressure, operation load; catalyst property, structure, size, and bed void factor; fuel property, temperature, pressure, air surplus coefficient, composition and temperature of turbine exhaust gas, and so on.

- Strong endothermic reaction
- The tubular reactor, also named as primary reformer and used in the industrial units, is heated from outside tubes.
- The tubes are filled with the nickel-based catalyst, to accelerate the natural gas reforming reaction and the flue gas generated in outside tube (chamber) by the combustion process provides heat to reformer tubes through the radiation heat transfer.

4.2.1 Schematic diagram of primary reformer (tubular reactor)

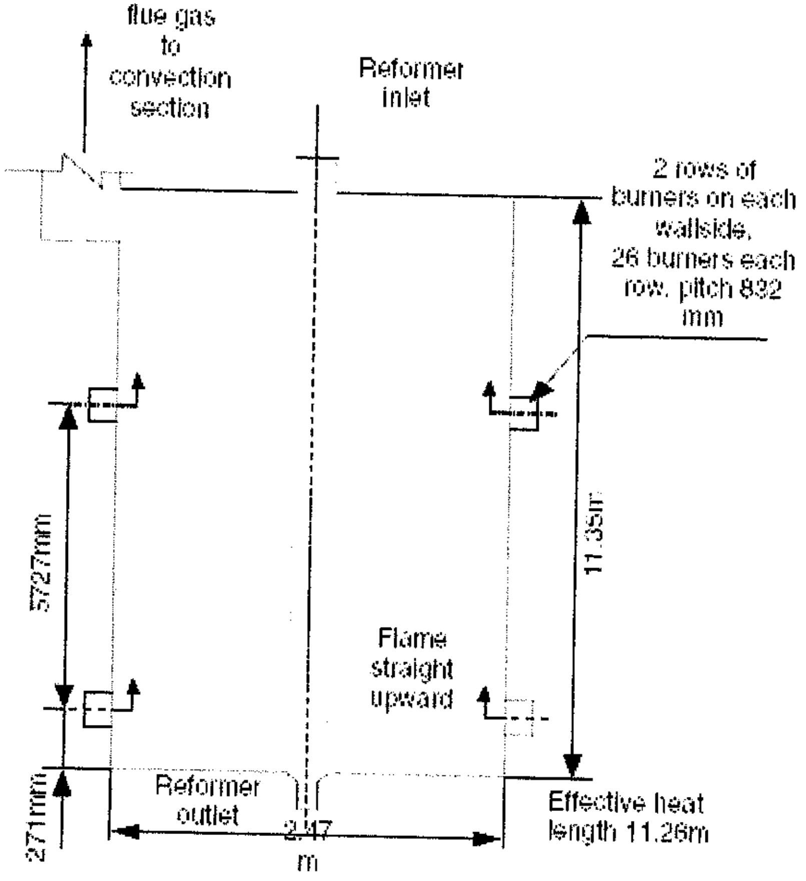


Figure 4.1: The structure of Selas reformer drawing

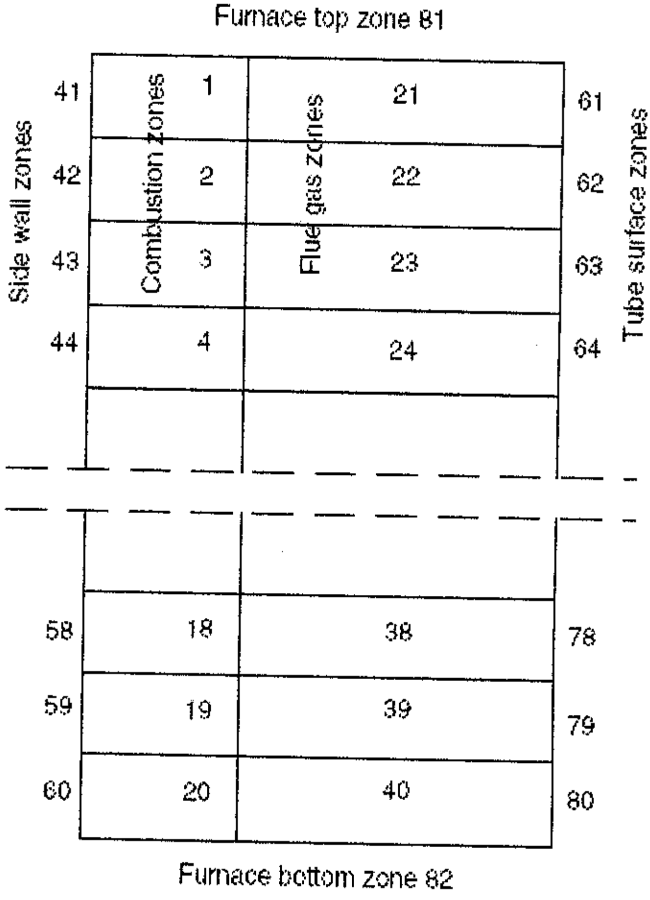


Figure 4.2: Selas reformer district schematic

4.2.2 Inside tube model

Reformer is a tubular packed bed reactor. Its tubes have internal diameter of 152 mm, height of 11.35 mm, filled with the catalyst particles of 16 x 6 x 16 mm (lower section) and 16 x 6 x 8 mm (upper section). At tube entrance reactant gas Reynolds number $Re>10^5$.

Assumptions have been made such as inside tube the gas flow can be considered as a steady state, tube wall effect is significant, temperature and concentrations distributions in radial direction are pronounced, so a two-dimension model is more reasonable. Since it difficult to obtain accurate two-dimension model parameters to describe the mass and heat transfer inside tube, the general way is to assume that the reforming reaction is pseudo-homogeneous phase.

4.2.3 Outside tube model

Selas reformer used in Urumqi Second Ammonia Plant is a furnace which has a single row of tubes, receives the radiation heat from burners installed on two sidewalls (each sidewall has two rows of burner). Its structure is shown if Figure 3.1. Inside reformer,

Chamber size: 11.35 m high, 2.45 m wide and 18 m long

88 tubes made by HP-50 compose a row in middle of the furnace, the inter-tube space is 0.25m, and the tube diameter is 172.6 x 10.3 mm

In the reformer, all 88 tubes have same temperatures at same horizontal altitude, therefore three-dimensional temperature distribution in the reformer can be simplified into two-dimensional one. Since tube arrangement in a Selas sidewall-burning furnace is symmetric, the simulation only needs to study half of tubes. Along the wall and tube, divide the height into 20 sections (each section represents a zone). Correspondingly, the space between the tube row and the wall is divided into 20 zones, the width direction is divided into two kinds of zones (combustion and flue gas zone), the width ratio of these two zones is 1:3, which is similar to the industrial unit. Therefore, the system is divided into 20 sidewall zones, 20 tube-surface zones, 20 combustion zones, 20 flue gas zones, a furnace top zone, and a furnace bottom zone; Its sums up to 82 zones. (see Figure 3.2). So, 82 zone temperatures need to be computed.

4.2.4 Algorithm for Solution of Complex Reactions in the primary reformer

Seldom is the reaction of interest the only one occurs that occurs in a tubular reactor. Typically, multiple reactions will occur, some desired and some undesired. One of the key factors in the economic success of a chemical plant is the minimization of undesired side reactions that occurs along with the desired reaction.

In complex reaction systems consisting of combinations of parallel and series reactions, the availability of software packages (ODE solvers) makes it much easier to solve problems using moles N_j or molar flow rates F_j rather than conversion. For gas systems, the molar flow rates are usually the preferred variable in the mole balance equation.

Below are the mole balance equations for complex reactions where r_A and r_B are the net rates of formation of A and B.

Mole Balance

$dN_A/dt = F_{A0} - F_A + \int^{V} r_A dV$ Equation 1

For packed bed reactor

$dF_A/dV = r_A$ $dF_B/dV = r_B$ Equation 2

4.2.4.1 Reactions

(1) Number each reaction

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ Methane reforming reaction (Reaction 1)

A B C 3D

$CO + H_2O \leftrightarrow CO_2 + H_2$ Water gas shift reaction (Reaction 2)

C B F D

4.2.4.2 Mole Balance

(b) Write mole balance on each and every species Equation 3

$dF_{CH4}/dW = r_{CH4}$ $dF_{H2O}/dW = r_{H2O}$ $dF_{CO}/dW = r_{CO}$

$dF_{H2}/dW = r_{H2}$ $dF_{CO2}/dW = r_{CO2}$

4.2.4.3 Net Rate Laws

(c) Write the net rate of reaction for each species

The key point for multiple reactions is to write the net rate of formation of each species. That is, we have to sum up the rates of formation for each reaction in order to obtain the net rate of formation. In general the net rate of reaction for every species is the sum of all rates of the reactions in which their species appears.

$r_{CH4} = r_{1CH4}$ Equation 4

$r_{H2O} = r_{1H2O} + r_{2H2O}$

$r_{CO} = r_{1CO} + r_{2CO}$

$r_{H2} = r_{1H2} + r_{2H2}$

$r_{O2} = r_{2O2}$

(d) Write rate law for one species in every reaction

The rate laws for each of the individual reactions are expressed in terms of concentrations, C_j, of the reacting species. A rate law is needed for one species in each reaction.

Reaction (1): $CH_4 + H_2O \overset{k_{1A}}{\leftrightarrow} CO + 3H_2$

Followed an elementary rate law, then the rate of disappearance of CH_4 in reaction 1 would be

$$-r_{1CH4} = k_{1CH4}C_{CH4}C_{H2O} \qquad \text{Equation 5}$$

Reaction (3): $CO + H_2O \leftrightarrow CO_2 + H_2$

$$-r_{2CO} = k_{2CO}C_{CO}C_{H2O} \qquad \text{Equation 6}$$

(e) In each reaction relate the rates of reaction of each species to one another.

Reaction (1): $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\quad -r_{1CH4} = k_{1CH4}C_{CH4}C_{H2O}$

Need to relate the rates of formation of other species in Reaction 1 to the given rate law.

$$\frac{r1CH4}{-1} = \frac{r1H2O}{-1} = \frac{r1CO}{1} = \frac{r1H2}{3} \qquad \text{Equation 7}$$

$$r_{1H2O} = r_{1CH4} = -\,k_{1CH4}C_{CH4}C_{H2O} \qquad \text{Equation 8}$$

$$r_{1CO} = -\,r_{1CH4} = k_{1CH4}C_{CH4}C_{H2O} \qquad \text{Equation 9}$$

$$r_{1H2} = 3\,(-r_{1CH4}) = 3\,k_{1CH4}C_{CH4}C_{H2O} \qquad \text{Equation 10}$$

Reaction (2): $CO + H_2O \leftrightarrow CO_2 + H_2$ $\quad -r_{3CO} = k_{3CO}C_{CO}C_{H2O}$

$r_{2H2O} = r_{2CO} = - k_{2CO}C_{CO}C_{H2O}$ Equation 11

$r_{2CO2} = - r_{2CO} = k_{2CO}C_{CO}C_{H2O}$ Equation 12

$r_{2H2} = -r_{2CO} = k_{2CO}C_{CO}C_{H2O}$ Equation 13

(f) Combine net rates, rate laws, and relative rates to write the net rates in terms of concentration.

We now substitute the rate laws for each species in each reaction to obtain the net rate of reaction for that species.

The net rates of reaction for species CH_4, H_2O, CO, H_2 are

$r_{CH4} = r_{1CH4} + r_{2CH4} = - k_{1CH4}C_{CH4}C_{H2O}$ Equation 14

$r_{H2O} = r_{1H2O} + r_{2H2O} = - k_{1CH4}C_{CH4}C_{H2O} - k_{2CO}C_{CO}C_{H2O}$ Equation 15

$r_{CO} = r_{1CO} + r_{2CO} = k_{1CH4}C_{CH4}C_{H2O} - k_{2CO}C_{CO}C_{H2O}$ Equation 16

$r_{H2} = r_{1H2} + r_{2H2} = 3\ k_{1CH4}C_{CH4}C_{H2O} + k_{2CO}C_{CO}C_{H2O}$ Equation 17

$r_{CO2} = r_{3CO2} = k_{3CO}C_{CO}C_{H2O}$ Equation 18

4.2.4.4 Stoichiometry: Concentrations

(g) If the reactions are gas-phase reactions, proceed as follows.

For ideal gases

$C_j = F_{TO}/v_O\ (F_j/F_T)(P/P_O)(T_O/T) = C_{TO}(F_j/F_T)(P/P_O)(T_O/T)$

Where $F_T = \sum_{j=1}^{n} F_j$

And $C_{TO} = P_O/RT_O$

*For isothermal system ($T=T_O$) with no pressure drop ($P=P_O$)

$C_j = C_{TO}\ (F_j/F_T)$

Now insert rate laws written in terms of molar flow rates into the mole balances. After performing this operation for each species, arrive at a coupled set of first-order ordinary differential equations to be solved for the molar flow rates as a function of reactor volume (distance along the length of the reactor)

Combining mole balance, rate laws and stoichiometry for species in the gas phase and for isothermal operation with no pressure drop gives us:

Coupled ODE

$$dF_1/dV = r_1 = \sum_{i=1}^{m} \quad r_{i1} = f_{n1}\,[C_{TO}\,(F_1/F_T), \ldots . C_{TO}F_j/F_T]$$

There are coupled ordinary differential equations that must be solved simultaneously with either a numerical package or by writing and ODE solver.

In combining the mole balance, rate laws, and stoichiometry, the results from (a) to (g) have been used. The total molar flow rate of all the gases is:

$$F_T = F_{CH4} + F_{H2O} + F_{CO} + F_{H2} + F_{CO2}$$

Equation 19

Rewrite mole balances on each species in the total molar flow rate.

- Mole Balance on CH_4

$$dF_{CH4}/dV = r_{CH4} = -\ k_{1CH4}C_{CH4}C_{H2O}$$

$$dF_{CH4}/dV = -k_{1CH4}C^2_{TO}\,(F_{CH4}/F_T)\,(F_{H2O}/F_T)$$

Equation 20

Mole Balance on H_2O

$$dF_{H2O}/dV = r_{H2O} = -\ k_{1CH4}C_{CH4}C_{H2O} - k_{2CO}C_{CO}C_{H2O}$$

$$= -k_{1CH4}C^2_{TO}\,(F_{CH4}/F_T)\,(F_{H2O}/F_T) - k_{2CO}C^2_{TO}\,(F_{CO}/F_T)\,(F_{H2O}/F_T)$$

Equation 21

- Mole Balance on CO

$$dF_{CO}/dV = r_{CO} = k_{1CH4}C_{CH4}C_{H2O} - k_{2CO}C_{CO}C_{H2O}$$

$= -k_{1CH4}C^2_{TO}(F_{CH4}/F_T)(F_{H2O}/F_T) - k_{2CO}C^2_{TO}(F_{CO}/F_T)(F_{H2O}/F_T)$

Equation 22

- **Mole Balance on H_2**

$dF_{H2}/dV = r_{H2} = 3\ k_{1CH4}C_{CH4}C_{H2O} + k_{2CO}C_{CO}C_{H2O}$

$= 3\ k_{1CH4}C^2_{TO}(F_{CH4}/F_T)(F_{H2O}/F_T) - k_{2CO}C_{TO}^2(F_{CO}/F_T)(F_{H2O}/F_T)$ Equation 23

- **Mole Balance on CO_2**

$dF_{CO2}/dV = r_{CO2} = k_{2CO}C_{CO}C_{H2O}$

$= - k_{2CO}C_{TO}^2(F_{CO}/F_T)(F_{H2O}/F_T)$

Equation 24

$C_{T0} = P_0/RT_o = 170.61\ mol/m^3$

4.2 Result

Table 4.1: ODE Solver Algorithm for Multiple Reactions

(1) $dF_{CH4}/dV = r_{CH4}$
(2) $dF_{H2O}/dV = r_{H2O}$
(3) $dF_{CO}/dV = r_{CO}$
(4) $dF_{H2}/dV = r_{H2}$
(5) $dF_{CO2}/dV = r_{CO2}$
(6) $r_{CH4} = - k_{1CH4}C_{CH4}C_{H2O}$
(7) $r_{H2O} = - k_{1CH4}C_{CH4}C_{H2O} - k_{2CO}C_{CO}C_{H2O}$
(8) $r_{CO} = k_{1CH4}C_{CH4}C_{H2O} - k_{3CO}C_{CO}C_{H2O}$
(9) $r_{H2} = 3\ k_{1CH4}C_{CH4}C_{H2O} + k_{2CO}C_{CO}C_{H2O}$
(10) $r_{CO2} = k_{2CO}C_{CO}C_{H2O}$
(11) $r_{1H2O} = r_{1CH4}$
(12) $r_{1CO} = - r_{1CH4}$
(13) $r_{1H2} = 3\ (-r_{1CH4})$
(14) $r_{2H2O} = r_{2CO}$
(15) $r_{2H2O} = r_{2CO}$
(16) $r_{2CO2} = - r_{2CO}$
(17) $r_{2H2} = -r_{2CO}$
(18) $r_{CH4} = r_{1CH4} + r_{2CH4}$
(19) $r_{H2O} = r_{1H2O} + r_{2H2O}$
(20) $r_{CO} = r_{1CO} + r_{2CO}$
(21) $r_{H2} = r_{1H2}$
(22) $r_{CO2} = r_{2CO2}$
(23) $C_{CH4} = C_{TO}F_{CH4}/F_T$
(24) $C_{H2O} = C_{TO}F_{CH4}/F_T$
(25) $C_{CO} = C_{TO}F_{CO}/F_T$
(26) $C_{H2} = C_{TO}F_{H2}/F_T$
(27) $C_{CO2} = C_{TO}F_{CO2}/F_T$
(28) $F_T = F_{CH4} + F_{H2O} + F_{CO} + F_{H2} + F_{O2} + F_{CO2}$
(29) $C_{T0} = 170.61$ mol/m^3
(30) $k_{CH4} = 0.179$ bar-1
(31) $k_{CO} = 40.91$ bar-1
(32) $F_{CH4} = 1781.25$ kmol/hr
(33) $F_{H2O} = 5343.75$ kmol/hr
(34) $F_{CO} = 0$ kmol/hr
(35) $F_{H2} = 0$ kmol/hr
(36) $F_{CO2} = 4.275$ kmol/hr

4.2.1 Result from Polymath:

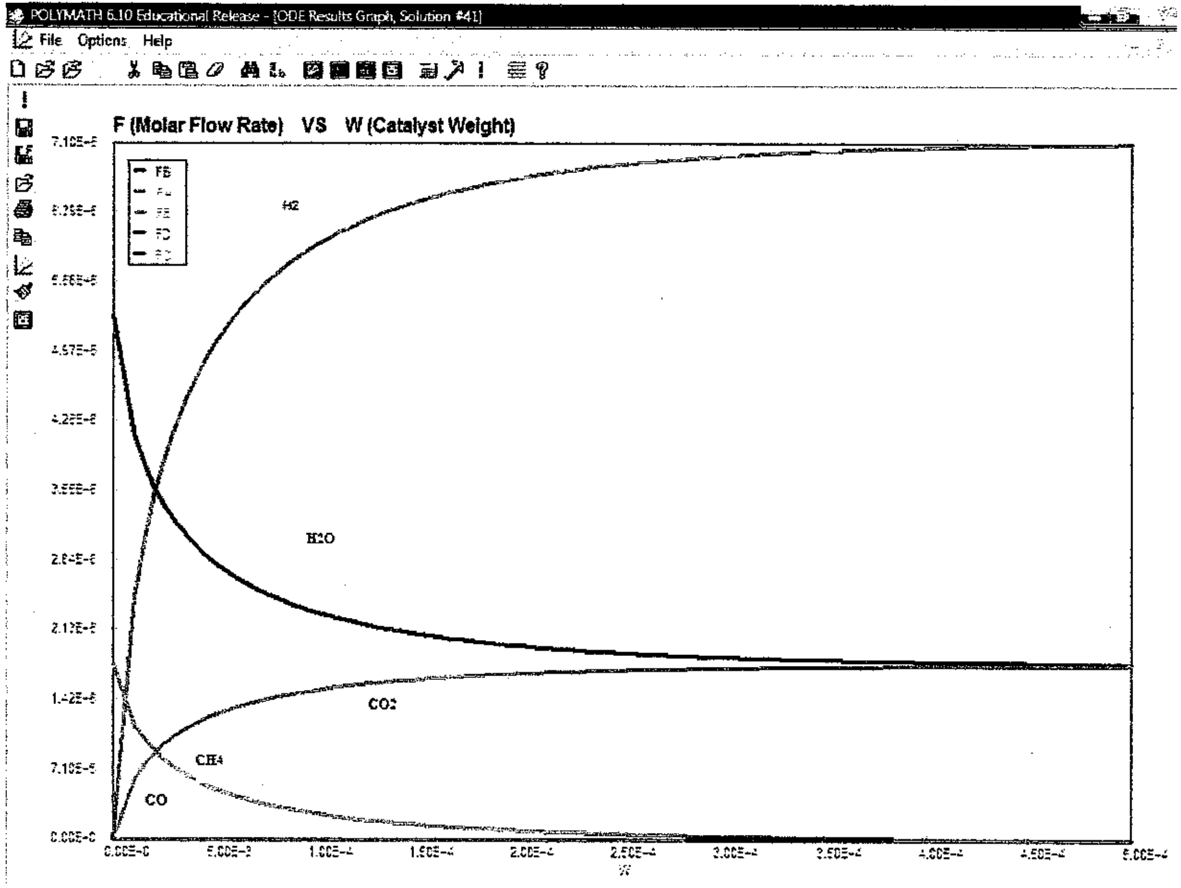


Figure 4.3: Graph F (Molar Flow Rate) VS W (Catalyst Weight)

Figure above is the graph for F, Molar flow rate of chemical species inside the primary reformer versus catalyst weight (W) that will be get after the optimum weight has been identified throughout this graph. From the graph we can consider that the weight of catalyst that produce highest molar flow rate for the hydrogen is the optimum weight for catalyst in the primary reformer. Hydrogen is the most desired chemical species in the primary reformer, so the highest molar flow rate of hydrogen can produce the highest conversion and yield of hydrogen.

So from the graph, it shows that we can get 7096 kmol/hr of hydrogen if 50,000g or 50 kg of catalyst used. So here we can conclude that 50kg of catalyst is the most optimum catalyst weight for the primary reformer.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The entering molar flow rates, F_{jo}, along with the entering temperature, T_o, and pressure, P_o are specified as are the specific reaction rates k_{ij}. Consequently, all the mole balance equations can be solved simultaneously with an ODE solver (Polymath). In fact, with almost all ODE solvers, the combine step can be eliminated as the ODE solver will do the work. In this case, the ODE solver algorithm is shown in Table 4.1.

From the graph, it shows that 7096 kmol/hr of hydrogen will be produced if 50,000g or 50 kg of catalyst been used. So here we can conclude that 50kg of catalyst is the most optimum catalyst weight for the primary reformer.

5.2 Recommendation

The process modeled and optimized here is an equilibrium model. That is, each reactor is assumed to be operating at equilibrium. In reality however, equilibrium cannot be reached, and an approached to equilibrium model should be adopted. The approach to equilibrium in the reformers is affected by choice of catalyst. Numerous catalysts of differing properties are available to suit specific purposes. Once a catalyst is chose, parameters such as catalyst activity, surface area, particle size, crush strength, and nickel content among others should be considered to more accurately model the process.

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APPENDICES

APPENDIX 1: REPORT FROM POLYMATH

LYMATH Report
dinary Differential Equations

No Title
01-Jun-2009

	Variable	Initial value	Minimal value	Maximal value	Final value
	CA	42.62692	0.1175844	42.62692	0.1175844
	CB	127.8808	28.6985	127.8808	28.6985
	CC	0	0	0.1045428	0.0005167
	CD	0	0	113.3804	113.3804
	CE	0.1023046	0.1023046	28.41302	28.41302
	CTo	170.61	170.61	170.61	170.61
	FA	1.781E+06	7358.629	1.781E+06	7358.629
	FB	5.344E+06	1.796E+06	5.344E+06	1.796E+06
	FC	0	0	5122.892	32.33887
0	FD	0	0	7.096E+06	7.096E+06
1	FE	4275.	4275.	1.778E+06	1.778E+06
2	FT	7.129E+06	7.129E+06	1.068E+07	1.068E+07
3	k1A	0.179	0.179	0.179	0.179
4	k2C	40.91	40.91	40.91	40.91
5	r1A	-975.7583	-975.7583	-0.6040348	-0.6040348
6	r1B	-975.7583	-975.7583	-0.6040348	-0.6040348
7	r1C	975.7583	0.6040348	975.7583	0.6040348
8	r1D	2927.275	1.812104	2927.275	1.812104
9	r2B	0	-359.3892	0	-0.6066894
0	r2C	0	-359.3892	0	-0.6066894
1	r2D	0	0	359.3892	0.6066894
2	r2E	0	0	359.3892	0.6066894
3	rA	-975.7583	-975.7583	-0.6040348	-0.6040348
4	rB	-975.7583	-975.7583	-1.210724	-1.210724
5	rC	975.7583	-1.572491	975.7583	-0.0026545
6	rD	2927.275	2.418794	2927.275	2.418794
7	rE	0	0	359.3892	0.6066894
8	W	0	0	5.0E+04	5.0E+04

d(FB)/d(W) = rB
d(FA)/d(W) = rA
d(FE)/d(W) = rE
d(FD)/d(W) = rD
d(FC)/d(W) = rC

```
1  k1A = 0.179
   bar^-1
2  CTo = 170.61
   mol/m^3
3  FT = FA+FB+FC+FD+FE
4  CC = CTo*FC/FT
5  CE = CTo*FE/FT
6  CD = CTo*FD/FT
7  k2C = 40.91
8  CB = CTo*FB/FT
9  r2C = -k2C*CC*CB
10 CA = CTo*FA/FT
   concentration
11 r2D = -r2C
12 rA = -k1A*CA*CB
   Net rates in terms of concentration
13 r1A = rA
14 r2E = -r2C
15 r1D = 3*(-r1A)
16 r1C = -r1A
17 r1B = r1A
18 r2B = r2C
19 rE = k2C*CC*CB
20 rB = -k1A*CA*CB-k2C*CC*CB
21 rD = (3*k1A)*CA*CB+k2C*CC*CB
22 rC = k1A*CA*CB-k2C*CC*CB
```

otal number of equations	27
umber of differential equations	5
umber of explicit equations	22
lapsed time	1.157 sec
olution method	RKF_45
tep size guess. h	0.000001
runcation error tolerance. eps	0.000001

ata file: c:\users\juls\documents\norzuliana.pol

APPENDIX 2: TABLE FROM POLYMATH

OLYMATH Polynomial Regression Migration Document

(Cat. weight	FD (H2)			
0	0	5015600.867	5015600.867	2.51563E+13
1067.666	2457000	5075196.647	2618196.647	6.85495E+12
1500.034	3001000	5099330.888	2098330.888	4.40299E+12
2033.254	3519000	5129094.561	1610094.561	2.5924E+12
2528.092	3899000	5156715.799	1257715.799	1.58185E+12
3010.033	4204000	5183617.142	979617.1425	9.5965E+11
3532.168	4481000	5212762.065	731762.0648	5.35476E+11
4094.15	4733000	5244131.197	511131.1968	2.61255E+11
4579.988	4920000	5271250.066	351250.066	1.23377E+11
5016.924	5069000	5295639.287	226639.2867	51365366278
5563.238	5234000	5326133.851	92133.85054	8488646415
6124.567	5383000	5357466.533	-25533.46712	651957943.2
6557.633	5486000	5381639.735	-104360.2649	10891064897
7026.057	5588000	5407786.577	-180213.4234	32476877984
7545.724	5691000	5436793.738	-254206.2618	64620823534
8040.473	5779000	5464410.008	-314589.9917	98966862897
8530.355	5860000	5491754.608	-368245.3915	1.35605E+11
9080.087	5942000	5522439.961	-419560.0392	1.76031E+11
9632.479	6018000	5553273.791	-464726.209	2.1597E+11
10010	6067000	5574346.541	-492653.4592	2.42707E+11
10600	6136000	5607279.602	-528720.3975	2.79545E+11
11010	6181000	5630165.289	-550834.7106	3.03419E+11
11590	6239000	5662540.164	-576459.8364	3.32306E+11
12050	6283000	5688216.788	-594783.212	3.53767E+11
12630	6334000	5720591.662	-613408.3378	3.7627E+11
13100	6373000	5746826.474	-626173.526	3.92093E+11
13550	6407000	5771944.911	-635055.0891	4.03295E+11
14020	6442000	5798179.723	-643820.2773	4.14505E+11
14660	6485000	5833903.722	-651096.2782	4.23926E+11
15110	6514000	5859022.159	-654977.8413	4.28996E+11
15610	6544000	5886931.533	-657068.467	4.31739E+11
16080	6570000	5913166.345	-656833.6551	4.3143E+11
16590	6597000	5941633.907	-655366.0933	4.29505E+11
17060	6621000	5967868.719	-653131.2815	4.2658E+11
17580	6646000	5996894.468	-649105.5322	4.21338E+11
18070	6667000	6024245.655	-642754.3454	4.13133E+11
18580	6689000	6052713.216	-636286.7836	4.04861E+11
19080	6710000	6080622.591	-629377.4093	3.96116E+11
19600	6729000	6109648.34	-619351.66	3.83596E+11
20120	6748000	6138674.089	-609325.9107	3.71278E+11
20640	6766000	6167699.839	-598300.1614	3.57963E+11
21160	6783000	6196725.588	-586274.4121	3.43718E+11
21510	6794000	6216262.15	-577737.8501	3.33781E+11
22030	6809000	6245287.899	-563712.1008	3.17771E+11
22570	6824000	6275430.023	-548569.9766	3.00929E+11
23100	6838000	6305013.96	-532986.0398	2.84074E+11
23640	6852000	6335156.084	-516843.9156	2.67128E+11
24180	6864000	6365298.209	-498701.7913	2.48703E+11
24540	6873000	6385392.958	-487607.0418	2.37761E+11
25080	6884000	6415535.082	-468464.9176	2.19459E+11
25620	6896000	6445677.207	-450322.7933	2.02791E+11
26170	6907000	6476377.518	-430622.4816	1.85436E+11
26540	6914000	6497030.455	-416969.5446	1.73864E+11
27080	6923000	6527172.58	-395827.4203	1.56679E+11
27640	6933000	6558431.079	-374568.9211	1.40302E+11
28000	6939000	6578525.828	-360474.1716	1.29942E+11
28560	6948000	6609784.328	-338215.6724	1.1439E+11

Coefficients	55.81875	5015600.867
Std.dev.s	5.447983	158887.7877
R2, SE (y)	0.517184	787632.6611
95% conf. int.	10.67805	311420.0638
Variance	6.2E+11	
Sum of Squares	6.08E+13	
Model	FD = a1 * W + a0	

29110	6956000	6640484.639	-315515.3606	99549942791
29680	6964000	6672301.326	-291698.6739	85088116363
30040	6969000	6692396.076	-276603.9244	76509731000
30610	6976000	6724212.762	-251787.2377	63396813068
31170	6983000	6755471.262	-227528.7385	51769326831
31550	6988000	6776682.386	-211317.614	44655133986
32110	6994000	6807940.885	-186059.1148	34617994190
32680	7000000	6839757.572	-160242.4281	25677635751
33050	7004000	6860410.509	-143589.4911	20617941946
33620	7010000	6892227.196	-117772.8044	13870433447
34000	7014000	6913438.32	-100561.6799	10112651461
34570	7019000	6945255.007	-73744.99317	5438324018
35140	7024000	6977071.694	-46928.30646	2202265947
35520	7027000	6998282.818	-28717.18199	824676541.3
36100	7032000	7030657.692	-1342.307789	1801790.199
36660	7036000	7061916.191	25916.19144	671648978.6
37050	7039000	7083685.503	44685.5034	1996794214
37620	7043000	7115502.19	72502.19011	5256567571
38010	7046000	7137271.502	91271.50207	8330487090
38580	7049000	7169088.189	120088.1888	14421173085
39160	7053000	7201463.063	148463.063	22041281070
39550	7055000	7223232.375	168232.3749	28302131979
40120	7058000	7255049.062	197049.0617	38828332699
40510	7061000	7276818.374	215818.3736	46577570390
41090	7064000	7309193.248	245193.2478	60119728773
41670	7066000	7341568.122	275568.122	75937789869
42050	7068000	7362779.246	294779.2465	86894804159
42640	7071000	7395712.308	324712.3082	1.05438E+11
43020	7073000	7416923.433	343923.4326	1.18283E+11
43610	7075000	7449856.494	374856.4943	1.40517E+11
44190	7077000	7482231.369	405231.3685	1.64212E+11
44580	7079000	7504000.68	425000.6805	1.80626E+11
45160	7081000	7536375.555	455375.5547	2.07367E+11
45550	7082000	7558144.867	476144.8666	2.26714E+11
46130	7084000	7590519.741	506519.7408	2.56562E+11
46520	7086000	7612289.053	526289.0528	2.7698E+11
47110	7088000	7645222.114	557222.1145	3.10496E+11
47690	7089000	7677596.989	588596.9887	3.46446E+11
48080	7091000	7699366.301	608366.3007	3.7011E+11
48670	7092000	7732299.362	640299.3623	4.09983E+11
49060	7093000	7754068.674	661068.6743	4.37012E+11
49640	7095000	7786443.548	691443.5485	4.78094E+11
50000	7096000	7806538.298	710538.298	5.04865E+11