Chemical Exergy Analysis on Ammonia Synthesis Reaction

by

Wansalma Useng

Dissertation submitted in partial fulfillment of
The requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2011

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Chemical Exergy Analysis on Ammonia Synthesis Reaction

by

WANSALMA USENG

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(AP Dr Shuhaimi Mahadzir)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK DARUL RIDZUAN

SEPTEMBER 2011

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.

Wansalma Useng

WANSALMA USENG

ACKNOWLEDGEMENT

The author wishes to take the opportunity to express her utmost gratitude to the individual that have taken the time and effort to assist the author in completing the project. Without the cooperation of these individuals, no doubt the author would have faced some minor complications throughout the course.

First and foremost, I would like to express my gratitude to Allah SWT for His Blessings and for granting me the opportunity to complete this Final Year Project (FYP). Secondly, I would like to thank my supervisor AP Dr Shuhaimi Mahadzir for his valuable guidance and advice while conducting this project. The willingness to spend his valuable time and effort to assist me has vastly contributed to the successful completion of the project.

I also acknowledge AP Dr Bambang Ari Wahjoedi, the fundamental science lecturer, who has provided all the necessary guidance for the basic knowledge and the calculation methodology used throughout the project. It really helps my understanding on how to acquire the vital model for the project.

I hope that this project will be beneficial and contribute greatly to the industry in the future.

ABSTRACT

The chemical exergy analysis method is based on the second law of thermodynamics. The method is introduced to the study of process design of chemical processes optimization. In this work, chemical exergy is used as a basis to assess reversible reactions. Ammonia synthesis reaction is selected as case study.

Chemical exergy analysis is applied to estimate the effect of the process parameters, which are operating pressure and temperature, on the trend of ammonia reaction conversion. The proposed method used for the study is based on Gibbs free energy and the calculation of chemical equilibrium. This study aims to be able to identify the optimal value of process conditions for ammonia production. The main objective of this research is to identify the optimal operating condition that gives the highest ammonia reaction conversion. The finding will provide information to improvement operation performance of an industrial ammonia production.

The exergy analysis result in this research shows that at 500 degree Celsius, which is the typical operating temperature used in industrial production, the ammonia yield tends to arise in a very small amount. This is resulting from the minimum reaction driving force or minimum work available for the reaction to take place in the respective temperature.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

Ex	Exergy
Ex_{phys}	Physical exergy
Ex^0_{chem}	Chemical exergy
ΔG	Gibbs free energy change
ΔG^0	Standard Gibbs free energy
ΔG^0_f	Standard Gibbs free energy of formation
ΔG_r	Gibbs free energy of reaction
H	Enthalpy
H_f	Enthalpy of formation
ΔH	Enthalpy change
K_{eq}	Equilibrium constant
P_0	Pressure at environment state
Q	Reaction quotient
R	Gas constant
S	Entropy
ΔS	Entropy change
T_0	Temperature at environment state
X	Production conversion ratio

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Production of ammonia is one of major production in petrochemical industry in the world. Ammonia is a chemical that is widely produced for upstream or downstream process in many chemical related industries such as fertilizer and pharmaceuticals.

The Haber process, which developed during WWI by the chemist Fritz Haber, is a method used to manufacture ammonia by taking molecular nitrogen (N_2) from air and combines it with molecular hydrogen (H_2) obtained from methane, natural gas, to form nitrogen gas, which the chemical formula is NH_3. The reversible reaction of ammonia synthesis is described by the equation (1-1)

$$N_{2\,(g)} + 3H_{2\,(g)} \leftrightarrow 2NH_{3\,(g)} \tag{1-1}$$

The industrial condition for producing ammonia requires temperature around 450 to 500 degree Celsius. The forward reaction is exothermic which mean if we remove heat as product by lowering the operating temperature, it will result in the equilibrium mixture that is richer in ammonia. Figure 1.1 describes the trend of ammonia production according to thermodynamic properties of reversible reaction as stated in Le Chatelier principle.

Figure 1.1: Trend of ammonia production with varied operating condition

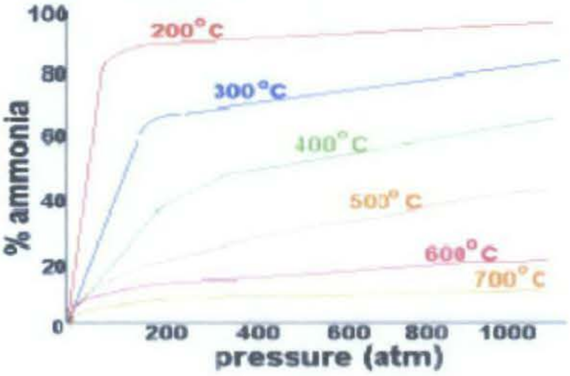


Figure source: http://www.ausetute.com.au/haberpro.html

In Haber process, the reaction conducted at 500 degree Celsius because higher temperature increases the rate of reaction. It's not applicable in the industrial production to have 90% ammonia yield if it takes all day to fill a production bucket full than to have 10% ammonia yield very quickly filled thousands of liters by the end of the day. And from the same principle, ammonia synthesis reaction is favored at high pressure, but it is too expensive to make a high pressure chemical plant above 200 atm with the greatest return value in addition. High pressure process is difficult to control as well. Since the reaction is restricted by the unfavorable position of the chemical equilibrium, heterogeneous type of iron catalyst is introduced to increase the rate of the reaction mixture to reach its equilibrium composition more quickly. However, not more than 20-25 % of the synthesis gas is converted to ammonia per pass.

Due to the thermodynamically limited to low conversion of ammonia production, industrial ammonia synthesis is designed with a recycle stream. Significant amount of reactants are recycled back to the upstream reactors, after the removal of ammonia at low temperatures. As a result, many modern ammonia production plants use well-developed thermodynamically designed process to improve the reaction heat utilization and reduced energy consumption costs.

In this project, the chemical exergy analysis method is applied to explore and evaluate the chemical equilibrium in a relationship with thermodynamic properties of substances to identify the optimal value of the production conditions.

1.1.1 Concept of Chemical Exergy

In order to make a preparation for performing a thermodynamic analysis of a process, the principle of such an analysis should be defined first. Exergy, generally, is defined as the ideal amount of work to perform a certain task. Exergy can have a physical and a chemical component called physical exergy and standard chemical exergy, which can be distinguished as shown in equation (1-2)

$$\mathbf{Ex} = \mathbf{Ex}_{\mathbf{phys}} + \mathbf{Ex}^{\mathbf{0}}_{\mathbf{chem}} \qquad \textbf{(1-2)}$$

The first term on the right-hand side of this equation, the physical exergy, expresses the amount of work available due to differences in the pressure and temperature with the environment.

The second term is the standard chemical exergy term, which expresses the amount of work available due to the differences in composition with respect to the environment. The superscript in Ex^0_{chem} expresses that the standard chemical exergy is considered at ambient conditions (Krishnan, et al., 2004).

The chemical exergy of a pure substance is the maximum amount of work that can be obtained by taking it to ***chemical equilibrium*** with the reference environment at constant temperature and pressure. The chemical exergy has two contributions: reactional exergy, resulting from the chemical reactions necessary to produce species existing as stable components in the environment, from the initial composition of the substance; and concentrational exergy, which results from the necessary processes to match the chemical concentration of the produced species to their chemical concentration in the environment. The quantity of the chemical exergy depends on the environmental model that is selected as reference. (Rivero, and Garfias, 2006)

The property exergy can be defined mathematically by the equation (1-3)

$$\mathbf{Ex = (H - T_0S)_{P,T} - (H - T_0S)_{Po,To} = \Delta H - T_0\Delta S} \qquad \mathbf{(1\text{-}3)}$$

where the term $\Delta H - T_0\Delta S$ often indicates the availability function. The availability function at environmental conditions can be identified as the ***Gibbs energy*** (Dincer, and Rosen, 2007), which is also the chemical potential that is minimized when a system reaches equilibrium at constant pressure and temperature and thus it indicates the spontaneity of a reaction. Some authors say that Gibbs free energy depends on both the enthalpy and entropy changes of a reaction, and they even refer to reactions as "energy driven" or "enthalpy driven" (Lower, 2010). It can also be defined by the equation (1-4)

$$\mathbf{\Delta G = \Delta H - T_0\Delta S} \qquad \mathbf{(1\text{-}4)}$$

Furthermore, the concept of exergy has a distinct advantage over the Gibbs energy of formation. The only difference between the two concepts is that their zero values are defined for different reference substances (Krishnan, et al., 2004). It can be seen from above equations and theories that the chemical exergy and Gibbs free energy are allied.

1.1.2 Application of Chemical Exergy Analysis

Exergy analysis is a general method for efficiency analysis of systems and processes by evaluating quantitatively the causes resulting in increases of exergy due to thermodynamic imperfections of thermal and chemical processes but the use of the exergy concept and the analysis of ultimate efficiencies of processes are more or less still limited to the academic world.

As mention previously, the chemical exergy of a reaction is the maximum work that can be obtained from it by taking it to chemical equilibrium with the reference environment at a constant temperature and pressure. For better understanding, the application of chemical exergy can be illustrated through researches which used chemical exergy analysis as tools of the study.

Refer to a research paper called "Computation of Chemical Exergy Potential in an Industrial AC Electric ARC Furnace" by Camdali and Tunc (2005), it is found that the chemical exergy destruction during the process occurred due to chemical reactions and combustions. In this study, the chemical exergy analysis conducted by calculating the chemical exergy potential in an electric arc furnace (EAF) and these potentials are distributed depending on production materials, emphasizing the chemical exergy concept. The author found that if the processes being analyzed do not involve chemical reactions, there are no changes in chemical composition of the streams crossing the control surface, and there is no exchange process of substances with the environment, thus the chemical component of exergy will not be taken into consideration.

Ozturk, et al., (2007) conducted a study to identify the best solution of how to reduce or completely eliminate emissions of greenhouse gases and other pollutants. The authors found out that those gases can be eliminated by substituting fossil fuels with a clean energy source, e.g. solar energy, which need the energy conversion into chemical energy carriers. In this research he established that water-gas shift reaction, as the main energy conversion reaction, in parabolic trough collector, is evaluated by using the heat exergy and chemical exergy analysis approach.

Furthermore, Zausner (2007) published the research called "Thermodynamic Analysis of CO_2 Capture Cycles Using Pre-Combustion Decarbonization and Membrane Technologies." The study focused on precombustion decarbonization cycles that reform syngas, separating the CO_2 using a membrane, and then burning hydrogen-rich fuel in a gas turbine. The author examined the overall performance of the syngas reforming section, it showed an efficiency loss of 8.4% and 10.6% compared to the baseline cycle for the high and low temperature CO_2 membrane cycles, since the operating temperatures of the membranes are limited by the exothermic CO shift reaction favoring lower temperatures. In this research, the chemical exergy analysis of the reformers in the decarbonization system is undertaken to understand the impact of fuel reforming.

There are no limits or any specific pattern on how the chemical exergy analysis approach can be introduced to the study. These researches raised above are only few illustration of the application of chemical exergy analysis.

1.2 PROBLEM STATEMENT

Since early studies, it was found that the conversion of ammonia synthesis is limited by thermodynamics. The gas volume decreases with reaction, hence, high operating pressures must be used to push equilibrium to the right in reaction according to the Le Chatelier principle.

Ammonia synthesis from nitrogen and hydrogen is also exothermic,

$$\mathbf{N_{2\,(g)} + 3\,H_{2\,(g)} \leftrightarrow 2\,NH_{3\,(g)} \qquad \Delta H = -92\ KJ/mol}$$

Therefore conversion to ammonia increases with decreasing temperature. However, to achieve industrially acceptable reaction rates, the reaction temperature must be high. The trade-off solution is to operate at temperatures in the range of 450 to 500°C, at which the equilibrium conversion is on the order of 10 to 15%. The reason behind this decision is that the low operating temperature has an effect on the rate of reaction. The lower the temperature, the slower the rate of reaction. This is because nearly all chemical reactions have some activation barrier which must be overcame before the reaction can proceed, and the high temperature helps to get over this barrier. However, the understanding of this reaction barrier is not well understood.

Thus the study on chemical reaction of reversible reaction and thermodynamics of ammonia synthesis in a relationship with chemical exergy is required in order to have a clear understanding on the nature of the reaction and be able to identify the optimum operating condition for ammonia production.

1.3 OBJECTIVES

1) To analyze and identify the optimum condition, i.e. operating temperature, for ammonia synthesis reaction
2) To construct graphical understanding of thermodynamic effect on ammonia synthesis reaction, e.g. Gibbs energy of reaction versus temperature, equilibrium conversion versus temperature, and amount of exergy versus temperature.

1.4 SCOPE OF STUDY

This study aims to determine the optimal value of process parameters which include the operating temperature and pressure of ammonia production. The area of knowledge in this research involves fundamental of chemical equilibrium and thermodynamics of reversible chemical reaction, which is needed to be comprehended clearly in order to be able to identify process variables which have effect on the equilibrium change of ammonia synthesis reaction. Furthermore, this research study ultimately aims to be able to determine the relationship between chemical exergy and the conversion in ammonia production.

CHAPTER 2

LITERATURE REVIEW

As mentioned earlier in this report, it has been realized that the concept of chemical exergy has a distinct advantage over the Gibbs free energy of formation; besides, the general equations of the chemical exergy and the Gibbs free energy are also allied. The only different between the two concepts is that their zero values are defined for different substances. Thus, in this research, the Gibbs free energy concept is chosen as the key model for the preliminary study stage.

The Gibbs free energy is a quantity that becomes more negative during the course of any natural process. The values of Gibbs energy is counted as the driving force for the reactions. As a chemical reaction takes place, the free energy will only fall and never become more positive. Eventually a point is reached where any further transformation of reactants into products will cause this free energy to increase. At this point where the free energy is at a minimum and no further net change can take place, the reaction is at equilibrium. (Lower, S., 2010)

This schematic approach allows us to define one of the fundamental statements of chemistry; *a system will come to equilibrium when it has reached its minimum free energy.* (Price, G., 1998)

In fact, many industrial reactions are not carried to equilibrium, thus the reactor design is based primarily on reaction rate, however, the choice of operating conditions may possibly still be influenced by equilibrium considerations. (Bejan, A., 1997)

Even from early studies, it is realized that from the Le Châtelier law alone, it is apparent that this exothermic reaction is favored by low temperature and high pressure. However, it was not as simple as that: the rate of any reaction increases with the temperature, so working with temperature alone, one has the choice between a high product yield achieved only very slowly or a very low yield quickly.

Let's now discuss on the basic understanding on the application of equilibrium criteria to chemical reactions. At the constant temperature and pressure conditions, chemical change will tend to occur in the direction that leads to a decrease in the value of the ***Gibbs free energy***. If the total free energy of reaction of a mixture, reactants and products, goes through a minimum value as the composition changes, then all net change will stop, the reaction system will be in a state of ***chemical equilibrium*** (Atkins, P., 2008). The relative concentration of reactants and products in the equilibrium state is expressed by the ***equilibrium constant*** which is determined the standard free energy change, as shown in equation (2-1)

$$\Delta G^{o} = RT \ln K_{eq} \qquad (2\text{-}1)$$

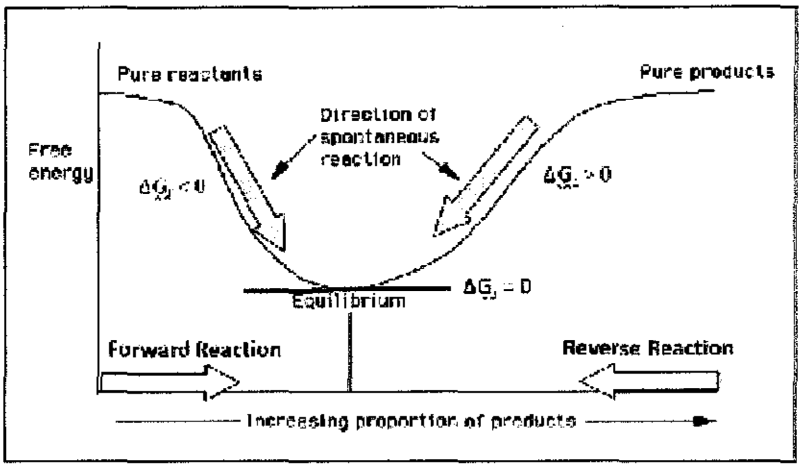
For a ***homogeneous chemical reaction***, the free energies of the reactants become more negative as the reaction proceeds and those of the products are more positive as the composition of the system changes. Eventually it reaches a minimum value at a system composition that defines the ***equilibrium composition*** of the system, after which time no further net change will occur (Lower, S., 2010).

Figure 2.1 below identify the characteristic of Gibbs energy of reaction (ΔG_r), it is defined as a slope of plot of Gibbs free energy versus the extent of reaction or amount of production conversion. The figure indicated the two distinctive features of the equilibrium state for a constant temperature and pressure. Values of ΔG_r indicate the direction of the reaction by equation (2-2)

$$\Delta G_r = RT \ln (Q/K_{eq}) \qquad (2\text{-}2)$$

Where, K_{eq} is the equilibrium constant and Q is the reaction quotient, both values are composition dependence.

If $\Delta G_r < 0$, the forward reaction is spontaneous and the reaction is exergonic, if $\Delta G_r > 0$, the reverse reaction is spontaneous and the reaction is endergonic, and at the equilibrium state ΔG_r is equal to 0.



(Figure source: http://www.shodor.org/unchem/advanced/thermo/)

Figure 2.1: The Gibbs free energy curve on relation to the reaction conversion

In figure 2.1 above, the chemical equilibrium is represented by Gibbs free energy value. The curve is a type of equilibrium models, since the key meaning of the curve is to show the trend of reaction equilibrium in variety reaction variables.

Apart from the important part where the variation of Gibbs energy with the composition of a system is determined, it is also essential to recognize how state changing, whereby temperature and pressure, affects the free energy.

Generally, the Gibbs energy expression with state change is defined as equation (2-3)

$$\mathbf{G = H - TS} \qquad \textbf{(2-3)}$$

When the system undergoes a change of state, Gibbs energy, G, may change, because enthalpy, H, temperature, T, and entropy, S, change. It confirms that Gibbs energy is an important quantity in chemical process because the pressure and temperature are usually the process variables which can be under control. In other words, Gibbs energy carries around the combined consequences of the First and Second Laws in a way that makes it particularly suitable for chemical application.

Furthermore, another concept of Gibbs energy is accounted when the reaction of a mixture started, the Gibbs energy of mixing of two perfect gases that form an ideal solution. The Gibbs energy of mixing is negative for all compositions and temperatures, so perfect gases mix spontaneously in all proportions. (Atkins, P., 2002)

Chemical equilibrium is usually explained either by minimization of Gibbs free energy or by using an equilibrium constant. In order to minimize the Gibbs free energy, constrained optimization methods are generally used; it requires an understanding of complex mathematical theories. Therefore, many recent thermodynamic equilibrium models are developed based on the equilibrium constant and not on the Gibbs free energy. (Barba, et al., 2011)

In this research, a propose structure for the model of study is, undoubtedly, the Gibbs free energy. By applying to this Gibbs free energy the conditions of multiple chemical equilibrium and thermodynamic stability, all the relevant statistical and thermodynamic equilibrium properties of the reversible chemical reaction are expected to be calculated. These properties include the location of the critical concentration and temperature.

The equilibrium model has already been used by many researchers for the analysis of the gasification process. Most of models were based on the minimization of Gibbs free energy. The other kind of equilibrium model is based on equilibrium constant. However, it is important to note that an equilibrium model based on the minimization of Gibbs free energy and one based on equilibrium constants are of the same concept. (Tang, et al., 2005)

Gasification is a kind of waste-to-energy conversion scheme that offers the most attractive solution to both waste disposal and energy problems. The theoretical analysis of the gasification is, somehow, common to the ammonia production on the aspect of energy analysis. Thus, the study on thermodynamics and chemical equilibrium of gasification is introduced in the studies review stage.

The first illustration starts from an equilibrium model for biomass gasification. Biomass gasification involves the production of a gaseous fuel by partial oxidation of a solid fuel. Clean synthesis (syn) gas, produced from partial combustion of biomass, can be burnt in a gas turbine combustion chamber to run a biomass based combined cycle power plant. A thermo-chemical model has been developed to predict the gas composition and performance of a biomass gasifier based on thermodynamic equilibrium concept for different biomass materials. A simplified numerical method is applied to solve the thermo-chemical equilibrium reactions. Furthermore, in this research, the chemical exergy analysis was also prepared since the system needs high exergy efficiency of biomass gasifier to obtain a high yield from the biomass (Srinivas, et al., 2009). The authors have also introduced the standard chemical exergy calculation incorporated with the thermo-chemical model.

The next illustration model is the equilibrium model from research on supercritical water gasification of biomass. In this research, a model is developed to estimate equilibrium composition for supercritical water gasification (SCWG) of biomass. Direct minimization of Gibbs free energy subject to the linear material balance constraints is reported to be very effective for complicated phase equilibrium and chemical equilibrium problems. The authors have formulated a thermodynamic model using direct Gibbs free energy minimization to predict the equilibrium composition of SCWG of biomass. (Tang, et al., 2005)

Jarungthammachote and Dutta (2007) have studied on the management of municipal solid waste (MSW) and the current status of world energy resources crisis are important problems. In this research, the thermodynamic equilibrium model based on equilibrium constant for predicting the composition of producer gas in a downdraft waste gasifier was developed. This is a constrained optimization problem that generally uses the Lagrange multiplier method. The authors have shown that an understanding of some mathematical theories is necessary for solving optimization and non-linear equation problems. For that reason, the present thermodynamic equilibrium model is developed based on the equilibrium constant and not on the Gibbs free energy.

Besides the methodology illustrated previously, which are the minimization of Gibbs free energy and the equilibrium constants approach, the study of equilibrium model can also be developed alternatively. Hildebrandt and Glasser (2004) have studied on predicting phase and chemical equilibrium using the convex hull of the Gibbs free energy. The authors clarified that while it is well known that the Gibbs free energy of a system is minimized at phase and chemical equilibrium, but the solution of this minimization problem is not straightforward. A geometric algorithm that uses a convex hull approach to minimize the Gibbs free energy, and thereby predict equilibrium, is presented in this paper. The algorithm, which can be used to predict either phase or simultaneous phase and chemical equilibrium, is a general method that does not have convergence problems. Furthermore, provided the thermodynamic data for all possible phases are included, the algorithm automatically generates both the number and types of phases present at equilibrium.

There is, actually, no limit or any specific pattern on how the equilibrium model is developed, it depends on how the result of model would be implemented to meet the objective of the study.

CHAPTER 3
METHODOLOGY

3.1 PRELIMINARY MODEL OF STUDY

The initial stage of this study aims to generate a model which is the Gibbs Energy curve with respect to the reaction conversion of ammonia production, to identify the best model representing the reaction equilibrium characteristics over variety of input variable i.e. temperature. Figure 3.1 shows the expected shape of the model of study.

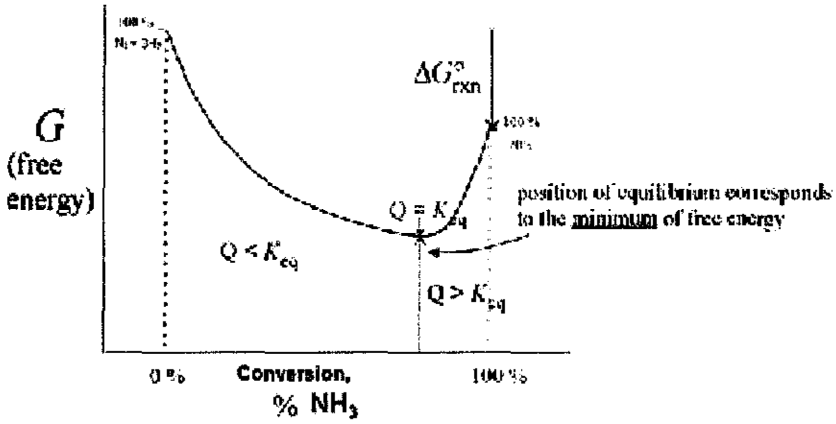


Figure source: http://guweb2.gonzaga.edu/faculty/cronk/chemistry/L00-index.cfm?L00resource=free-energy

Figure 3.1: The proposed model of study

Ammonia synthesis reaction:

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$$

To generate the Gibbs Energy curve with composition dependence, the author needs to generate 2 graphs, i.e. a plot of Gibbs energy of reaction and a plot of Gibbs energy of mixing, as base values of the Gibbs free energy curve.

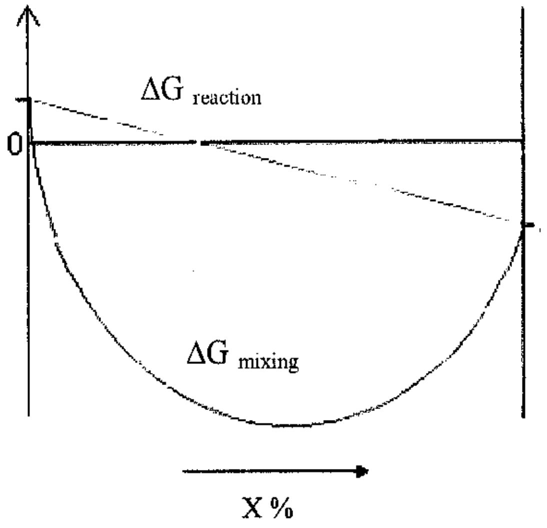


Figure 3.2: Plot of Gibbs energy of reaction and Gibbs energy of mixing curves in a relationship with percentage of reaction conversion

The main equations used to construct the Gibbs free energy curve are;

$$\Delta G_{mixing} = -RT\,\Sigma(x_i \ln x_i) \qquad (3\text{-}1)$$

$$\Delta G_{reaction} = \Delta H_{reaction} + T\Delta S_{reaction} \qquad (3\text{-}2)$$

$$\Delta G_{mixture} = \Delta G_{mixing} + x_i\,\Delta G_{reaction\,(i)} \qquad (3\text{-}3)$$

To construct a plot of Gibbs energy of reaction line, $\Delta G_{reaction}$, Kirchoff's equation is introduced in order to identify enthalpy values, H, at different temperatures.

Kirchoff's Equation:

$$\Delta H = \Delta H^0 + \Delta C_p\,(Tf - Ti) \qquad (3\text{-}4)$$

Unit in KJ/Kg-mol

The heat capacity, C_p, of a pure substance can be calculated by using Polynomial equation.

Polynomial equation:

$$C_p = A + BT + CT^2 + DT^3 + ET^4 \qquad (3\text{-}5)$$

Unit T in K, Cp in KJ/Kg-mol-K

Table 3.1: Polynomial coefficients for calculating heat capacity of ammonia as a function of temperature

Coefficient	**Value**
A	34.20
B	-2.21 x 10^{-2}
C	1.21 x 10^{-4}
D	-1.09 x 10-^{7}
E	3.20 x 10^{-11}

Source: Chemical Engineering Research Information Center, Korea

The following table shows the calculated heat capacity values of ammonia and tabulated heat capacity values of nitrogen and hydrogen.

Table 3.2: Heat capacity of Ammonia, Nitrogen, and Hydrogen, as a function of temperature

T (^{0}C)	**T (^{0}K)**	**Cp_{NH3}**	**Cp_{N2}**	**Cp_{H2}**
25	298	35.78	29.14	28.86
100	373	37.82	29.19	28.99
200	473	40.98	29.29	29.13
300	573	44.34	29.46	29.18
400	673	47.65	29.68	29.23
450	723	49.23	29.83	29.26
500	773	50.74	29.97	29.29
550	823	52.17	30.12	29.32
600	873	53.51	30.27	29.35

For entropy of reaction, Third Law of Thermodynamics is introduced

$$\Delta S = \int_{Ti}^{Tf} \frac{Cp}{T} dT \qquad \textbf{(3-6)}$$

Unit in KJ/Kg mol-K

3.2 RESEARCH FRAMEWORK

Figure 3.3 below illustrates 6 steps of research framework

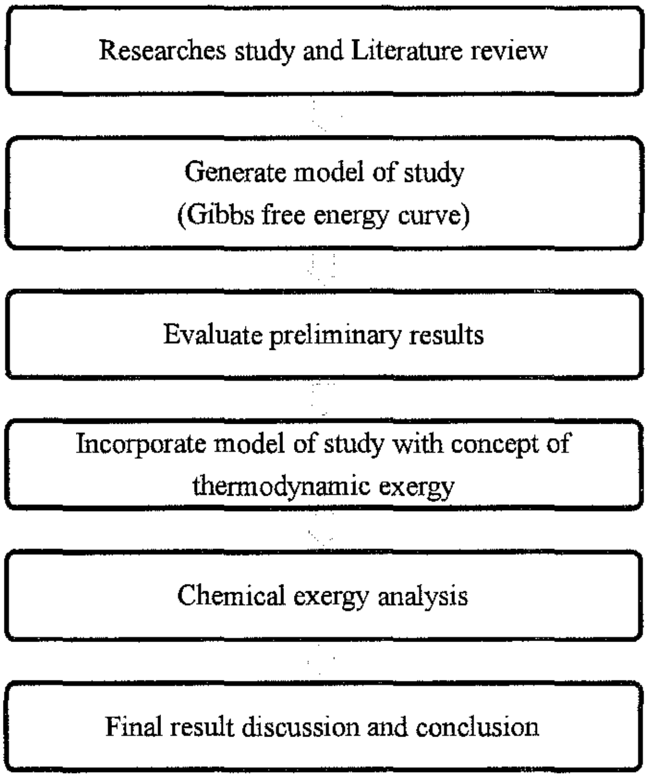


Figure 3.3: Research process flow diagram

3.2.1 Project Activities

In the first phase, the conceptual study on thermodynamics and chemical exergy and Literatures review on theories related to the project scope was performed in order to build up fundamental understanding of the research. Then, the methodology identification was performed. Relevant studies were determined to be used along with the proposed method in order to obtain better result for analysis.

The next phase was the preliminary research model generation. The finding conceptual study phase shows that concept of exergy has a distinct advantage over the Gibbs energy of formation. As well, equations and theories of the chemical exergy and Gibbs free energy are proved that they are allied. Thus, a plot of Gibbs free energy curve in a relationship with chemical reaction conversion was proved to be chosen as a preliminary model of study.

After a type of model has been determined, literatures and detailed theories required for the construction of model were explored. Whilst, trial and error calculations for model equations were developed to get the most suitable equations used for model construction as proposed.

Results of calculations from model developed were identified as desired results for the preliminary phase. It was done by comparing and evaluating the most accurate results with respect to the theories and literatures reviewed.

Finally, the vital stage, the chemical exergy concept was introduced and implemented with research analysis. The result analysis from the Gibbs free energy curves, as the preliminary model of study was brought and integrated with chemical exergy concept. The final result from chemical exergy analysis approach, as expected, provided useful discussion with respected to the problem statement.

3.2.2 Project Progress Timeline

To make the project run smoothly and be successful as planned, disciplinable schedule and Gantt chart are needed. The preliminary model of study was identified as planned, in the early stage of FYP2. As well as the final result of this study, was delivered within week 12, as expected. The overall project progress was running as scheduled. The key milestones and project's Gantt chart can be referred in the Appendix.

CHAPTER 4

RESULT AND DISCUSSION

4.1 MODEL IDENTIFICATION

The preliminary result of this study obtained from a model of study presented in curve-shape plot of Gibbs free energy (G) versus reaction conversion ratio (X).

Table 4.1: Mole fraction calculation over conversion fraction

Conversion fraction	**Mole fraction**						
	H_2, in	**N_2, in**	**H_2, out**	**N_2, out**	**H_2, react**	**N_2, react**	**NH_3, out**
0.10	0.75	0.25	0.71	0.24	0.04	0.01	0.05
0.20	0.75	0.25	0.67	0.22	0.08	0.03	0.11
0.30	0.75	0.25	0.62	0.21	0.13	0.04	0.18
0.40	0.75	0.25	0.56	0.19	0.19	0.06	0.25
0.50	0.75	0.25	0.50	0.17	0.25	0.08	0.33
0.60	0.75	0.25	0.43	0.14	0.32	0.11	0.43
0.70	0.75	0.25	0.35	0.12	0.40	0.13	0.54
0.80	0.75	0.25	0.25	0.08	0.50	0.17	0.67
0.90	0.75	0.25	0.14	0.05	0.61	0.20	0.82
1.00	0.75	0.25	0.00	0.00	0.75	0.25	1.00

Table 4.1 express the mole fraction values calculated for ammonia production with respect to the reaction conversion fraction from 0.1 [10%] to 1 [100%]

The Gibbs free energy curve generated by using following equations;

1. $\Delta G_{mixing} = -RT\,\Sigma(x_i \ln x_i)$
2. $\Delta G_{reaction} = \Delta H_{reaction} + T\Delta S_{reaction}$
3. $\Delta G_{mixture} = \Delta G_{mixing} + x_i\,\Delta G_{reaction\ (i)}$

The first result shows in Table 4.2 is the calculated values of Gibbs energy of mixing which followed the equation, $\Delta G_{mixing} = -RT\ \Sigma(x_i \ln x_i)$

Table 4.2: Calculated result of Gibbs free energy of mixing, ΔG_{mixing}, unit KJ

Conversion	ΔG_{mixing}								
	25°C	100°C	200°C	300°C	400°C	450°C	500°C	550°C	600°C
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1	-1941.25	-2429.82	-3081.25	-3732.67	-4384.10	-4709.81	-5035.53	-5361.24	-5686.95
0.2	-3111.32	-3894.38	-4938.44	-5982.51	-7026.58	-7548.61	-8070.65	-8592.68	-9114.72
0.3	-3925.46	-4913.41	-6230.68	-7547.95	-8865.21	-9523.85	-10182.50	-10841.10	-11499.80
0.4	-4458.32	-5580.38	-7076.47	-8572.55	-10068.60	-10816.70	-11564.70	-12312.70	-13060.80
0.5	-4731.03	-5921.72	-7509.32	-9096.91	-10684.50	-11478.30	-12272.10	-13065.90	-13859.70
0.6	-4737.47	-5929.79	-7519.54	-9109.3	-10699.10	-11493.90	-12288.80	-13083.70	-13878.60
0.7	-4445.96	-5564.91	-7056.84	-8548.78	-10040.70	-10786.70	-11532.60	-12278.60	-13024.60
0.8	-3784.82	-4737.38	-6007.45	-7277.53	-8547.60	-9182.64	-9817.68	-10452.70	-11087.80
0.9	-2584.37	-3234.80	-4102.04	-4969.28	-5836.52	-6270.14	-6703.76	-7137.37	-7570.99
1.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

The value of ΔG_{mixing} was calculated at nine different temperatures which are 25, 100, 200, 300, 400, 450, 500, 550, and 600 degree Celsius. Values varied parabolically as the composition of the gas mixture changed.

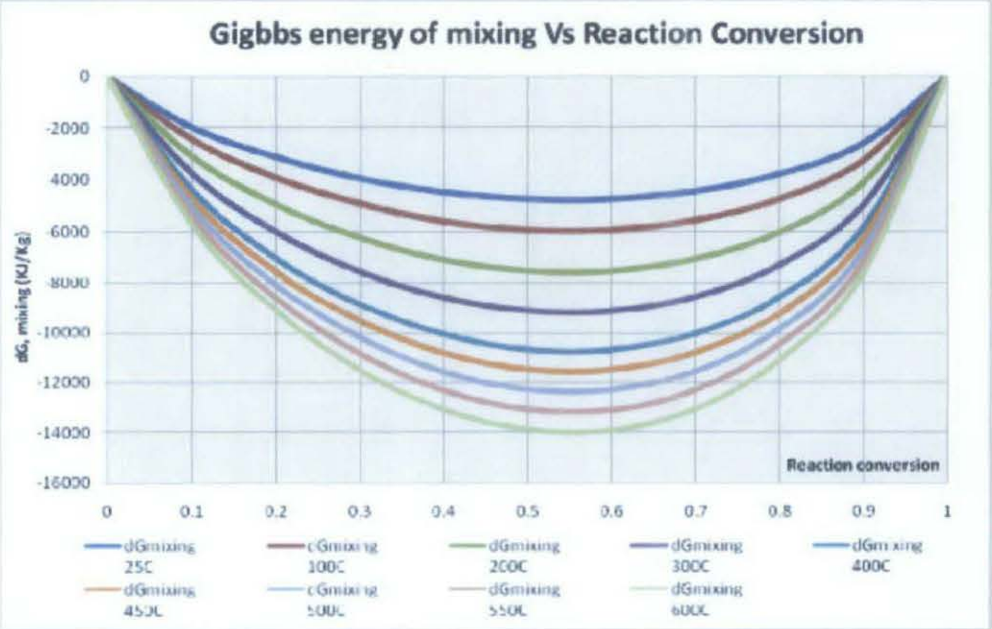


Figure 4.1: Gibbs free energy of mixing values versus reaction conversion, at various temperatures

Table 4.3: Calculation results of Enthalpy, Entropy, and Gibbs free energy of reaction

T (C)	T (K)	dH$_r$ (KJ/mol)	dS$_r$ (KJ/mol.K)	dG$_r$ (KJ/mol)
25	298	-92220.00	-198.76	-32988.90
100	373	-95259.10	-207.86	-17727.90
200	473	-98297.00	-214.81	3305.93
300	573	-100009.00	-217.28	24492.35
400	673	-100496.00	-216.74	45370.43
450	723	-100355.00	-215.73	55615.81
500	773	-99989.70	-214.35	65705.58
550	823	-99433.50	-212.72	75635.04
600	873	-98714.50	-210.90	85403.02

In table 4.3, the Gibbs free energy of reaction was calculated at nine different temperatures which are 25, 100, 200, 300, 400, 450, 500, 550, and 600 degree Celsius. The equation used to calculate is $\Delta G_{reaction} = \Delta H_{reaction} + T\Delta S_{reaction}$.

Result of calculation shows in Table 4.4 is the values of Gibbs energy of reaction with respect to temperatures. To make the Gibbs energy values relate to reaction conversion for the plot, it needed to be multiplied with the reaction conversion fraction.

Table 4.4: Calculation results of Gibbs energy of reaction with respect to reaction conversion.

Conversion (xi)	$x_i\,\Delta G_{reaction\,(i)}$								
	25^0C	100^0C	200^0C	300^0C	400^0C	450^0C	500^0C	550^0C	600^0C
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1	-3298.89	-1772.79	330.59	2449.24	4537.04	5561.58	6570.56	7563.50	8540.30
0.2	-6597.78	-3545.58	661.19	4898.47	9074.09	11123.16	13141.12	15127.01	17080.60
0.3	-9896.68	-5318.37	991.78	7347.70	13611.13	16684.74	19711.67	22690.51	25620.91
0.4	-13195.60	-7091.16	1322.37	9796.94	18148.17	22246.33	26282.23	30254.02	34161.21
0.5	-16494.50	-8863.95	1652.96	12246.17	22685.22	27807.91	32852.79	37817.52	42701.51
0.6	-19793.40	-10636.70	1983.56	14695.41	27222.26	33369.49	39423.35	45381.02	51241.81
0.7	-23092.20	-12409.50	2314.15	17144.64	31759.30	38931.07	45993.90	52944.53	59782.11
0.8	-26391.10	-14182.30	2644.74	19593.88	36296.35	44492.65	52564.46	60508.03	68322.41
0.9	-29690.00	-15955.10	2975.33	22043.11	40833.39	50054.23	59135.02	68071.54	76862.72
1.0	-32988.90	-17727.90	3305.93	24492.35	45370.43	55615.81	65705.58	75635.04	85403.02

The plot in Figure 4.2 shows that values of Gibbs energy of reaction varies linearly with the composition of components in the gas mixture. The characteristic of the lines are, obviously, split as the reaction conversion increases. At the temperature 200 ^{0}C and above, values of Gibbs energy increases positively as the temperature increases. While at temperature below 200 ^{0}C, Gibbs energy values tend to decrease, approach more negative value, as the temperature increases.

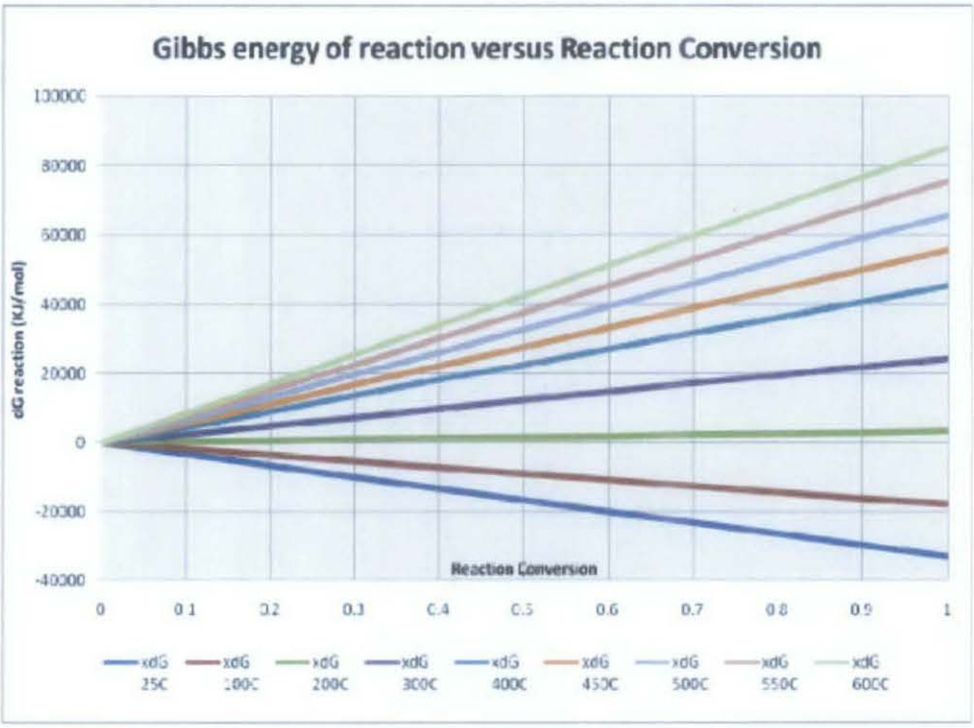


Figure 4.2: Gibbs free energy of reaction values at various temperatures (G vs. X).

4.2 EQUILIBRIUM CONVERSION

Values shown in table 4.5 are the calculation results of Gibbs free energy of mixture which is the proposed model of study. The calculation was done for nine different temperatures which are at 25, 100, 200, 300, 400, 450, 500, 550, and 600 degree Celsius.

Table 4.5: Calculation results of Gibbs free energy curves with respect to temperature in unit KJ/mol

Conversion	**Gibbs Energy (KJ/mol)**								
	25^{0}C	**100^{0}C**	**200^{0}C**	**300^{0}C**	**400^{0}C**	**450^{0}C**	**500^{0}C**	**550^{0}C**	**600^{0}C**
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1	-5240.14	-4202.61	-2750.66	-1283.44	152.94	851.77	1535.03	2202.26	2853.35
0.2	-9709.11	-7439.96	-4277.26	-1084.04	2047.51	3574.55	5070.47	6534.33	7965.89
0.3	-13822.10	-10231.80	-5238.90	-200.24	4745.92	7160.90	9529.19	11849.40	14121.16
0.4	-17653.90	-12671.50	-5754.09	1224.39	8079.55	11429.66	14717.52	17941.27	21100.42
0.5	-21225.50	-14785.70	-5856.36	3149.26	12000.71	16329.60	20580.69	24751.63	28841.82
0.6	-24530.80	-16566.50	-5535.99	5586.11	16523.21	21875.56	27134.54	32297.34	37363.25
0.7	-27538.20	-17974.40	-4742.70	8595.87	21718.60	28144.39	34461.26	40665.92	46757.54
0.8	-30176.00	-18919.70	-3362.71	12316.35	27748.74	35310.01	42746.78	50055.32	57234.66
0.9	-32274.40	-19189.90	-1126.71	17073.83	34996.87	43784.10	52431.27	60934.16	69291.72
1.0	-32988.90	-17727.90	3305.93	24492.35	45370.43	55615.81	65705.58	75635.04	85403.02

As mentioned earlier, value of Gibbs energy of mixture is the sum of Gibbs energy of mixing and Gibbs energy of reaction with respect to the reaction conversion. Values highlight in RED are the minimum values of Gibbs energy at a certain conversion fraction with respect to the temperature. The minimum value of Gibbs energy indicates the equilibrium reaction conversion of the process.

It is observed that the Gibbs energy values of reaction at 400 ˉ 600 ^{0}C give very low production yield, or reaction conversion, most likely less than 10% conversion. To be more accurate, detailed calculation has been made to acquire most precise solution. Table 4.6 shows detailed calculation results for Gibbs energy values of reaction at 400 ˉ 600 ^{0}C, the equilibrium conversion for all temperatures are at 6%.

Table 4.6: Calculation results for Gibbs energy values of reaction at 400 - 600 ^{0}C

Conversion	Gibbs Energy (KJ/mol)				
	400^{0}C	450^{0}C	500^{0}C	550^{0}C	600^{0}C
0.00	0.00	0.00	0.00	0.00	0.00
0.01	-4138.07	-4376.75	-4617.00	-4858.84	-5102.31
0.02	-6821.83	-7191.16	-7563.60	-7939.25	-8318.13
0.03	-8912.11	-9367.98	-9828.53	-10293.90	-10764.10
0.04	-10519.30	-11025.80	-11538.50	-12057.70	-12583.30
0.05	-11621.30	-12141.00	-12668.40	-13203.90	-13747.40
0.06	-12103.60	-12590.40	-13086.40	-13592.10	-14107.50
0.07	-11730.70	-12121.00	-12522.10	-12934.60	-13358.30
0.08	-10046.50	-10243.00	-10451.80	-10673.50	-10908.20
0.09	-6050.98	-5881.81	-5726.66	-5585.92	-5459.73
0.10	4537.04	5561.58	6570.56	7563.50	8540.30

The following, Figure 4.3, shows the combined plot of Gibbs free energy curves calculated at nine different temperatures, namely, 25, 100, 200, 300, 400, 450, 500, 550, and 600 degree Celsius. The black dot on each curve shows the equilibrium reaction conversion point at various temperature inputs.

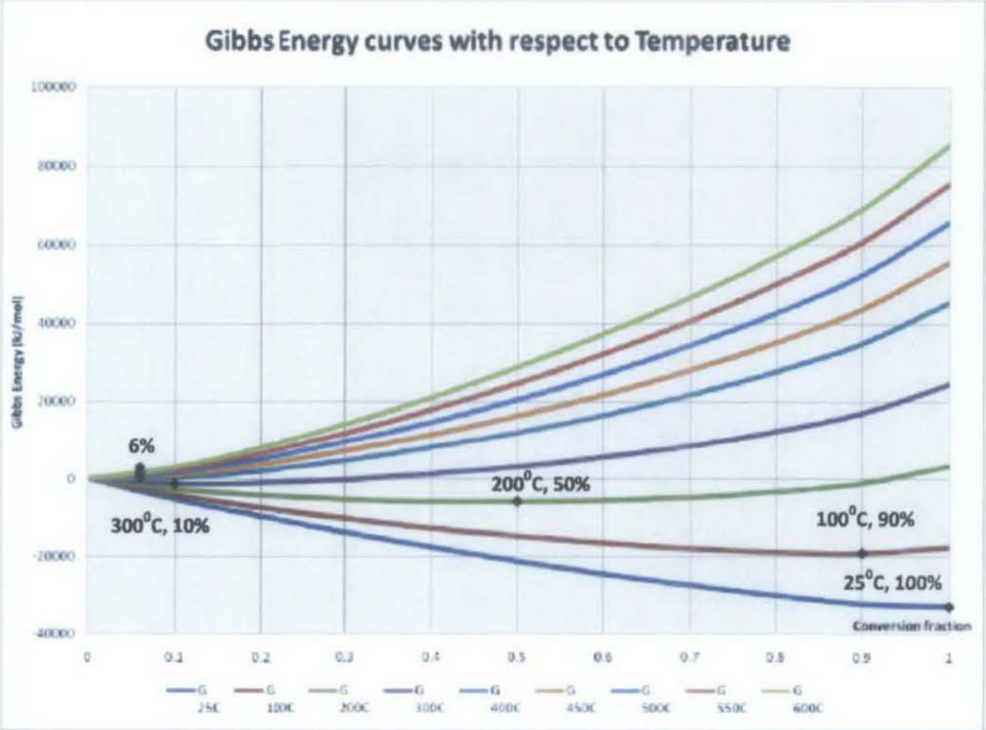


Figure 4.3: The Combined plot of Gibbs free energy curves at various temperatures.

From the plot, it is observed that at the ambient temperature, 25^0C, the reaction spontaneously converted reactants to ammonia at complete 100% conversion. The percentage conversion decreases as temperature increases. At the temperature between 100^0C and 300^0C, the percentage of reaction conversion tends to decrease rapidly, then, slowly decreases for reaction at the temperature above 400^0C. This observation can be seen from the characteristic of black points on the plot and the graphical trend in Figure 4.4. The following Figure 4.4 shows the trend of equilibrium conversion as the temperature changes.

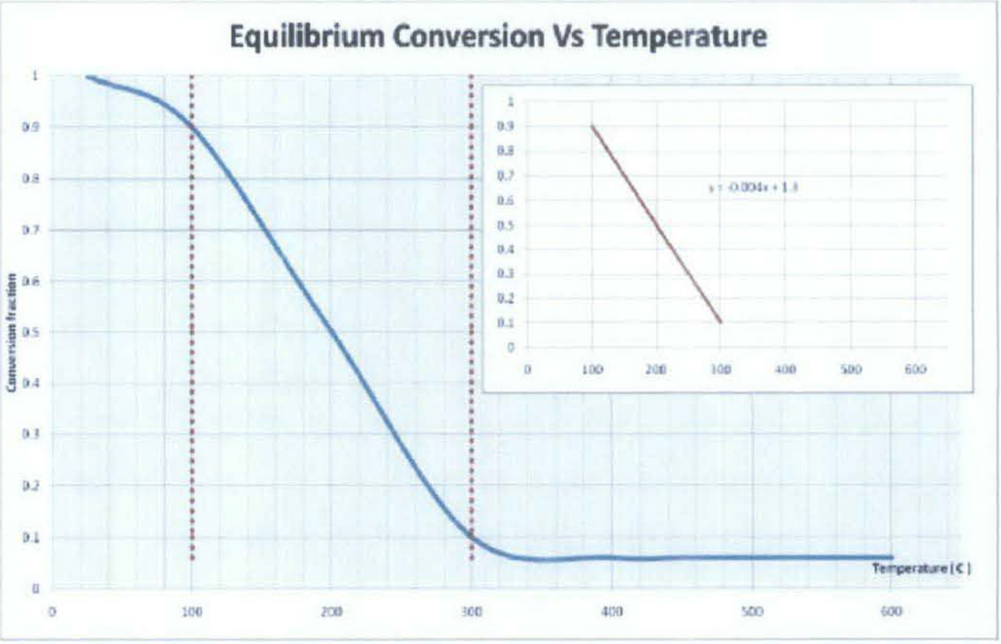


Figure 4.4: Trend of equilibrium conversions versus temperature in degree Celsius

It can be observed from the trend above that the equilibrium conversion rapidly falls from 90% to 10% conversion in temperature range between 100^0C and 300^0C. The linear slope value is 0.004, nearly zero. Thus, we can interpret that from the preliminary model of study, Gibbs energy concept, the acceptable range of ammonia production operating temperature is between 100^0C and 300 ^{0}C.

4.3 EXERGY ANALYSIS

The earlier finding can, further, be explained through chemical exergy analysis. Generally, the chemical exergy analysis is a method for efficiency analysis of systems and processes by evaluating quantitatively the causes resulting in decreases of exergy due to thermodynamic imperfections of thermal and chemical processes. It is also indicate the energy driving force for the reaction.

Exergy values of the reaction can be defined by using two separated exergy concepts which are the physical exergy, expresses the amount of work available due to differences in the pressure and temperature with the environment, and the standard chemical exergy, which expresses the amount of work available due to the differences in composition with respect to the environment.

The standard chemical exergy was calculated from equation;

$$\mathbf{Ex_{,chem}(NH_3) = G_{,f}(NH_3) + Ex_{,chem}(N_2) + 3Ex_{,chem}(H_2)}$$

The tabulated data for calculation and result of calculation for standard chemical exergy for ammonia reaction is shown below.

$Ex_{,ch}(N_2)$	0.72	KJ/mol
$Ex_{,ch}(H_2)$	236.1	KJ/mol
$G_{,f}(NH_3)$	-46.11	KJ/mol
$Ex_{,ch}(NH_3)$	331.455	KJ/mol

The following Table 4.7 presents the calculation result of the physical exergy term and the ultimate value of chemical exergy analysis, $Ex_{,Total} = Ex_{,phy} + Ex^0_{,chem}$. The physical exergy was calculated from equation;

$$\mathbf{Ex_{,phy} = (H - T_0S)_{P,T} - (H - T_0S)_{Po,To} = \Delta H - T_0\Delta S,}$$

Where;

$H_0(NH_3)$	-92220	KJ/mol
$S_0(NH_3)$	-198.76	KJ/mol.K
T_0	298 K	

Table 4.7: The calculation result of the physical exergy term and the total exergy, unit in KJ/mol

T (C)	T (K)	H (KJ/mol)	S (KJ/mol.K)	$Ex_{,phy}$	$Ex_{,Total}$
25	298	-92220.0	-198.8	0.0	331.5
100	373	-95259.1	-207.9	-328.4	3.1
200	473	-98297.0	-214.8	-1296.1	-964.6
300	573	-100009.0	-217.3	-2270.7	-1939.3
400	673	-100496.0	-216.7	-2918.2	-2586.8
450	723	-100355.0	-215.7	-3079.5	-2748.0
500	773	-99989.7	-214.4	-3123.4	-2792.0
550	823	-99433.5	-212.7	-3054.0	-2722.6
600	873	-98714.5	-210.9	-2876.7	-2545.3

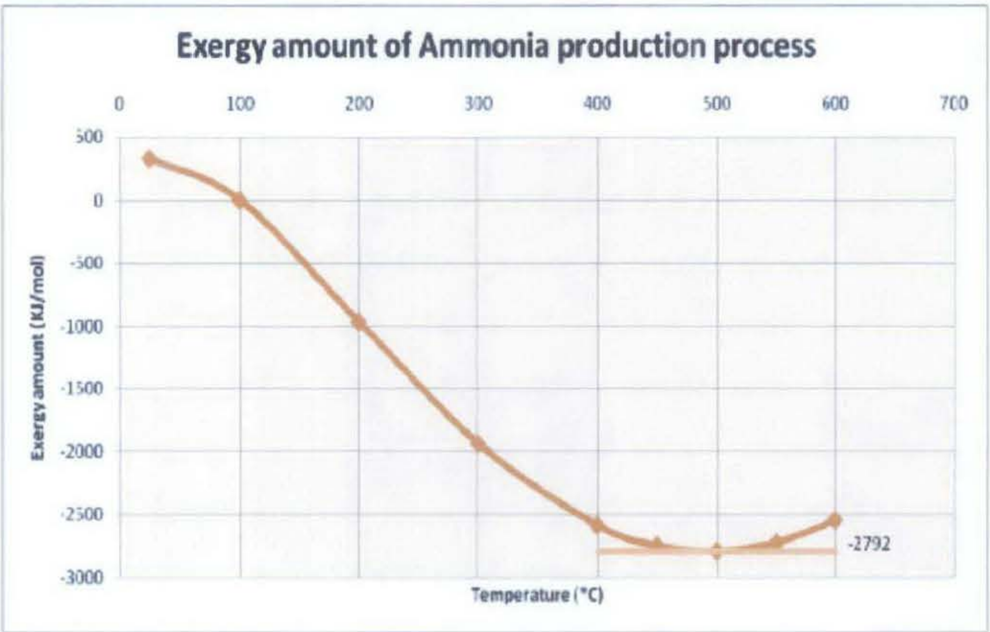


Figure 4.5: The trend of exergy amount of ammonia production process versus temperature in degree Celsius

From the plot above, it is observed that amount of exergy for ammonia synthesis reaction tends to fall as temperature increases until it reaches the minimum point, which appeared at 500^0C. Then the trend started to rise again. Since the amount of exergy is defined as amount of energy available for the process to be used, thus, it can be concluded that at 500^0C, which the process conveys the minimum amount of potential work, the ammonia reaction would provide the least performance to convert reactants to a product of ammonia.

4.4 RESULT DISCUSSION

Gibbs energy curves have been calculated at nine different temperatures, namely, 25, 100, 200, 300, 400, 450, 500, 550, and 600 degree Celsius. It is observed that as the composition approaches the equilibrium, value of Gibbs free energy, which denotes the spontaneity of the forward reaction, approaches more negative value. This observation can be seen for a certain range of temperature, which is below 200 degree Celsius, while Gibbs energy of processes above 200 degree Celsius tends to increase positively as the temperature increases. The more negative value of free energy the easier the reaction can shift to the equilibrium state. The most negative value on the Gibbs energy curve indicates the equilibrium reaction conversion.

In accordance with the results, the higher the temperature input, the higher is the free energy value obtained. This means the less the operating temperature, the easier the ammonia production reaches the equilibrium. Thus, the acquired results are in agreement with thermodynamics theory. The trend of equilibrium conversion versus temperature showed that the acceptable range of operating temperature for ammonia production is between 100 and 300 degree Celsius.

Furthermore, the study on exergy amount of ammonia production, which indicates work available or energy driving force for the process, illustrates the least amount of exergy occurs at the temperature of 500 degree Celsius. From this finding, we can conclude that at 500 degree Celsius, ammonia production is likely to give the most undesired production performance due to the least energy driving force.

The results obtained tend to oppose the experimental records for ammonia production which proved that the optimal industrial operating temperature for ammonia synthesis is at 500 degree Celsius with 20-25 percent ammonia yields. In fact, current industrial ammonia production is designed with recycle stream and iron catalyst in order to improve the production yield.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The main objective of this research is to identify the optimal operating condition that gives the highest ammonia yield from the synthesis reaction and to construct graphical understanding of thermodynamic effect on ammonia synthesis reaction.

The chemical exergy analysis method is proposed to identify the optimal solution for operating condition of industrial ammonia synthesis and to provide theoretical explanations to improve the thermodynamics limit of ammonia production. It is found that the general concept of chemical exergy and Gibbs free energy is allied and as well, can be incorporated through its general equation.

Furthermore, it has been realized that the production equilibrium is restricted by its thermodynamics, thus the application of equilibrium criteria to chemical reaction is introduced in this report. The less is the Gibbs free energy value, the easier for the reaction to reach the equilibrium state.

Therefore, the Gibbs free energy curve in a relationship with reaction conversion is selected as a preliminary model of study. Since chemical exergy and Gibbs free energy are related in terms of calculation equation, therefore, the key to success of the project is depended strongly on the equations used for model generation.

The vital process of this research is to construct the graphical understanding which deals with chemical exergy analysis. Results from the graphical model of study show that thermodynamics has an influence to the trend of amount of ammonia yield, it also identify the optimal range of operating temperature, thus, objectives of the research are satisfied.

Even though, the experimental records show that the optimal operating temperature for ammonia production is between 450 and 500 degree Celsius, but it is somehow oppose the theoretical proof which shows that at the respective temperature the reaction gives the least amount of ammonia yields.

Additionally, to improve the outcome of the research project, it is recommended that the future project work should consider more detailed on other operation additives which industrial ammonia production used to improve the ammonia synthesis capacity, i.e., iron catalyst and recycle stream. This is to assure that the research study accurately meet the experimental records.

REFERENCES

Agarwal, P. (2011). *Ammonia the next step.* Retrieved June 2011, from CHEresources.com/forum: http://www.cheresources.com/ammonia.shtml

Atkins, P. W. (2008). *Thermodynamic principles.* AccessScience. McGraw-Hill Companies, Retrieved June 29, 2011 from: http://www.accessscience.com

Atkins, P. W. (2002). *Physical Chemistry.* Oxford University Press Inc.

Barba, D., Prisciandaro, M., et al. (2011). *The Gibbs Free Energy Gradient Method for RDF gasification modelling.* Journal of Fuel Research 90(4): 1402-1407.

Bejan, A.(1997) *Advanced Engineering Thermodynamics*, J. Wiley, 1988.

Camdali, U. and M. Tunc (2005). *Computation of Chemical Exergy Potential in an Industrial AC Electric ARC Furnace.* Journal of Energy Resources Technology 127(1): 66-70.

Chemical Engineering Research Information Center Korea (2011). *Pure Components Properties (Queriable database).* Retrieved 10 November 2011 from http://www.cheric.org/research/kdb/hcprop/showcoef.php?cmpid=1918&prop=CPG

Chen, G. Q., & Ji, X. (2007). *Chemical exergy based evaluation of water quality.* Ecological Modelling, 200(1-2), 259-268.

D'Amboise, M. (1998). *Beginning Calculations in Physical Chemistry (Johnson, Barry R.; Scott, Stephen K.).* Journal of Chemical Education 75(5): 549.

Dincer, I., & Rosen, M. A. (2007). *Energy, environment, and sustainable development.* Exergy. Elsevier.

Dincer, I. (2000). *Thermodynamics, exergy and environmental impact.* Energy Sources, *22*(8), 723-732.

Hildebrandt, D. and D. Glasser (1994). *Predicting phase and chemical equilibrium using the convex hull of the Gibbs free energy.* The Chemical Engineering Journal and the Biochemical Engineering Journal 54(3): 187-197.

Jarungthammachote, S. and A. Dutta (2007). *Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier.* Energy 32(9): 1660-1669.

Kirova-Yordanova, Z. (2004). *Exergy analysis of industrial ammonia synthesis.* Energy, 29(12-15), 2373-2384.

Krishnan S., Jakob de S. A., & Hedzer J. van der K. (2004). *Sec. 6 Exergy, a convenient concept*. Efficiency and sustainability in the energy and chemical industries. CRC Press.

Krishnan S., Jakob de S. A., & Hedzer J. van der K. (2004). *Sec. 7 Chemical exergy*. Efficiency and sustainability in the energy and chemical industries. CRC Press.

Lima da Silva, A., Malfatti, C. d. F., & Müller, I. L. (2009). *Thermodynamic analysis of ethanol steam reforming using gibbs energy minimization method: A detailed study of the conditions of carbon deposition*. International Journal of Hydrogen Energy, 34(10)

Lower, S. (2010). *Free energy and equilibrium*. Retrieved June 21, 2011, from Chem1 Virtual Textbook: http://www.chem1.com/acad/webtext/thermeq

Mountouris, A., E. Voutsas, et al. (2006). *Solid waste plasma gasification: Equilibrium model development and exergy analysis*. Energy Conversion and Management 47(13-14): 1723-1737.

Ozturk, M., I. Ucgul, et al. (2007). *Heat and Chemical Exergy Analysis of Parabolic Trough Collector*. AIP Conference Proceedings 899(1): 425-426.

Pellegrini, L. F. and J. S. de Oliveira (2007). *Exergy analysis of sugarcane bagasse gasification*. Energy 32(4): 314-327.

Piotrowski, J., Kozak, R., & Kujawska, M. (1998). *Thermodynamic model of chemical and phase equilibrium in the urea synthesis process*. Chemical Engineering Science, 53(1), 183-186.

Price, G. (1998). *Thermodynamics of Chemical Processes*. Oxford University Press Inc., new York.

Rivero, R., & Garfias, M. (2006). Standard chemical exergy of elements updated. Energy 31(15): 3310-3326.

Robert, M., & Panoff, P. (2008). *Chemical thermodynamics*. Retrieved June 16, 2011, from UNC-Chapel Hill Chemistry Fundamentals Program: http://www.shodor.org/unchem/index.html

Rosen, M. A.(2007). *Encyclopedia of energy engineering and technology*. Exergy: Analysis (pp. 645-654)

S.Bastianoni, A. Facchini, L. Susani, E. Tiezzi (2007) *Emergy as a function of exergy*. Energy 32, 1158–1162.

Srinivas, T., A. V. S. S. K. S. Gupta, et al. (2009). *Thermodynamic Equilibrium Model and Exergy Analysis of a Biomass Gasifier.* Journal of Energy Resources Technology 131(3): 031801-031807.

Tang, H. and K. Kitagawa (2005). *Supercritical water gasification of biomass: thermodynamic analysis with direct Gibbs free energy minimization.* Chemical Engineering Journal 106(3): 261-267.

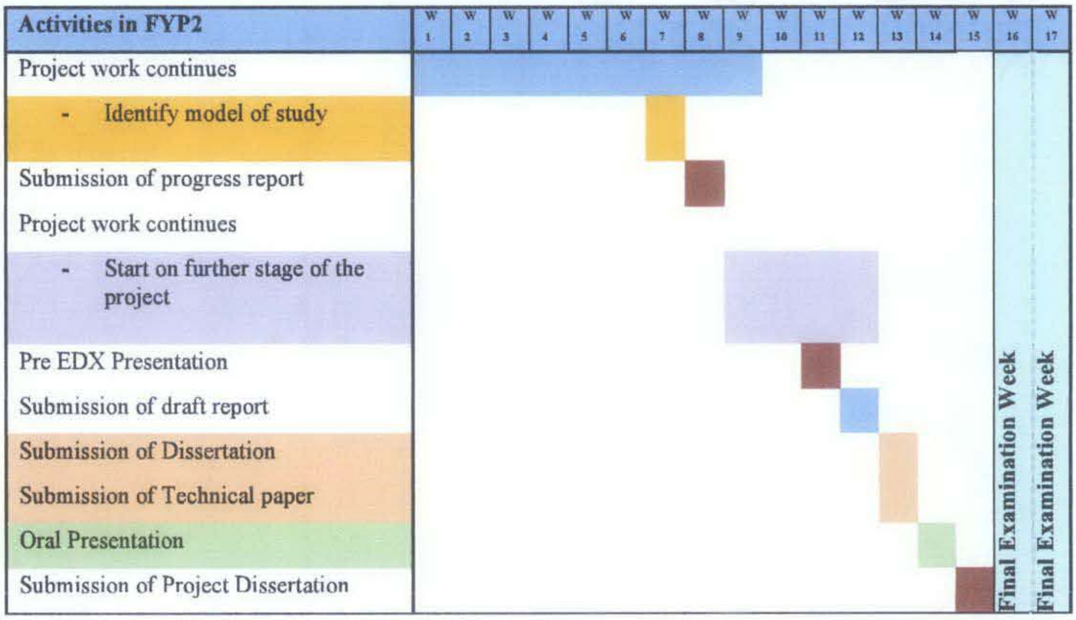
Zausner, J. (2007). *Thermodynamic Analysis of CO_2 Capture Cycles Using Pre-Combustion Decarbonization and Membrane Technologies.* ASME Conference Proceedings 2007(47926): 393-402.

APPENDICES

APPENDIX 1: KEY MILESTONES FOR FYP II

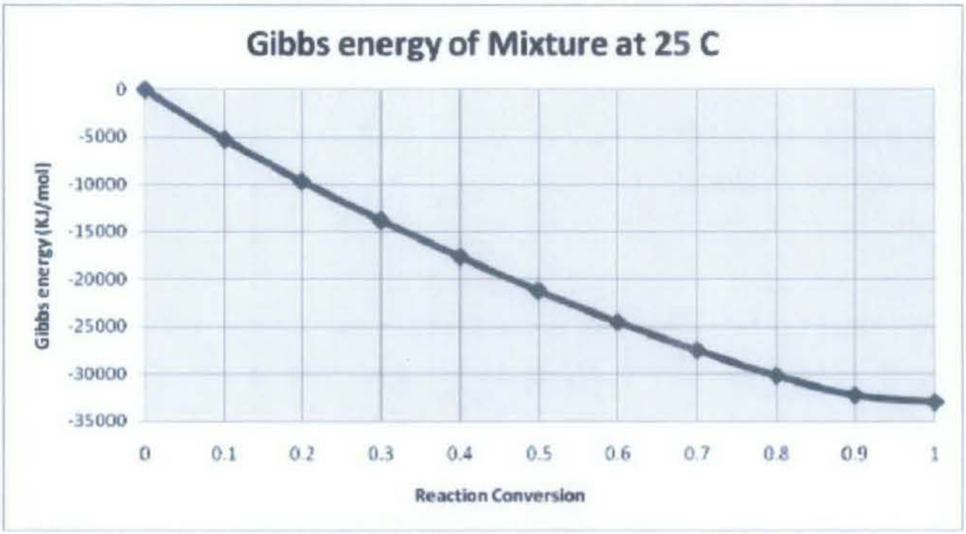
No	Action Item	Date
1	Project work commences	3/10/2011
2	Briefing & update on students progress	5/10/2011
3	Submission of Progress Report	14/11/2011
4	Poster Presentation	14/12/2011
5	Submission of Draft Dissertation	14/12/2011
6	Submission of Dissertation (CD Softcopy & Softbound)	19/12/2011
7	Final Oral Presentation/Viva	28/12/2011
8	Submission of Technical Paper	6/01/2012
9	Submission of hardbound Dissertation	13/01/2012

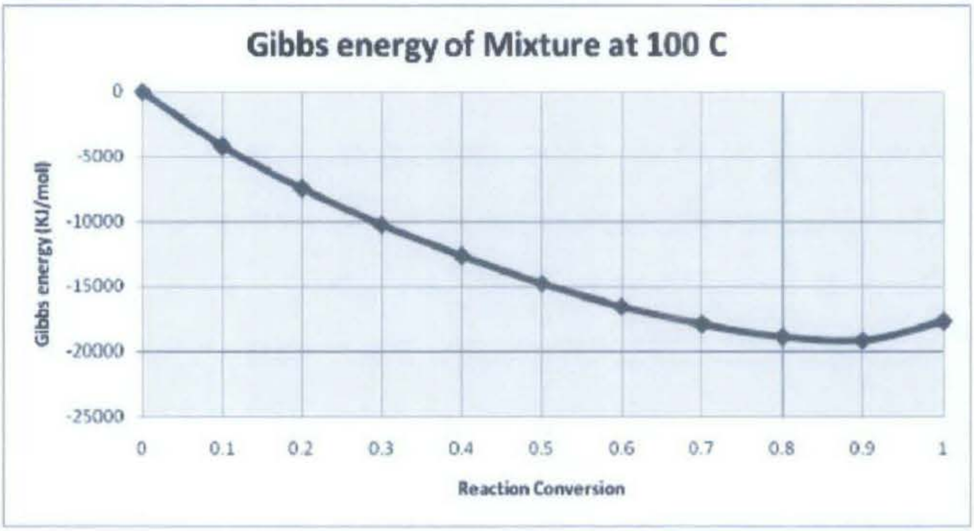
APPENDIX 2: GANTT CHART FOR FYP II

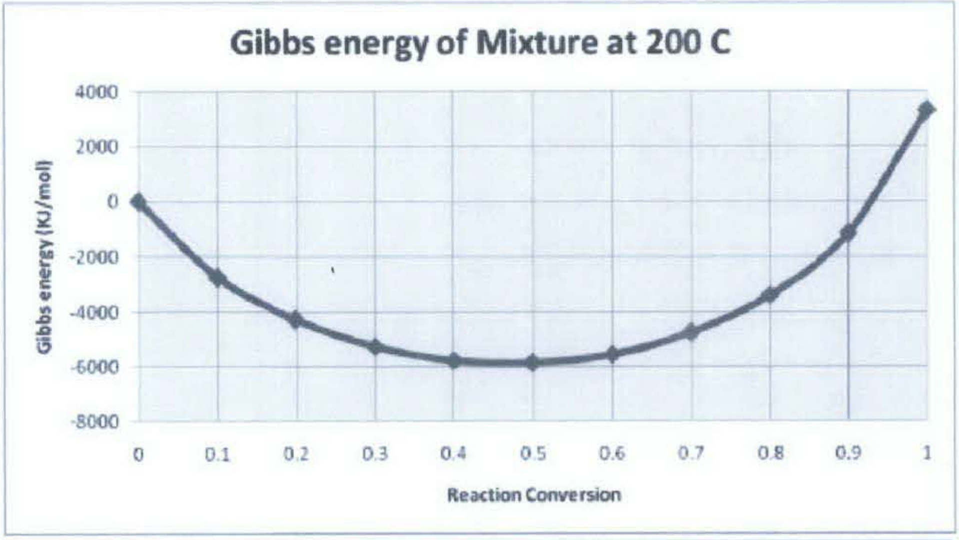


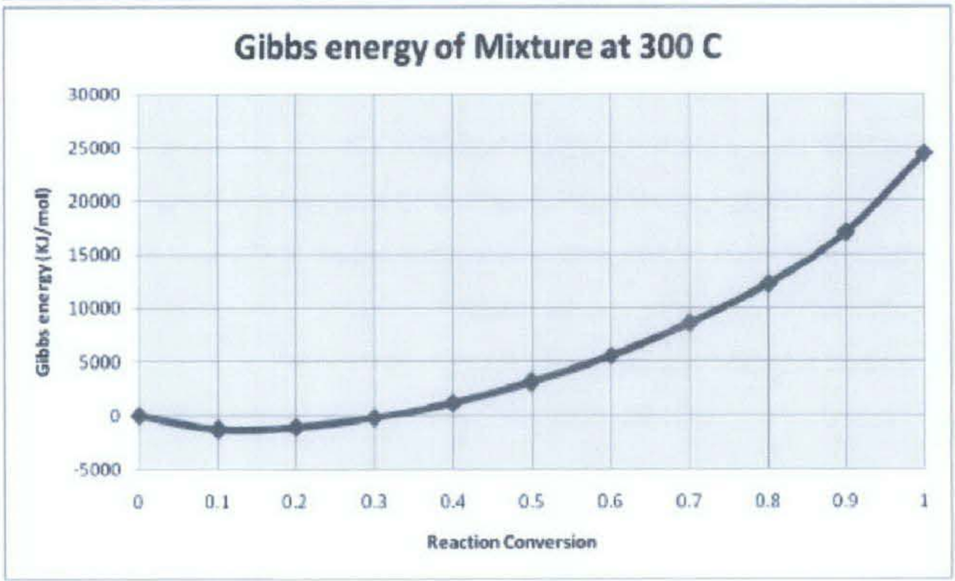
Activities in FYP2	W 1	W 2	W 3	W 4	W 5	W 6	W 7	W 8	W 9	W 10	W 11	W 12	W 13	W 14	W 15	W 16	W 17
Project work continues	■	■	■	■	■	■	■	■	■							Final Examination Week	Final Examination Week
- Identify model of study							■										
Submission of progress report								■									
Project work continues																	
- Start on further stage of the project									■	■	■	■					
Pre EDX Presentation											■						
Submission of draft report												■					
Submission of Dissertation													■				
Submission of Technical paper													■				
Oral Presentation														■			
Submission of Project Dissertation															■		

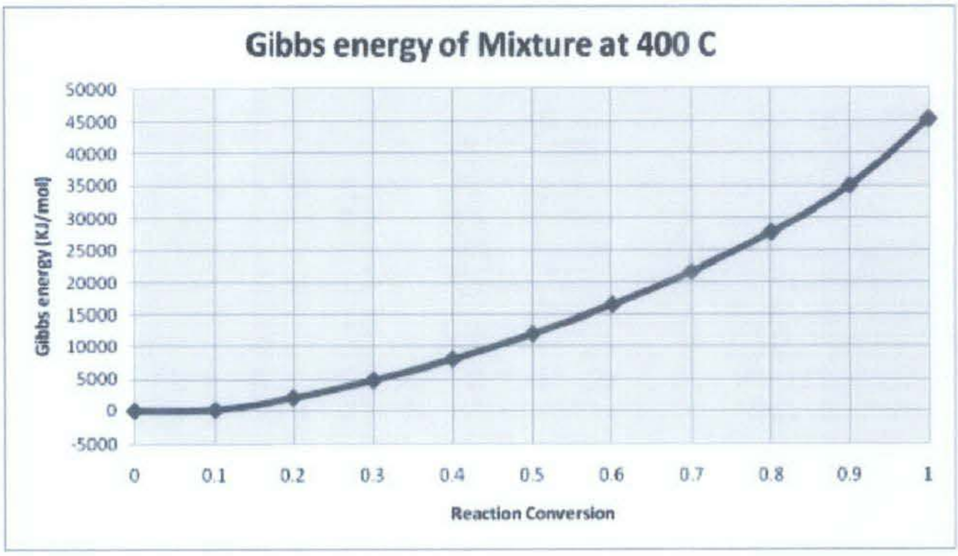
APPENDIX 3: PRELIMINARY MODEL OF STUDY FOR VARIOUS TEMPERATURE INPUTS

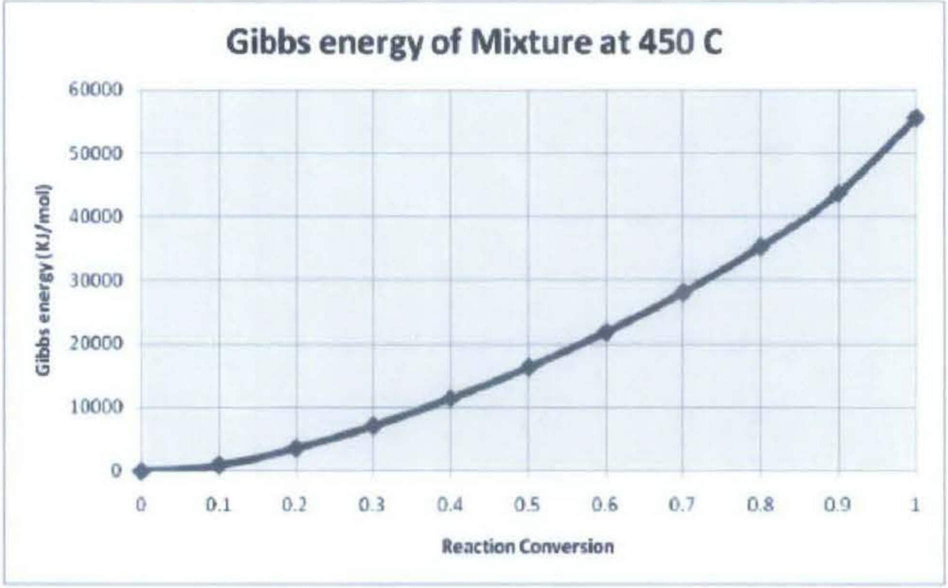


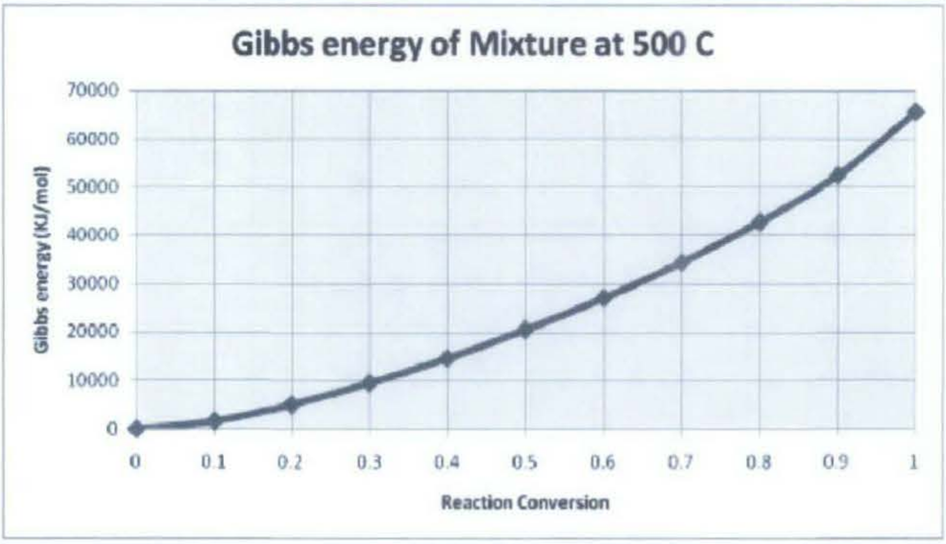


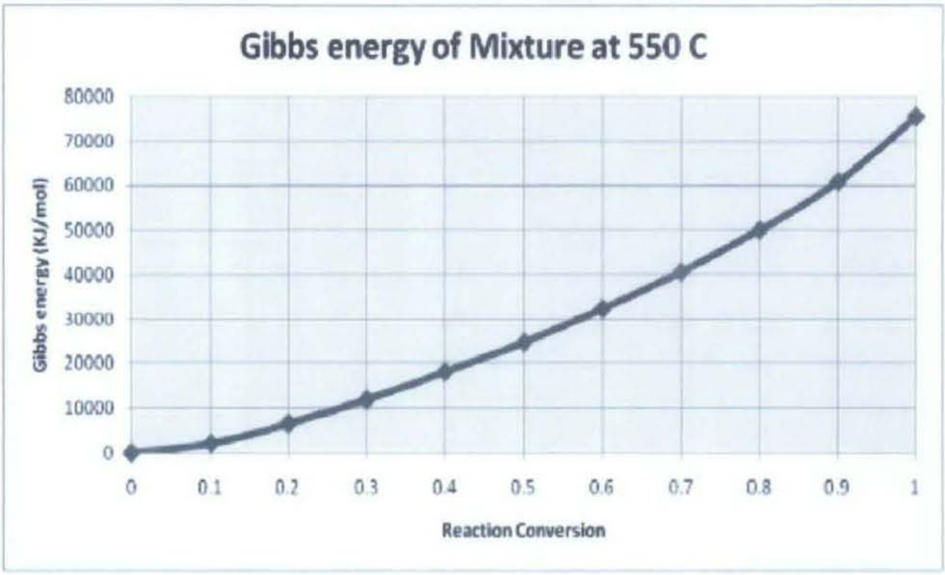

Gibbs energy of Mixture at 200 C
Gibbs energy (KJ/mol)
4000
2000
0
-2000
-4000
-6000
-8000
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Reaction Conversion

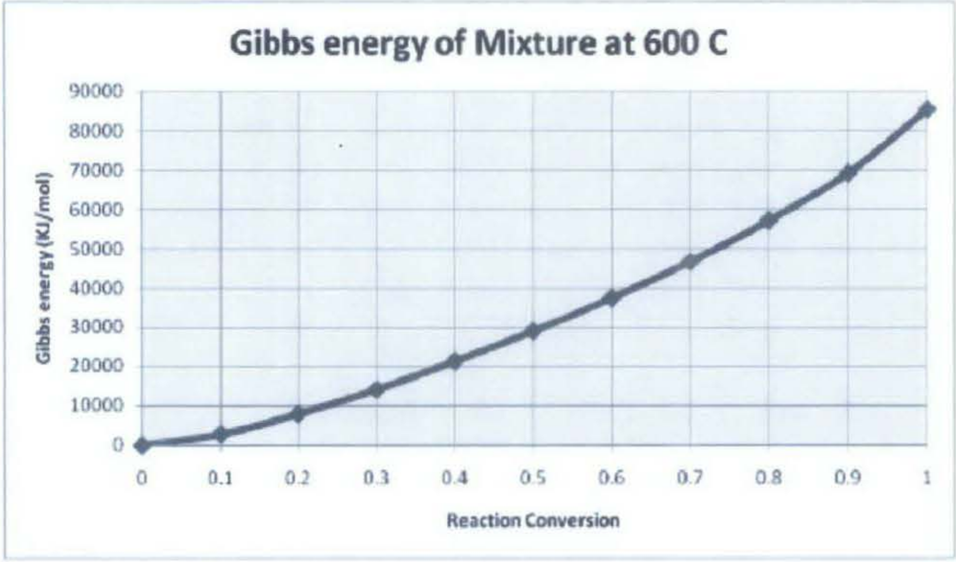

Gibbs energy of Mixture at 300 C
Gibbs energy (KJ/mol)
30000
25000
20000
15000
10000
5000
0
-5000
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Reaction Conversion


Gibbs energy of Mixture at 400 C
Gibbs energy (KJ/mol)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Reaction Conversion


Gibbs energy of Mixture at 450 C


Gibbs energy of Mixture at 500 C


Gibbs energy of Mixture at 550 C



APPENDIX 4: GIBBS ENERGY OF THE PROCESS AT 100 TO 300^{0}C

A. Calculation results for Gibbs energy of the process

Conversion	Gibbs energy (KJ/mol)						
	25C	100C	120C	140C	160C	180C	200C
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.1	-5240.14	-4202.61	-3916.55	-3627.77	-3336.83	-3044.29	-2750.66
0.2	-9709.11	-7439.96	-6816.08	-6186.75	-5553.12	-4916.28	-4277.26
0.3	-13822.10	-10231.80	-9246.21	-8252.44	-7252.23	-6247.20	-5238.90
0.4	-17653.90	-12671.50	-11305.40	-9928.31	-8542.64	-7150.56	-5754.09
0.5	-21225.50	-14785.70	-13021.50	-11243.60	-9455.04	-7658.43	-5856.36
0.6	-24530.80	-16566.50	-14386.40	-12189.90	-9980.56	-7761.55	-5535.99
0.7	-27538.20	-17974.40	-15358.40	-12723.30	-10073.10	-7411.74	-4742.70
0.8	-301760	-18919.70	-15843.00	-12744.40	-9628.64	-6500.05	-3362.71
0.9	-32274.40	-19189.90	-15616.30	-12018.10	-8400.52	-4768.53	-1126.71
1.0	-32988.90	-17727.90	-13564.50	-9373.75	-5161.52	-933.27	3305.93

B. Trend of Gibbs energy curves for the process and the equilibrium conversion position