

**Kinetic Parameter Estimation of Ammonia Synthesis Using Hybrid Dynamic
Global and Local Combined Particle Swarm Optimization**

by

Thian Jun Yi

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

MAY 2013

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr Periyasamy Balasubramaniam)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2013

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.

THIAN JUN YI

ABSTRACT

In this paper an industrial ammonia synthesis reactor has been modelled. The reactor under study is a fixed-bed reactor. The model is developed based on the fractional conversion of the nitrogen in the reaction. Calculation on material balance is then performed across the bed of iron catalysts before the model equation of the reaction is obtained in the form of an initial value problem. The second part of this project is the kinetic parameter estimation of the ammonia synthesis reaction. The expression for the rate of ammonia formation at pressures ranging from 150 atm. to 300 atm. derived here is the simplest yet available for a modern catalyst. It is suitable for design, optimization, and control studies, and is believed to be as accurate as the most complex expression in the composition, temperature, and pressure regions of commercial importance. The rate expression is based on the Temkin and Pyzhev expression corrected for high pressures and fitted to recently reported kinetic measurements of Nielsen, Kjaer, and Hansen for an industrially used catalyst. The pre-exponential factor of the rate expression is calculated using transitional state theory and thermo dynamical statistics. Activation energy of the reaction is the only kinetic parameter estimated through Hybrid Dynamic Global and Local Combined Particle Swarm Optimization method.

ACKNOWLEDEGEMENT

The author would like to express his utmost gratitude to Dr Periyasamy Balasubramaniam who is his supervisor for this project, without whom this report was almost impossible. The author is deeply indebted to his supervisor for his proper guidance, commitment, enthusiastic encouragement and useful critiques of this project. It was his advice and assistance which kept the progress on schedule and this project a successful one. His willingness to spare his time so generously has been very much appreciated. Besides, the author would also like to extend his thanks to all his friends in helping him directly or indirectly to complete this project. Finally, the author wishes to thank his parents for their continuous support and encouragement.

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CHAPTER 1

INTRODUCTION

1.1 PROJECT BACKGROUND

Ammonia synthesis is a vital process in chemical complexes. Ammonia is the raw material for a variety of industries. It is used in the production of chemical fertilizers, explosive materials, polymers, acids and even coolant. Among all, it is worth mentioning that ammonia synthesis is specifically crucial to the production of hundreds million tons of fertilizer per year which in turn responsible for sustaining one-third of the Earth's population. Ammonia is generated by plants (predominantly the legumes) and certain bacteria naturally, which extract nitrogen from the atmosphere in a process known as nitrogen fixation. Natural nitrogen fixation occurs at ambient temperatures and pressures, but artificial nitrogen fixation via the Haber-Bosch process requires high pressures (150-250 atmospheres) and high temperatures (300-550 degrees Celsius) to produce the vast quantities of ammonia necessary to satisfy global demand.

Various types of wastes, manures or their decomposition products, as well as ammonium sulphate from the coking of coal, were the primary sources of agricultural nitrogen before the existence of synthetic nitrogen fixation.(Austin, 1984) During the first decade of the twentieth century, the existent supply for nitrogen based fertilizers was not able to meet the worldwide demand. The largest source of the chemicals necessary for fertilizer production was found in a huge guano deposit (essentially sea bird droppings) that was 220 miles in length and 5 feet thick, located along the coast of Chile. During the development of inexpensive nitrogen fixation processes, many principles of chemical and high-pressure processes were clarified and the field of chemical engineering emerged. Scientists had long desired to solve the problem of the world's dependence on this fast disappearing natural

sources of ammonia and nitrogenous compounds. Priestly and Cavendish then passed electric sparks through air and produced nitrates by dissolving the oxides of nitrogen thus formed in alkalis. Commercial development of this process had proved elusive, for much electrical energy was consumed at low efficiency.(Austin, 1984) Nitrogen had been fixed as calcium cyanamide, but the process was too expensive except for producing chemicals requiring the cyanamide configuration. Other processes, such as thermal processing to mixed oxides of nitrogen (NOX), cyanide formation, aluminium nitride formation and decomposition to ammonia, etc., showed little commercial promise although they were technically possible. It was Fritz Haber, along with Carl Bosch, who finally solved this problem and made intensive ammonia synthesis possible.

In 1909, Haber invented a large-scale catalytic synthesis of ammonia from elemental hydrogen and nitrogen gas, reactants which are abundant and inexpensive.(Rossignol, 2009) Haber could force relatively unreactive gaseous nitrogen and hydrogen to combine into ammonia by using high temperature (around 500°C) and high pressure (approximately 150-200 atm) reactor assisted by iron catalyst. This furnished the essential precursor for many important substances, particularly fertilizers and explosives used in mining and warfare. Carl Bosch, with his technical ingenuity, developed suitable high-pressure equipment and production methods for large-scale production of ammonia. The collaborative efforts of Haber and Bosch made the commercial high-pressure synthesis of ammonia possible by 1913. The first commercial plant with a capacity of 30 tons per day was set up by the German chemical giant BASF (Badische Aniline und Soda Fabrik) in Oppau, Germany (Appl, 1986). This energy-intensive process has undergone considerable modification in recent years, resulting in prices which have not escalated as rapidly as energy prices in general. Today, synthetic ammonia produced from reaction between nitrogen and hydrogen is the base from which virtually all nitrogen-containing products are derived. The worldwide production of ammonia exceeds 210 million metric tonnes in year 2012 and is the sixth largest chemical produced.(Buckley, 2012)

Dr Steve Jenkins, of the Department of Chemistry at the University of Cambridge, said: "The Haber-Bosch process was developed in the early twentieth

century but has changed little since that time. Clearly, given the massive scale of worldwide ammonia production, even a tiny improvement in the efficiency of the ammonia synthesis process can have massive implications, not only for the economics of fertilizer production, but also for global energy demand."(University of Cambridge, 2010) It is for this reason that ammonia synthesis reaction has been studied over a wide range of conditions, including conditions of vital importance for industrial use of the process ever since the Haber-Bosch process was created. It was dated back to the year 1963 when a few researchers from the research laboratory of Haldor Topsoe in Hellerup, Denmark who did experiments on the rate equation and mechanism of ammonia synthesis at industrial conditions.(Anders Nielsen, 1964) In 1967, D.C.Dyson and J.M.Simon from the chemical engineering department of Rise University published a journal on the kinetic expression with diffusion correction for ammonia synthesis on industrial catalyst. The researchers have tried to estimate the kinetic parameters using linear regression analysis. However, parameter estimation through Hybrid Dynamic Global and Local Combine Particle Swarm Optimization (HDGLCPSO) was never carried out for it is a rather new and advance optimization method. Thus, it is one of the main objectives of this project to calculate the pre-exponential factor in the ammonia rate equation, A from transitional state theory and statistical thermodynamics. At the same time, the activation energy of the reaction, E_a will be estimated via HDGLCPSO. Through this project, the researchers are hoping to have some breakthrough in making the operation yield of ammonia synthesis higher than before.

1.2 PROBLEM STATEMENT

The yield of ammonia synthesis will remain the same for years if the reaction is not optimized using a rather advance or more comprehensive method. The yield of ammonia in a reaction is directly affected by the efficiency of the reactor. In order to improve the overall efficiency of the fixed bed reactor in industrial ammonia synthesis, kinetic model of the reactor must first be developed and parameter of the reaction has to be estimated. Previous works using the linear regression analysis is not sufficient to prove the accuracy and consistency of the experimental results obtained. Thus, the technique of HDGLCPSO is applied in the kinetic parameter estimation of ammonia synthesis.

1.3 OBJECTIVES

- To develop a kinetic model for ammonia synthesis reactor
- To calculate the pre-exponential factor of the ammonia synthesis reaction through transition state theory and statistical thermodynamics
- To estimate activation energy of the ammonia synthesis reaction through HDGLCPSO

1.4 SCOPE OF STUDY

The scope of study for the first part of this project includes the modelling of the ammonia synthesis reactor as well as the calculation of the frequency factor in the rate expression of ammonia synthesis. Knowledge on reaction engineering, transitional state-theory and also statistical thermodynamics is required. On the other hand, the scopes of studies for the second part of this project are mainly on the kinetic parameter estimation of ammonia synthesis using HDGLCPSO. The researcher needs to have a good introduction into the subject of particle swarm optimization as well as the Levenberg-Marquardt algorithm. Besides, MATLAB tools are used in the optimization of the parameter estimation. All of the calculations done will need to be translated into computer codes.

CHAPTER 2

LITERATURE REVIEW

The kinetic modelling of industrial ammonia synthesis reactor is nothing new to researchers in this particular field. According to (Ali Dashti, 2006), a horizontal type of reactor under the license of Kellogg Company was studied. The reactor was equipped with three axial flow catalysts beds and an internal heat exchanger in accompany with a cooling flow. Temperature, concentrations, and pressure profiles were obtained through the modelling of the reactor. The testing of the model based on the mentioned parameters is achieved at the end of each bed as industrial data are not usually available along the length of the bed. In order to calculate the rate of reaction, modified Temkin equation offered by Dyson & Simon in 1968 has been used.(Anders Nielsen, 1964)

$$R_{NH_3} = 2k \left[K_a^2 a_{N_2} \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^\alpha - \left(\frac{a_{NH_3}^2}{a_{H_2}^3} \right)^{1-\alpha} \right]$$

in which

α : Constant which takes a value from 0.5 to 0.75 in literature

k : Rate constant for reverse reaction in $N_2 + 3H_2 \rightarrow 2NH_3$

K_a : Equilibrium constant

a_i : Activity

Parameter estimation through HDGLCPSO was not involved in previous researchers work. Earlier on, researchers estimated the pre-exponential factors, A, and activation energies E_a , of ammonia synthesis reaction by linear regression method as HDGLCPSO method is only available after 1995. Conversely, A is calculated from transitional state theory and statistical thermodynamics in this project. The absolute

translational entropy, $S_{transl}^{o,f}$ must first be calculated before the next step can be taken. Critical properties of ammonia are required together with the aid of the Sackur-Tetrode equation in calculating $S_{transl}^{o,f}$. The entropy at the standard state, $\Delta S^{o,\neq}$ is then one third of the $S_{transl}^{o,f}$. This is because the molecule loses one degree of freedom in the reverse reaction.

PSO algorithm was originally proposed by Dr Kennedy and Dr Eberhart in 1995 based on social behaviour of swarm. Their first intention was to graphically simulate the choreography of a bird flock or fish school when they found that their model can be used as an optimizer. Each of the swarm represent particle, moving along the search space and exchange information with other particle.(Xiaohui Hu, 2003)

$$v_{p,d}^{k+1} = wv_{p,d}^k + c_1r_1(x_{p,d}^{ind} - x_{p,d}^k) + c_2r_2(x_d^{glo} - x_{p,d}^k) \dots\dots\dots (i)$$

$$x_{p,d}^{k+1} = x_{p,d}^k + v_{p,d}^{k+1} \dots\dots\dots (ii)$$

Both of the equations shown above are the governing equation in PSO. In equation (i) and (ii), p denotes the particle, d is the research direction, k represents the iteration number, v is the velocity (or pseudo velocity) of the particle and x is the position of particle. X^{ind} and x^{glo} represents the regions of the search space where the objective function attains low (optimum) values. X^{ind} is the best position found by the particle itself, while x^{glo} is the best position found by whole swarm. r_1 and r_2 are two random numbers with uniform distribution in the range of $[0,1]$. w , c_1 and c_2 are the cognition and the social parameters. However, there are several disadvantage of the PSO method, for example high number of objective function evaluations, which requires longer computation times when compared to the traditional methods. Besides, PSO algorithm is not very sensitive to initial guesses of model parameters which makes it less appealing when large number of unknown parameters are present in the model.(Bai, February 2010)

In order to cope with the drawbacks of PSO algorithm, Hybrid Dynamic Global and Local Combine Particle Swarm Optimization (HDGLCPSO) algorithm is introduced for the parameter estimation. HDGLCPSO is the combination of DGLCPSO algorithm and Levenberg –Marquardt algorithm. Initial guesses will be randomly

generated using DGLCPSO algorithm. Once the simulation is started, the particle will conduct a global search over the parameter space or known as search space. As the iterations evolve, the particle concentrate around the more promising region found during the exploration stage and it leads to improvement of the global minimum during the exploitation stage. Afterwards, the solution obtained using DGLCPSO algorithm is given as initial guesses to the Levenberg-Marquardt algorithm to determine the improved optimal values.(V.Kumar, 2009)The Levenberg-Marquardt (LM) algorithm is an iterative technique which locates the minimum of a multivariate function that is expressed as the sum of squares of non-linear real valued functions. It has become a standard technique for non-linear least squares problems and it is widely adopted in a broad spectrum of disciplines. LM can be thought of as a combination of steepest descent and the Gauss-Newton Method. The algorithm behaves like a steepest descent method which is slow but guaranteed to converge when the current solution is far from the correct one. However, when the current solution is close to the correct solution, it becomes a Gauss-Newton method. (Roweis, 2002)

CHAPTER 3

METHODOLOGY

3.1 PROJECT FLOW



Figure 1: Project Flowchart

The flowchart shown in previous page summarizes the scheduled activities completed within the given time frame for this project. Detailed activities which were carried out in different stages of the project are further explained and elaborated in the later part of this report.

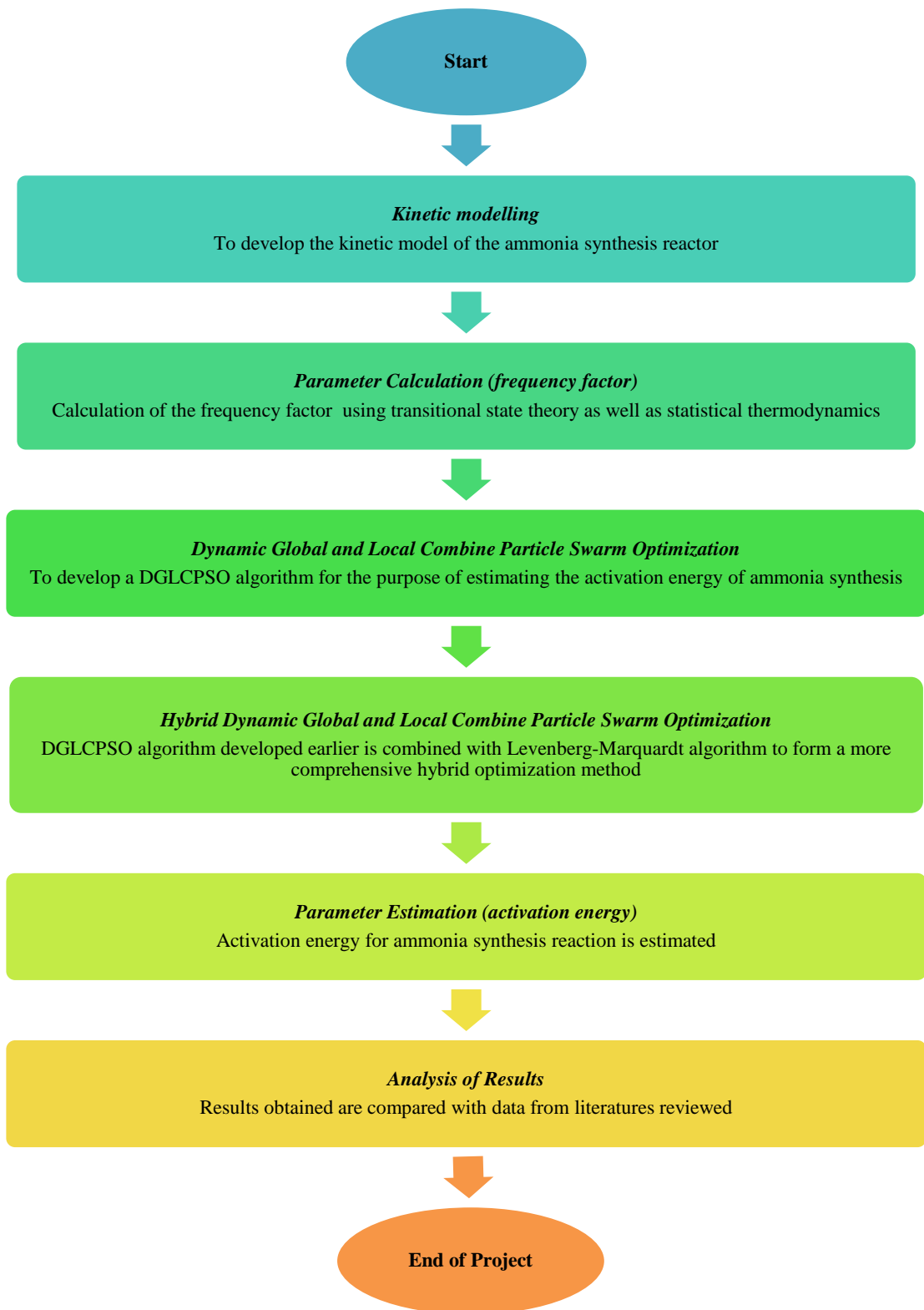
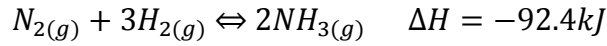


Figure 2: Detailed Flowchart

This project is mainly on MATLAB coding development as well as simulation. The project first started with a proper research on the latest technology on ammonia synthesis using plug flow reactor. Journals, technical papers, and other online resources were referred to have a better insight on the research topic. The frequency factor of the rate expression is then calculated using the transitional state theory as well as statistical thermodynamics. Certain manual calculations and derivations are unavoidable in this project. The second part of the project is more on kinetic modelling using a method call Hybrid Dynamic Global and Local Combine Particle Swarm Optimization (HDGLCPSO). The HDGLCPSO algorithm must first be developed before the kinetic parameter mentioned can be estimated. The results obtained are compared with data from literature.

3.2 MODELLING OF AMMONIA SYNTHESIS REACTOR

The stoichiometric equation for the reversible reaction of ammonia synthesis is as shown below:



The rate of reaction can be written as the rate of disappearance of nitrogen gas or hydrogen gas and this is equal to the rate of formation of ammonia gas.

$$\frac{r_{N_2}}{-1} = \frac{r_{H_2}}{-3} = \frac{r_{NH_3}}{2}$$

The kinetic model is developed based on the fractional conversion, x of the key element in the reaction, which is nitrogen gas, N_2 .

$$x = \frac{F_{N_2}^{in} - F_{N_2}}{F_{N_2}^{in}} \times 100$$

$F_{N_2}^{in}$ = inlet flow of nitrogen gas

F_{N_2} = outlet flow of nitrogen gas

x = fractional conversion of nitrogen
across the reactor

Inert gases such as argon and methane is taken into account when finding the mole fraction of individual component in the reaction in terms of flow rate. These inert gases are added into the reaction to regulate the heat released from the exothermic reaction.

Flow rate of individual component:

$$F_{N_2} = F_{N_2}^{in} - xF_{N_2}^{in}$$

$$F_{H_2} = F_{H_2}^{in} - 3xF_{N_2}^{in}$$

$$F_{NH_3} = F_{NH_3}^{in} + 2xF_{N_2}^{in}$$

$$F_{CH_4} = F_{CH_4}^{in}$$

$$F_{Ar} = F_{Ar}^{in}$$

$$\text{Let } = \frac{F_{H_2}^{in}}{F_{N_2}^{in}},$$

$$F_{N_2} = F_{N_2}^{in}(1 - x)$$

$$F_{H_2} = F_{N_2}^{in}(\beta - 3x)$$

$$F_{NH_3} = F_{NH_3}^{in} + 2xF_{N_2}^{in}$$

$$F_{CH_4} = F_{CH_4}^{in}$$

$$F_{Ar} = F_{Ar}^{in}$$

$$F_T = F_{N_2} + F_{H_2} + F_{NH_3} + F_{CH_4} + F_{Ar}$$

$$F_T = F_{N_2}^{in}(1 - x + \beta - 3x + 2x) + F_{NH_3}^{in} + F_{CH_4}^{in} + F_{Ar}^{in}$$

$$F_T = F_{N_2}^{in}(1 + \beta - 2x) + F_{NH_3}^{in} + F_{CH_4}^{in} + F_{Ar}^{in}$$

The mole fraction of each individual component can then be represented as below:

$$y_{N_2} = \frac{F_{N_2}^{in}(1-x)}{F_{N_2}^{in}(1+\beta-2x)+F_{NH_3}^{in}+F_{CH_4}^{in}+F_{Ar}^{in}} = \frac{F_{N_2}^{in}(1-x)}{F_T}$$

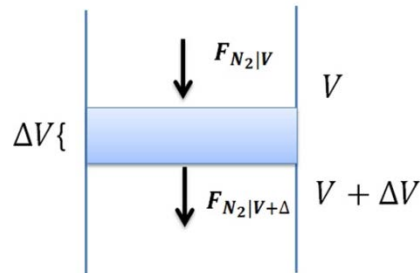
$$y_{H_2} = \frac{F_{N_2}^{in}(\beta-3x)}{F_T}$$

$$y_{NH_3} = \frac{F_{NH_3}^{in}+2xF_{N_2}^{in}}{F_T}$$

$$y_{CH_4} = \frac{F_{CH_4}^{in}}{F_T}$$

$$y_{Ar} = \frac{F_{Ar}^{in}}{F_T}$$

Material balance or mass balance calculation is then performed across the catalyst bed. An element with volume of ΔV equal to the catalysts bed that is similar to the fix bed reactor in the experiment is considered:



$$F_{N_2|V} - F_{N_2|V+\Delta V} + r_{N_2}\eta\Delta V = 0$$

Taking the limit of the equation above result in the relation below:

$$\lim_{\Delta V \rightarrow 0} \left(\frac{F_{N_2|V+\Delta V} - F_{N_2|V}}{\Delta V} \right) = -r_{N_2}\eta$$

$$-\frac{dF_{N_2}}{dV} = -r_{N_2}\eta$$

Then,

$$\frac{dF_{N_2}}{dV} = -\frac{1}{2}r_{NH_3}\eta \text{ since } r_{N_2} = -\frac{r_{NH_3}}{2}$$

The developed model equation is thus:

$$\frac{dx}{dv} = \frac{r_{NH_3}\eta}{2F_{N_2}^{in}}$$

3.3 PARAMETER CALCULATION (frequency factor)

The rate of equation for ammonia synthesis is accurately described in the modified Temkin equation. (Dyson & Simon, 1968)

$$r_{NH_3} = 2k \left[K_a^2 a_{N_2} \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^\alpha - \left(\frac{a_{NH_3}^2}{a_{H_2}^3} \right)^{1-\alpha} \right]$$

Where α is a constant which take value from 0.5 to 0.75 in the literature.

$$\log_{10} K_a = -2.691122 \log_{10} T - 5.519265 \times 10^{-5} T + 1.848863 \times 10^{-7} T^2 \\ + \left(\frac{2001.6}{T} \right) + 2.6899$$

The equation shown above has been developed by Gillespie and Beattie to calculate the equilibrium constant.

The equation of reversible ammonia synthesis has been considered in base of Arrhenius format.

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

Pre-exponential factor in the rate equation is to be calculated using the transitional state theory as well as statistical thermodynamics.

$$A = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{0,\ddagger}}{R}\right)$$

However, Sackur-Tetrode equation must first be applied to calculate the absolute translational entropy.

$$S_{transl}^{o,f} = R \ln \left\{ \frac{V_m}{N_A} \left[\frac{2\pi \left(\frac{M_w}{N_A} \right) k_B T}{h^2} \right]^{\frac{3}{2}} \right\} + \frac{5}{2} R$$

Prior to that, the molar volume V_m must first be calculated using Redlich-kwang equation of state where

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$

$$a = 0.42747 \frac{R^2 T_c^{2.5}}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$A = \frac{aP}{R^2 T^{0.5}}$$

$$B = \frac{bP}{RT}$$

and

$$T_c = 405.37K$$

$$P_c = 11,280,000Pa$$

$$T = 714K$$

$$P = 24,412,992.19Pa$$

Substituting these values into the equations above, we are able to find Z , the compressibility factor which is then used to calculate V_m , the molar volume. V_m is found to be $2.21639 \times 10^{-4} \frac{m^3}{mol}$.

It is worth mentioning that $Z^3 - Z^2 + Z(A - B - B^2) - AB = 0$.

The largest root after solving the cubic equation is taken to be the value of Z while the other two values are just complex number. Substituting the value of Z into the equation $PV_m = ZRT$, we can finally find V_m of ammonia which is then substituted back into the Sackur-Tetrode equation to calculate absolute translational entropy.

$$\Delta S^{o,\neq} = \frac{1}{3} S_{transl}^{o,f}$$

The entropy at the standard state is then one third of the $S_{transl}^{o,f}$. This is because the molecule loses one degree of freedom in the reverse reaction. The final value of A is calculated to be $4.89507 \times 10^{16} \frac{mol}{m^3s}$.

3.4 PARAMETER ESTIMATION (activation energy)

The activation energy required for the decomposition of ammonia into nitrogen and hydrogen can be calculated by minimizing the residual sum of squares errors between the experimental data and model calculated values. (Kennedy & Eberhart, 1995) Thus, the objective function for the parameter estimation can be represented as minimising the function below:

$$f(E_{Act}) = \sum_{i=1}^{nobs} (y_{NH_3,exp} - y_{NH_3,model})^2$$

The gradient based optimization methods such as Levenberg-Marquardt algorithm can be applied to estimate the kinetic constants included in a model by minimizing the above-mentioned objective function. However, the Levenberg-Marquardt method is highly sensitive with the initial guess of a parameter to be estimated. This algorithm minimizes the objective function by the optimal compromise between the steepest descent and Gauss-Newton methods. Moreover, the poor initial guess leads the Levenberg-Marquardt algorithm to determine the incorrect solution. But, the global optimization methods such as genetic algorithm, simulated annealing, particle swarm optimization and so on provide global minimum for the optimization problem. These methods do not determine the exact global minimum due to the randomness of

initial guesses. However, these methods provide good approximation of the searched optimal solution. Therefore, it is most suitable to use a hybrid dynamic global and local combined particle swarm optimization method for the estimation of activation energy in an ammonia synthesis reaction. A hybrid optimization algorithm is a combination of heuristic method followed by Levenberg-Marquardt algorithm. The former method is used to conduct a global search in a parameter space, and the latter method performs local search around the global minimum.

3.5 HYBRID DYNAMIC GLOBAL AND LOCAL COMBINED PARTICLE SWARM OPTIMIZATION

The particle swarm optimization(PSO) is a heuristic or empirical method and is related to the bird flocking, fish schooling and swarm theory. In PSO, the initial particles are randomly generated and each particle in the parameter space is associated with a velocity. The particles fly through the parameter space with velocities which are dynamically adjusted according to their historical behaviour during the search process. The equations for the updates of particle velocity and position are the same as in equation (i) and (ii) mentioned previously.

The original PSO shares the information of individual particle with best performance in the swarm, and the best performance of the swarm. However, it does not utilize the information about the performance of neighbourhood particles in the swarm. In dynamic global and local combined particle swarm optimization (DGLCPSO), the information of their neighbourhood particles is also considered along with the particle's individual performance. This will enable the optimizer to reach the global minimum in the early stage of iteration. Thus, the formulas to update the particle velocity in the swarm and position are given by

$$v_p^{i+1} = w^i v_p^i + r_1 (a + 1 / (endgen + 1 - i)) (x_p^{ind} - x_p^i) + (b - 1 / (endgen + 1 - i)) (x_p^{loc} - x_p^i) + cr_2 (x^{glo} - x_p^i) \dots\dots(iii)$$

$$x_p^{i+1} = x_p^i + v_p^{i+1} \dots\dots(iv)$$

In a hybrid minimization algorithm, first DGLCPSO starts with the randomly generated initial guess, and it performs the global search in a parameter space to determine the global minimum as the solution. Afterwards, the Levenberg-Marquardt

method utilizes the global minimum determined from DGLCPSO as an initial guess, and performs local search around the global minimum to determine the exact optimal solution. The hybrid DGLCPSO algorithm is implemented in MATLAB along with *lsqcurvefit* solver available in MATLAB for Levenberg-Marquardt method.

3.6 PROJECT ACTIVITIES AND KEY MILESTONES (FYP I)

Detail of Activities	Week Number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of project title	*	*												
Preliminary research work and literature review		*	*	*	*									
Submission of extended proposal						*								
Preparation for proposal defense							*							
Proposal defense								*	*					
Detailed literature review								*	*	*	*	*		
Preparation of interim report			*	*	*	*	*	*	*	*	*	*		
Submission of interim report (draft)													*	
Submission of interim report														*

Table 1: Activities and milestone (FYP1)

Detail of Activities	Week Number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Parameter calculation (frequency factor)	*	*	*	*	*	*	*							
Progress report submission								*						
Parameter estimation (activation energy)						*	*	*	*	*	*			
Pre-SEDEX presentation											*			
Submission of dissertation (draft)												*		
Submission of technical paper													*	
Oral presentation (viva voce)														*
Submission of project dissertation														*

Table 2: Activities and milestone (FYP2)



-Completed Milestone

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PARAMETER ESTIMATION

The hybrid particle optimization algorithm parameters are presented in Table 3. In parameter estimation, the model calculated values are determined by numerically solving the mass balance equation under isothermal condition using *ode23s* solver available in MATLAB. It is supposed that the effectiveness factor for the commercial iron catalysts is equal to one for the laboratory kinetic experimental data as a result of smaller catalyst particles used. Also, the α value is assumed as 0.5 for all three iron catalysts according to Temkin, and Dyson and Simon.

Kinetic experiments were carried out by Guacciet *al.* in Montedison laboratory using the catalysts such as FNMS, FN and so on with the particle size of 0.42-0.5 mm. In the present work, FNMS and FN catalyst data are considered for the model validation. The volume of the catalyst bed used is 2 cm³ and the number of observations available for FNMS and FN catalysts is 7 and 12, respectively. The FNMS catalyst contains 60% Fe₂O₃, 32.6% FeO and remaining as the promoter (Al₂O₃, CaO, SiO₂, MgO and K₂O). The catalyst particle density is 4.89 g/cm³. The activation energy of an ammonia synthesis reaction is estimated through hybrid optimization algorithm using FNMS catalyst experimental data and the estimated value is presented in Table 4. The estimated activation energy for an ammonia synthesis reaction using FNMS catalyst is 37,279 ± 184 cal/mol. The residual sum of squares value obtained for this optimization problem is 0.35 and higher *F*-value for the global significance of regression is observed. The parity diagram obtained for FNMS catalyst data is shown in Figure 3. The isothermal mass balance equation described in this paper has a best fit with the experimental data. The residual error and per cent relative error plots obtained for the model validation with FNMS

catalyst experimental data are depicted in Figure 4. Here, the residual errors obtained for the mole fraction of ammonia in the laboratory reactor is lower than ± 0.4 and the per cent relative errors are within $\pm 4\%$. The reported pre-exponential factor and activation energy for an ammonia synthesis reaction by Guacciet *al.* are 5.131×10^{14} , and 39,057 cal/mol, respectively at $\alpha = 0.55$. Furthermore, the estimated activation energy through hybrid DGLCPSO is close to the value reported by Guacciet *al.*

The FN catalyst contains 66.8% Fe₂O₃, 27.9% FeO and remaining as the promoter (Al₂O₃, CaO, SiO₂, MgO and K₂O). The catalyst particle density is 4.88 g/cm³ and twelve experimental observations at different pressure, temperature and space velocity are used to estimate the activation energy of an ammonia synthesis reaction. The estimated activation energy value is given in Table 4. The estimated activation energy using FN catalyst experimental data is $38,007 \pm 300$ cal/mol. The residual sum of squares errors obtained for this optimization problem is low and the F-value obtained here is significant. The parity diagram obtained for an ammonia synthesis reaction using FN catalyst data is depicted in Figure 5. It is observed that the present model shows best fit with the experimental data. The residual error and percent relative error plots obtained for the FN catalyst experimental data are shown in Figure 6. Here, the percent relative errors obtained for the mole fraction of ammonia in the reactor are lower than $\pm 9\%$. The reported pre-exponential factor and activation energy for an ammonia synthesis reaction by Guacciet *al.* are 7.6683×10^{17} , and 49,951 cal/mol, respectively at $\alpha = 0.55$. Here, the estimated activation energy for the FN catalyst data through hybrid DGLCPSO is lower than the reported parameters by Guacciet *al.*

In the third case study, the proposed kinetic model is validated with Nelson *et al.* kinetic data using KMIR Haldor Topsøe catalyst. The catalyst volume and particle size used are 2.5 cm³ and 0.3-0.7 mm, respectively. The range of operating conditions covered by Nelson *et al.* experiments as follow:

Pressure: 149-309 atm

Temperature: 330-495°C

Space velocity: 13200-105600 V/V/h

Ratio H₂:N₂: 6.23-1.15.

This catalyst contains 95%Fe, 2% Al₂O₃, 1.5% K₂O, and 1.5% CaO with traces of MgO and SiO₂. The density of KMIR Haldor Topsøe catalyst is 2.35 g/cm³. In this parameter optimization, 32 experimental observations are used to estimate the activation energy of an ammonia synthesis reaction through hybrid DGLCPSO. The estimated activation energy is presented in Table 4. The estimated activation energy for an ammonia synthesis reaction using KMIR Haldor Topsøe catalyst data is 40,131 ± 156 cal/mol. The residual sum of squares obtained for this optimization problem is high and the F-value observed here is significant. The parity diagram obtained for the model validation using KMIR Haldor Topsøe catalyst data is depicted in Figure 7. The residual error and percent relative error plots obtained for this type of catalyst are shown in Figure 8. Here, the percent relative errors for the comparison between the experimental data with the model calculated values are lower than ± 32%. The hike in the percent relative errors is due the variation of hydrogen to nitrogen molar flow rate considered in the kinetic experiments from 1.15 to 6.23. Also, the variation in the pressure, inlet flow rate of the gaseous mixture (H₂-N₂) and temperature caused this effect. In 1968, Dyson and Simon estimated the kinetic parameters for an ammonia synthesis reaction using Nelson *et al.* data through linear regression. The reported values for the pre-exponential factor and activation energy of an ammonia synthesis reaction by Dyson and Simon are 8.849×10¹⁴ and 40,765 cal/mol, respectively at $\alpha = 0.5$. Also, Guacciet *al.* estimated the pre-exponential factor and activation energy for ammonia synthesis reaction using KMIR Haldor Topsøe catalyst data through nonlinear regression. The reported parameter values are 1.6066×10¹⁵, and 42,893 cal/mol for the pre-exponential factor and activation energy, respectively at $\alpha = 0.692$. By comparing these results with the present model validation, the estimated activation energy for KMIR Haldor Topsøe catalyst data through hybrid DGLCPSO is very close to the value of activation energy reported by Dyson and Simon.

Parameter	Value
number of iteration	300
number of particles	60
<i>a</i>	1
<i>b</i>	1
<i>c</i>	2
lower limit for DGLCPSO weighing factor	0.35
upper limit for DGLCPSO weighing factor	0.9
lower limit for activation energy (cal/mol)	30000
upper limit for activation energy (cal/mol)	50000

Table 3: DGLCPSO parameters

Parameter	Catalyst		
	FNMS	FN	KMIR HaldorTopsøe
Activation energy (cal/mol)	37,279	38,007	40,131
	95% confidence interval		
Lower limit	37,095	37,707	39,975
Upper limit	37,463	38,307	40,287
	Variance analysis		
Total sum of squares	914	1,629	10,184
Regression sum of squares	912	1,604	10,555
Residual sum of squares	0.35	3.14	116.3
F-value	15,806	5,621	2,812

Table 4: Estimated activation energy for an ammonia synthesis reaction

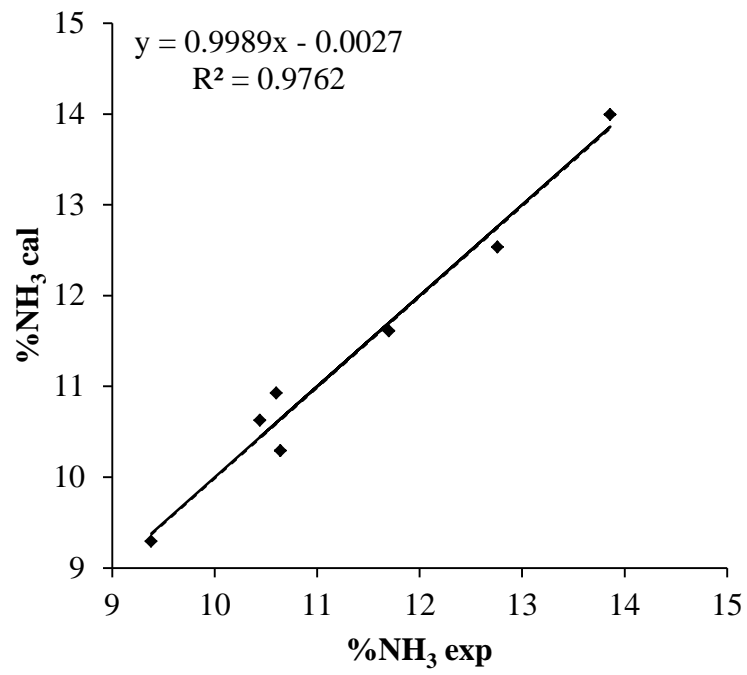
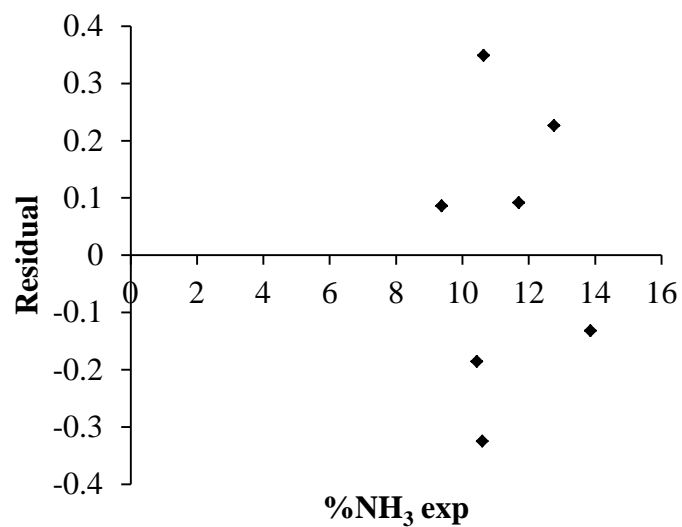
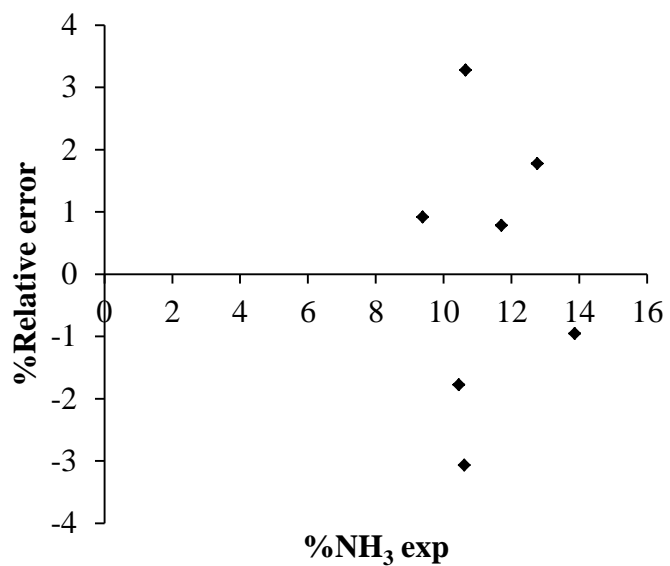


Figure 3: Parity diagram obtained for an ammonia synthesis reaction using FNMS catalyst experimental data



(a)



(b)

Figure 4: Error analysis plots obtained for an ammonia synthesis reaction using FNMS catalyst experimental data. (a) residual, and (b) relative error.

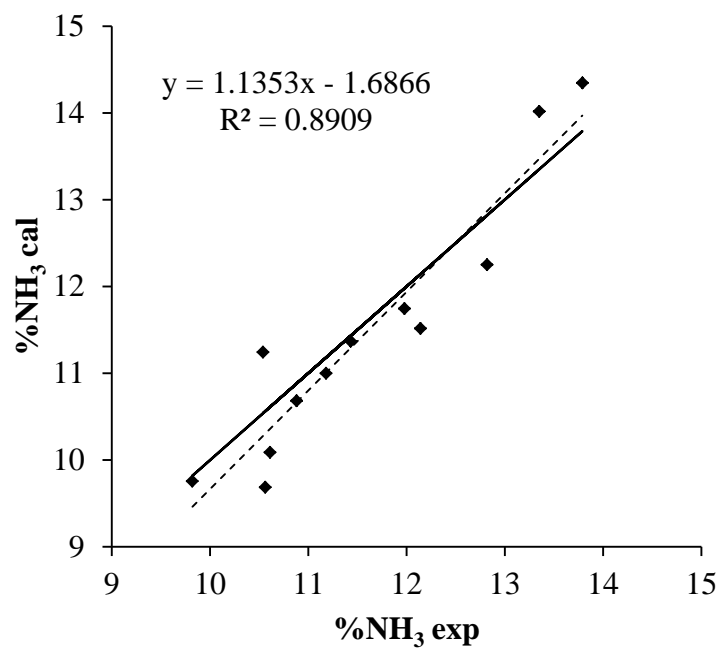
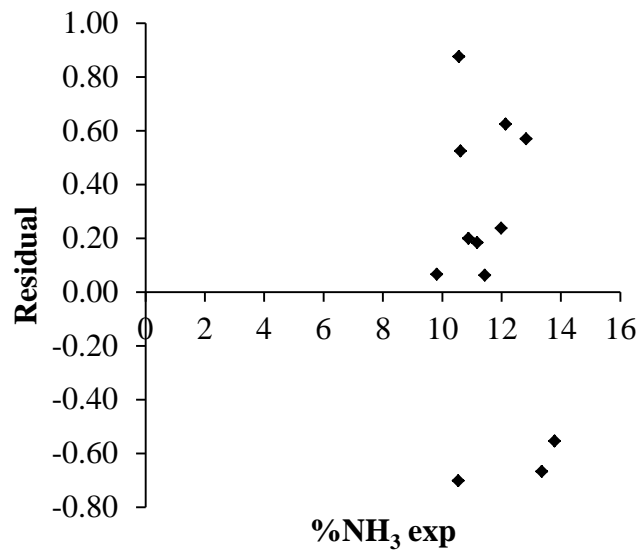
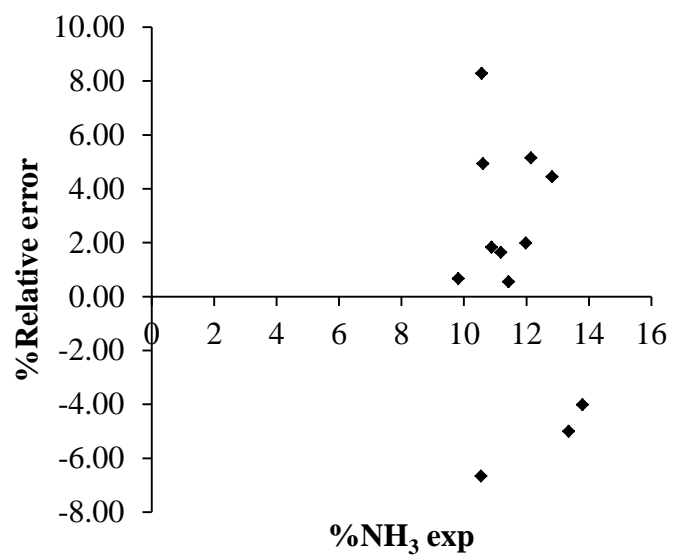


Figure 5: Parity diagram obtained for an ammonia synthesis reaction using FN catalyst experimental data



(a)



(b)

Figure 6: Error analysis plots obtained for an ammonia synthesis reaction using FN catalyst experimental data. (a) residual, and (b) relative error

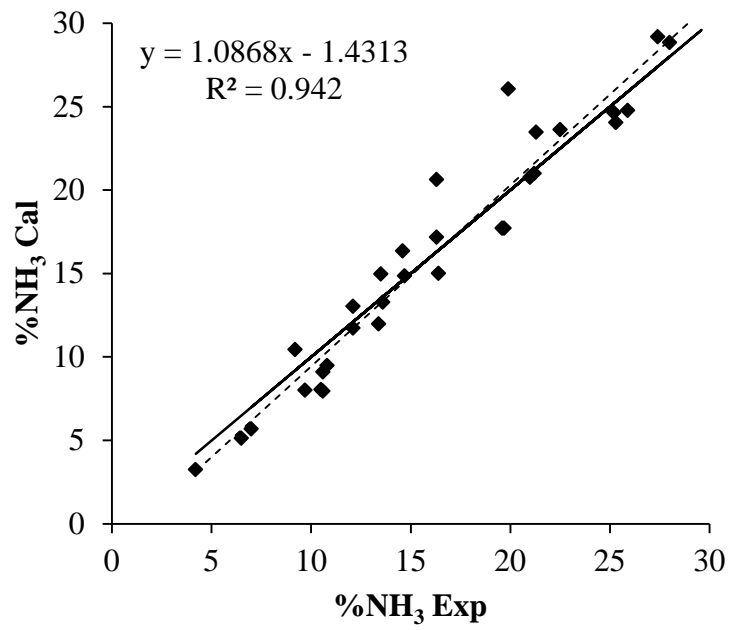
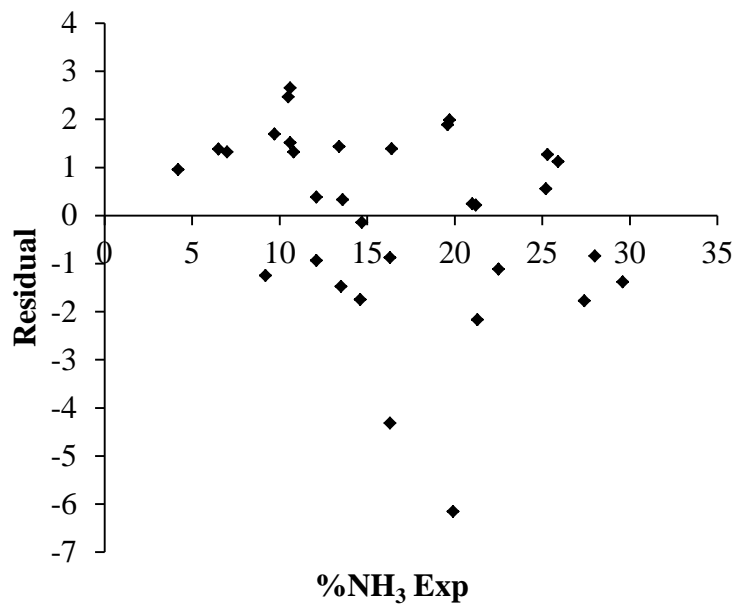
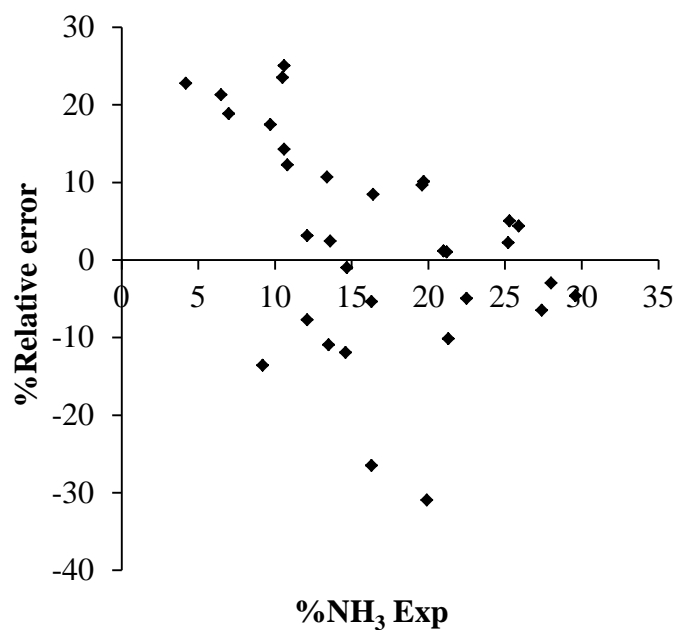


Figure 7: Parity diagram obtained for an ammonia synthesis reaction using KMIR HaldorTopsøe catalyst experimental data



(a)



(b)

Figure 8: Error analysis plots obtained for an ammonia synthesis reaction using KMIR HaldorTopsøe catalyst experimental data

CHAPTER 5

CONCLUSION AND RECCOMENDATION

The kinetic model of an ammonia synthesis reactor has been modelled successfully. The pre-exponential factor of the reaction is calculated through transition state theory and statistical thermodynamics concepts. The activation energy required for the decomposition of ammonia into nitrogen and hydrogen is estimated using three different types of commercial iron catalyst experimental data through HDGLCPSO. The results obtained have shown high consistency when compared with the data obtained from literature.

It is suggested to use different types of commercial catalysts other than those tested in this project in the HDGLCPSO to estimate the kinetic parameter. This might help to discover better or a more suitable type of catalysts for ammonia synthesis. Besides, a fourth degree Levenberg-Marquardt algorithm shall be used instead of a two degree Levenberg-Marquardt algorithm in future works. In a nutshell, this project is well completed within the given time frame and has achieved all the objectives.

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APPENDICES

(A.1) Equilibrium Constant(Dyson & Simon, 1968)(Guacci, Traina, Buzzi Ferraris, & Barisone, 1977)

The equilibrium constant, K_a can be calculated using Gillespie and Beattie correlation.

$$\log_{10} K_a = -2.691122 \log_{10} T - 5.519265 \times 10^{-5} T + 1.848863 \times 10^{-7} T^2 + \frac{2001.6}{T} + 2.6899$$

(A.2) Activity (Dyson & Simon, 1968)(Guacci, Traina, Buzzi Ferraris, & Barisone, 1977)

The following formula can be used to calculate the activity of each component involved in the ammonia synthesis reaction.

$$a_i = y_i \gamma_i P, \quad \text{for } i = \text{N}_2, \text{H}_2, \text{ and } \text{NH}_3$$

(A.3) Activity Coefficient(Dyson & Simon, 1968)(Guacci, Traina, Buzzi Ferraris, & Barisone, 1977)

The activity coefficient for hydrogen can be calculated using Cooper and Shaw and Wones correlation and is given by

$$\gamma_{\text{H}_2} = \exp \left\{ \frac{\exp(-3.8402T^{0.125} + 0.541)P - \exp(-0.1263T^{0.5} - 15.980)P^2 + 300[\exp(-0.011901T - 5.941)]\exp\left(-\frac{P}{300} - 1\right)}{300[\exp(-0.011901T - 5.941)]\exp\left(-\frac{P}{300} - 1\right)} \right\}$$

(A.4) & (A.5) Activity Coefficients for Nitrogen and Ammonia

For nitrogen and ammonia, the activity coefficients can be calculated using the correlations of Cooper and Newton. They are

$$\gamma_{\text{N}_2} = 0.93431737 + 0.3101804 \times 10^{-3} T + 0.295896 \times 10^{-3} P - 0.2707279 \times 10^{-6} T^2 + 0.4775207 \times 10^{-6} P^2$$

$$\gamma_{\text{NH}_3} = 0.1438996 + 0.2028538 \times 10^{-2} T - 0.4487672 \times 10^{-3} P - 0.1142945 \times 10^{-5} T^2 + 0.2761216 \times 10^{-6} P^2$$

NOMENCLATURES

a_i = Activity of the component i ($i = \text{N}_2, \text{H}_2$ and NH_3)

A_{Pre} = Pre-exponential factor (s^{-1})

E_{Act} = Activation energy (cal/mol)

$endgen$ = Maximum iteration number in DGLCPSO

C = Concentration (kmol/m^3)

c = Search parameter in DGLCPSO

f_i = Fugacity of component i ($i = \text{N}_2, \text{H}_2$ and NH_3)

$F_{\text{N}_2}^{In}$ = Initial molar flow rate of nitrogen entering to the reactor (kmol/s)

$F_{\text{NH}_3}^{In}$ = Initial molar flow rate of ammonia entering to the reactor (kmol/s)

$F_{\text{CH}_4}^{In}$ = Initial molar flow rate of methane entering to the reactor (kmol/s)

F_{Ar}^{In} = Initial molar flow rate of argon entering to the reactor (kmol/s)

F_{N_2} = Molar flow rate of nitrogen leaving from the reactor (kmol/s)

F_T = Total molar flow rate (kmol/s)

k = Kinetic constant for the reverse reaction ($\text{kmol}/\text{m}^3\text{s}$)

K_a = Equilibrium constant

k_B = Boltzmann's constant ($= 1.38065 \times 10^{-23}$ J/K)

h = Planck constant ($= 6.62607 \times 10^{-34}$ J.s)

M_w = Molecular weight of a molecule

N_A = Avogadro's number ($= 6.023 \times 10^{23}$ mol⁻¹)

N_{iter} = Total number of iterations considered in DGLCPSO

N_{pt} = Total number of particles considered in DGLCPSO

n_{obs} = Number of observations

P = Pressure (atm)

r = Particle radius ($= 2.85 \times 10^{-3}$ m)

r_1, r_2 = Random numbers

r_{NH_3} = Rate of reaction for ammonia (kmol/m³s)

R = Gas constant ($= 1.987$ cal/mol K)

S_r^o = Absolute translational entropy of a molecule

$\Delta S^\#$ = Change in entropy of a molecule at transition state

T_c = Critical temperature of a molecule (K, NH₃ = 405.37 K)

T = Reaction temperature (K)

v = Velocity of a particle

V = Volume of catalyst bed (m³)

V_m = Molar volume of a molecule (m³/mol)

ΔV = Change in volume

w^i = Weighing factor in DGLCPSO at iteration i $\left(w^i = w_{\max} - \frac{w_{\max} - w_{\min}}{N_{iter}} i \right)$

w_{min} = Minimum value of the weighing factor in DGLCPSO

w_{max} = Maximum value of the weighing factor in DGLCPSO

x = Fractional conversion of nitrogen in a reactor

x^{ind} = Individual particle position in DGLCPSO

x^{loc} = Local neighborhood particle position in DGLCPSO

x^{glo} = Global particle position in DGLCPSO

X_i = Mole fraction of component i in the catalyst pellet ($i = \text{N}_2, \text{H}_2, \text{NH}_3, \text{CH}_4$ and Ar)

y_i = Mole fraction of component i leaving from the reactor ($i = \text{N}_2, \text{H}_2, \text{NH}_3, \text{CH}_4$ and Ar)

α = Constant (= 0.5 for all iron catalysts)

β = Ratio of molar flow rate of hydrogen to nitrogen entering into the reactor

γ_i = Activity coefficient of the component i , ($i = \text{N}_2, \text{H}_2$ and NH_3)

ρ_{cat} = Catalyst particle density (kmol/m^3)