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KINETIC PARAMETER ESTIMATION IN AMMONIA SYNTHESIS REACTION THROUGH NONLINEAR REGRESSION.

DISSERTATION

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CERTIFICATION OF APPROVAL

KINETIC PARAMETER ESTIMATION IN AMMONIA SYNTHESIS REACTION THROUGH NONLINEAR REGRESSION.

by

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A project dissertation submitted to the
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Approved by,

(Dr ABRAR INAYAT)
Course coordinator FYP 2

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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.

(DANESHWARAN A/L SATIMURTY

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ABSTRACT

Ammonia synthesis optimization is of high interest in industry as market expands and demand increases. The optimization is made possible through fractional conversion of nitrogen in a reaction. Material balance is performed across bed of KMIR HaldorTopsoe catalyst before model equation of reaction is obtained. Next part of this project is kinetic parameter estimation in ammonia synthesis reaction. The two main parameters estimated are the pre- exponential factor and activation energy. The rate expression is done through Temkin equation 1950. Transitional state theory and statistical thermodynamics are used to obtain pre-exponential factor calculation. Sackur- Tetrode equation is used to calculate translational entropy and Yamada and Gunn (1973) correlation is used to calculate molar volume. The activation energy is calculated by minimizing residual sum of squares errors between experimental data and model calculated values.

ACKNOWLEDGEMENT

First and foremost, I would like to thank Universiti Teknologi Petronas for providing me with the opportunity to perform the final year project. I would also like to extend my highest gratitude to my supervisor, Dr. Periyasamy Balasubramaniam, who throughout the duration of my final year project has tirelessly aided and guided me for the project. Additionally, I am also grateful to the post-graduate students who have helped me through guidance and advice for my project. I would also like to thank my parents for their continuous support and encouragement which enabled me to complete the project.

INTRODUCTION

Ammonia synthesis is an important process in chemical developments. Ammonia is the initial chemical material for variety of industries. It is used in chemical fertilizers production, explosive materials, polymers, acids and even coolers. Kinetic modeling can play an important role to give an insight of the industrial units and hence modeling of Ammonia unit is very important to help us investigate different operation modes of this unit which better understanding off its bottleneck can led us to make the operation yield higher than before.

Supply for nitrogen based fertilizers was not able to meet the worldwide demand in twentieth century. Scientists step up to solve the problem of the world's dependence on fast disappearing natural sources of ammonia. Processes such as thermal processing to mixed oxides of nitrogen, cyanide formation, aluminum nitride formation and decomposition to ammonia showed little commercial promise. In the end, Fritz Haber and Carl Bosch completed ammonia synthesis.

Catalytic synthesis of ammonia was developed by Haber by utilizing hydrogen and nitrogen gas which are abundant and inexpensive. (Rossignol, 2009) This synthesis could force unreactive gases nitrogen and hydrogen to combine into ammonia using high temperature and high pressure in reactor assisted by iron catalyst. The Haber-Bosch process for ammonia synthesis was successfully operated in September 1913, was the decisive step into the age of mineral fertilizers. This innovation became a key driver in the development of the industrialized society and is still securing the nutrition of billions of people today. The realization of industrial ammonia synthesis involved high entrepreneurial risks and demanded great staying power. Process and equipment for this pioneering technology had to be developed from scratch.

Given the massive scale of ammonia production, tiny improvement in efficiency of ammonia synthesis process can have massive implications for global energy demand. Researches worldwide have tried to estimate kinetic parameters through various methods such as orthogonal collocation method combined with Broyden method, polythermal-temperature-ramping reactor (PTR), hybrid dynamic global and local combined particle swarm optimization. Activation energy and pre-exponential factor are the two important parameters estimated through non-linear regression.

PROBLEM STATEMENT

Yield of ammonia synthesis will remain the same for years if reaction is not optimized. Efficiency of the reactor is the core factor that affects the yield of ammonia in a reaction. Hence, kinetic model of reactor and the parameter of the reaction have to be developed and estimated to improve overall efficiency of a fixed bed reactor in industrial ammonia synthesis. Previous analysis is not sufficient to prove accuracy and consistency of experimental results obtained. As a trial measure, non-linear regression is applied in ammonia synthesis estimation.

OBJECTIVE

To estimate kinetic parameters such as pre exponential factor and activation energy included in an ammonia synthesis reaction.

SCOPE OF STUDY

Scope of study for this project involves ammonia synthesis reactor modeling and calculation of frequency factor in rate expression of ammonia synthesis. Previously learned knowledge on reaction engineering, transitional state-theory and statistical thermodynamics is required. Once it is done, the kinetic parameter estimation of ammonia synthesis executed using nonlinear regression. MATLAB tools are used in optimization of parameter estimation where the calculations done are translated into computer codes.

LITERATURE REVIEW

Optimization of ammonia synthesis process highly relies on accurate system model. Launching a proper mathematical model of ammonia synthesis process is a key problem of operation optimization. It has received considerable attention since last century. Heterogeneous simulation models imitating different types of ammonia synthesis reactors have been developed for design, optimization and control. Through modeling of the reactor, temperature, concentrations, and pressure profile is obtained. As industrial data is not available along the length of bed, model testing based on mentioned parameters is achieved at the end of each bed. As mentioned earlier, the rate of reaction is expressed through Temkin equation 1950.

$$R_{NH3} = 2k[K_a^2 a_{N_2}\left(\frac{a_{H_2}^3}{a_{NH_3}^2}\right)^{\alpha} - \left(\frac{a_{NH_3}^2}{a_{H_2}^3}\right)^{1-\alpha}]$$

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_α: Equilibrium constant

α_i : Activity

Parameter estimation through non-linear regression was not involved in previous researchers work. Researchers valued pre-exponential factors, A, and activation energies E_a, of ammonia synthesis reaction by linear regression method in early stages, and advanced to HDGLCPSO method which is available after 1995. On the other hand, A is calculated from transitional state theory and statistical thermodynamics in this project. $S^{o,f}_{transl}$ must first be calculated before the next step can be taken. Critical properties of ammonia are required together with aid of Sackur-Tetrode equation in calculating $S^{o,f}_{transl}$. The entropy at the standard state,$\Delta S^{o,\neq}$ is then one third of $S^{o,f}_{transl}$. This is because the molecule loses one degree of freedom in the reverse reaction.

An accuracy of kinetic model generally functions of number of independent parameters. Its popularity in relation to the process application is an indicative of its mathematical simplicity. Undoubtedly, linear regression analysis has frequently been employed in accessing the kinetic modeling of reactor and parameters estimation, primarily owing to its wide usefulness in variety of modeling process. This reflects the appealing simplicity of its equation. However, during the last few years, development interest in utilization of non-linear regression in optimization modeling has been noted. A number of researchers have been sponsored to investigate efficiency of linear and non-linear regression methods for kinetic parameter estimation in ammonia synthesis reaction through application of Sackur Tetrode equation, Temkin equation, Levenberg-Marquardt and Redlich-kwang equation.

METHODOLOGY

PROJECT FLOW

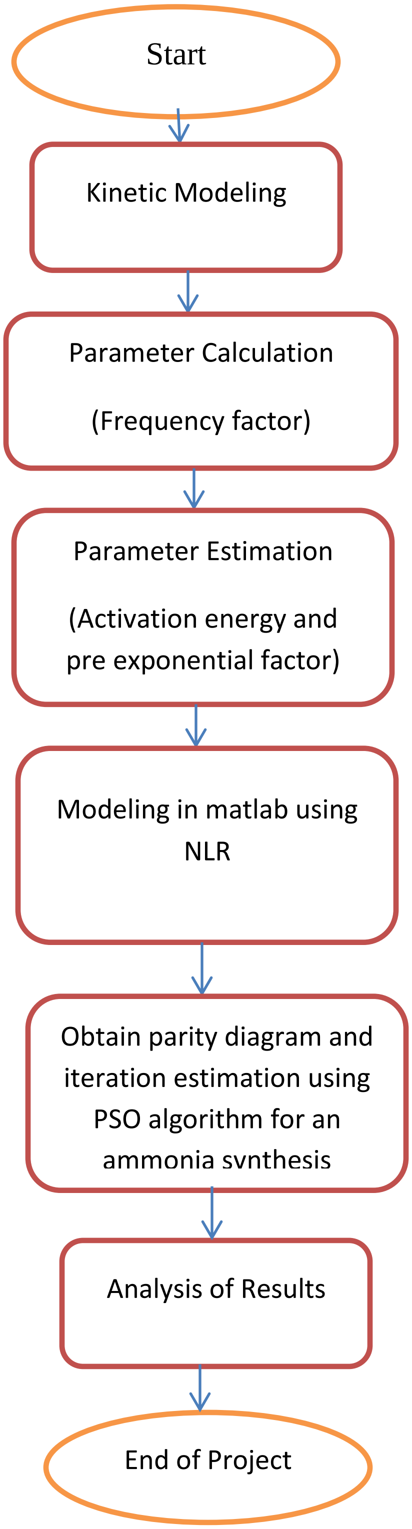


Figure 1: Project flow

Modeling of Ammonia Synthesis Reactor

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

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

Fractional conversion, x of the key element in the reaction, which is nitrogen gas, N_2.

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

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

$$F_{N_2} = oulet\ flow\ of\ nitrogen\ gas$$

$$x = fractional\ conversion\ of\ nitrogen$$
$$across\ the\ reactor$$

Outlet flow rates of each species

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

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

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

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

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

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

Hence,

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

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

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

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

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

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

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

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

Mole fraction of each individual component represented as:

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

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

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

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

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

Developed model equation is:

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

Rate expression

Temkin equation 1950 is the rate of equation for ammonia synthesis

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

Where constant $\alpha = 0.5$

$$\log_{10} K_a = -2.691122\log_{10} T - 5.519265\times10^{-5}T + 1.848863\times10^{-7}T^2 + \left(\frac{2001.6}{T}\right) + 2.6899$$

Activity coefficient

Activity coefficient is calculated as follows using the following formula:

$\alpha_i = y_i \gamma_i P$

Activity coefficient for Nitrogen and Ammonia using Cooper and Newton correlation:

$$\gamma N_2 = 0.93431737 + 0.3101804\times10^{-3}\,T + 0.295896\times10^{-3}\,P - 0.2707279\times10^{-6}\,T^2 + 0.4775207\times10^{-6}\,P^2$$

$$\gamma NH_3 = 0.1438996 + 0.2028538\times10^{-2}T - 0.4487672\times10^{-3}\,P - 0.1142945\times10^{-5}\,T^2 + 0.2761216\times10^{-6}\,P^2$$

Activity coefficient for Hydrogen using Cooper and Shaw and Wones:

$$\gamma H_2 = \exp\,[\,\exp\,(-3.8402T^{0.125} + 0.541\,)\,P - \exp\,(\,-0.12635T^{0.5} - 15.98\,)\,P^2 + 3w\,(\,\exp\,(\,-0.011901T - 5.941)\,]\,\exp\,(-P/3w - 1)]$$

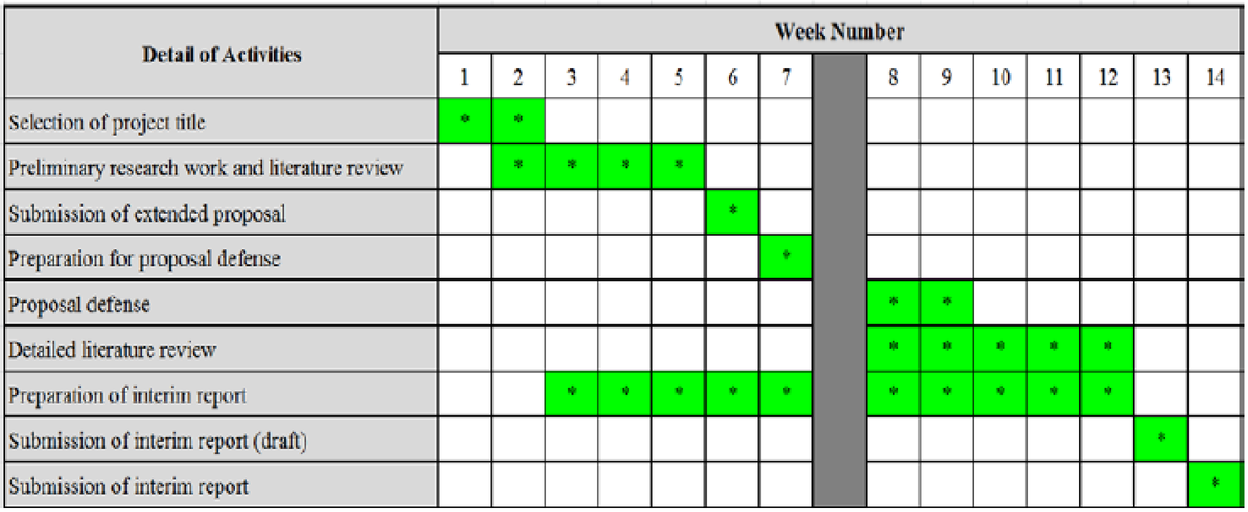
Final expression

Relation between pre-exponential factor and activation energy.

$$K = A_{ref} \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{av}}\right)\right)$$

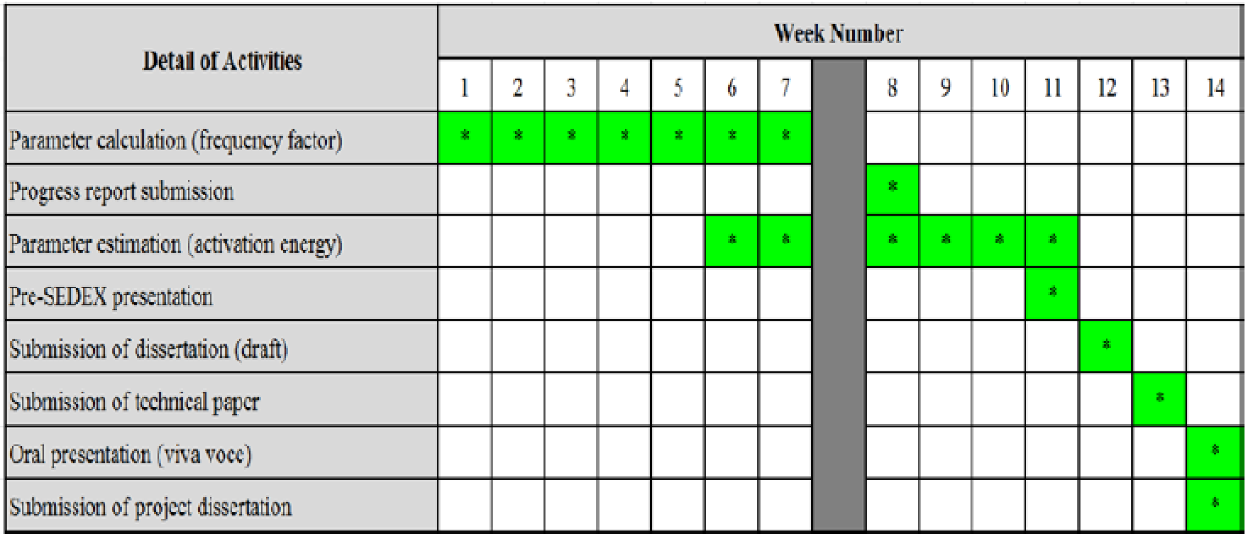
$$\text{Where } A_{ref} = A \exp\left(-\frac{E}{RT_{av}}\right)$$

Project activities and key milestones (FYP 1 and FYP 2)



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)

RESULTS AND DISCUSSION

The non-linear regression parameters are presented in Table below. Model calculated values are determined numerically solving mass balance equation under isothermal condition using ode23s solver available in MATLAB. Effectiveness factor for commercial KMIR Haldor Topsoe catalyst is equal to one for laboratory kinetic experimental data. α value is assumed 0.5 for the KMIR Haldor Topsoe catalyst according to Temkin, Dyson and Simon.

Kinetic model validated with Nelson et al. kinetic data using KMIR Haldor Topsoe catalyst. This catalyst contains 95%Fe, 2%Al_2O_3, 1.5% K_2O and 1.5% CaO with traces of MgO and SiO_2. Density of KMIR Haldor Topsoe catalyst is 2.35 g/cm^3. The estimated activation energy for an ammonia synthesis reaction using KMIR Haldor Topsoe catalyst is 38174 cal/mol. The calculated pre-exponential factor is $3.6374 \times 10^{10.}$ Residual sum of squares obtained is high and F-value is significant. The range of operating conditions covered by Nelson et al. experiments is as follow:

Pressure: 149-309 atm

Temperature: 330-495^{0}C

Space velocity: 13200-105600 V/V/h

Ratio H_2:N_2: 6.23-1.15.

The reported values for pre-exponential factor and activation energy for ammonia synthesis reaction by Dyson and Simon are 8.849×10^{14} and 40765 cal/mol at $\alpha = 0.5$. When comparing results reported by Dyson and Simon with our obtained value, the estimated activation energy and pre-exponential factor for KMIR HaldorTops∅e catalyst through non-linear regression is very close.

PARAMETER	VALUE
Number of iteration	100
Number of particles	10
Number of search dimension	1
a	1
b	1
c	2
Minimum weighing factor	0.35
Maximum weighing factor	0.9
Assumed initial global error	1000

Table 3: DGLCPSO parameters

Parameter	KMIR HaldorTops∅e catalyst
Reference Pre-exponential factor, A	0.075
Calculated pre-exponential factor	3.6374×10^{10}
Activation energy, E (cal/mol)	38174
95% confidence interval	
Lower limit	0.067,34580
Upper limit	0.083,41759
Variance analysis	
Total sum of squares	10183.91
Regression sum of squares	10488.86
Residual sum of squares	111.8
F-value	1407.32

Table 4: Estimated activation energy for an ammonia synthesis reaction

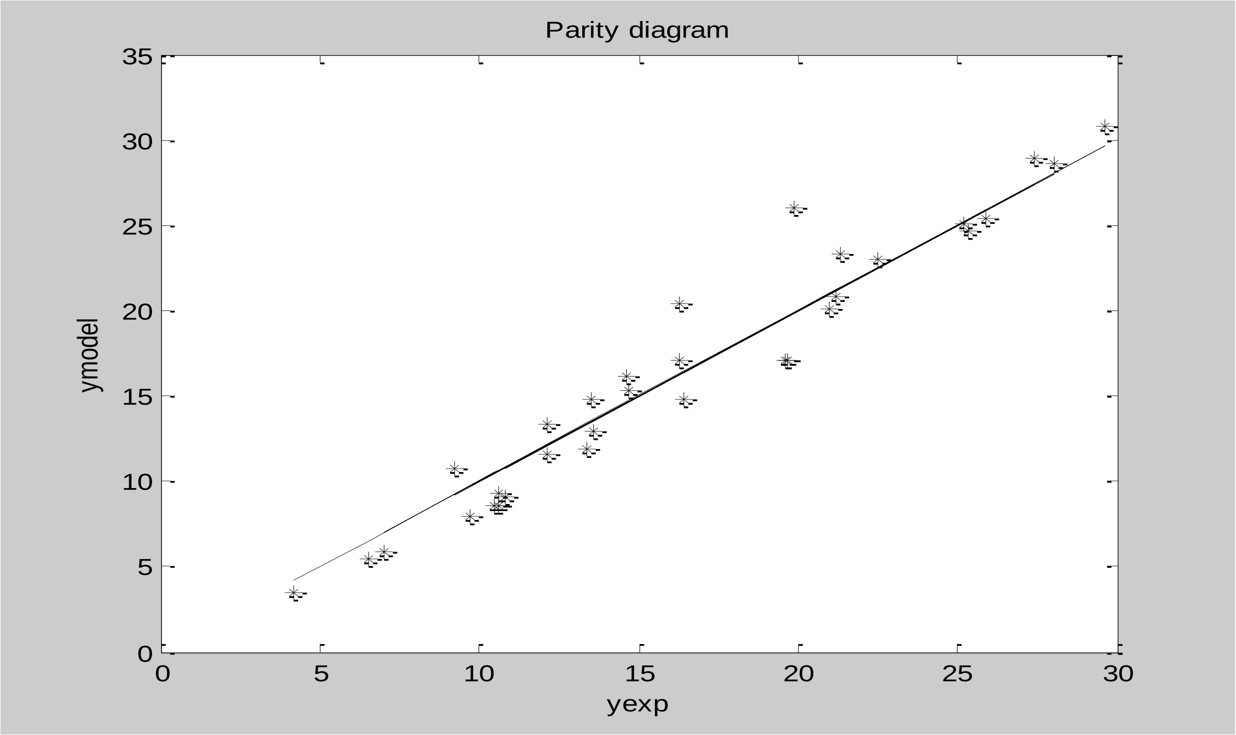


Figure 2 : Parity diagram obtained for an ammonia synthesis reaction using KMIR HaldorTops∅e catalyst

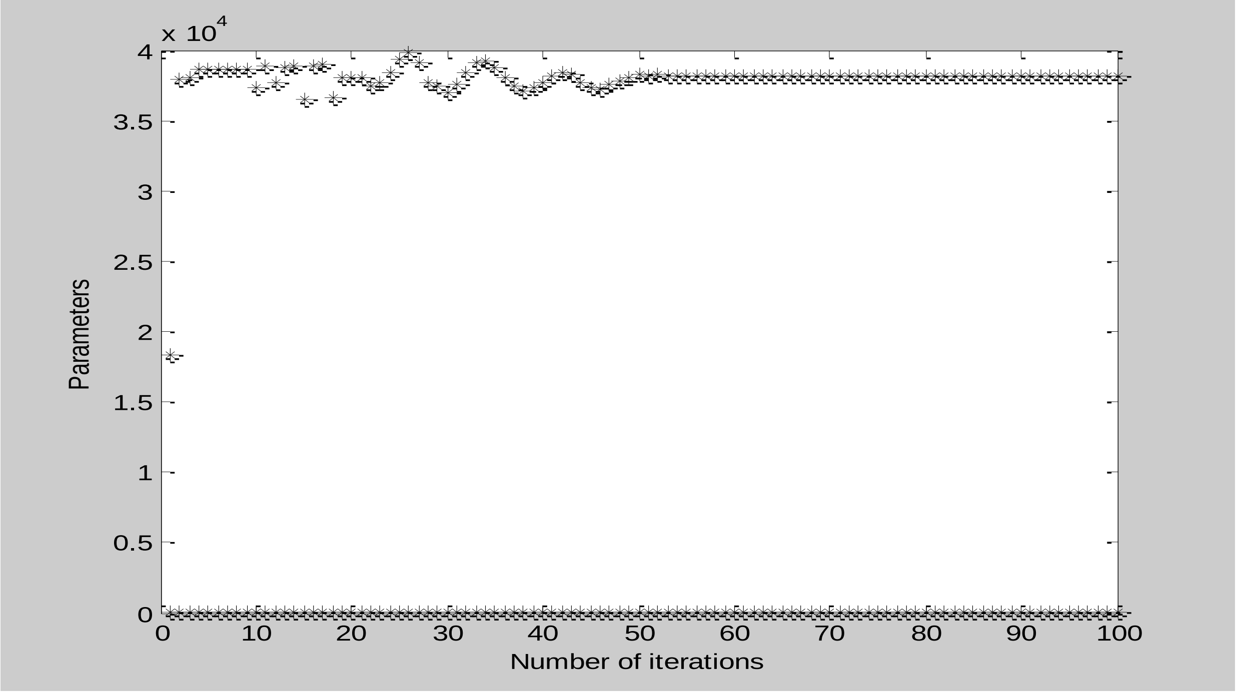


Figure 3: Number of iterations estimated using PSO algorithm

CONCLUSION

The pre-exponential factor of reaction calculated through transition state theory and statistical thermodynamics concept. Activation energy for decomposition of ammonia into nitrogen and hydrogen is estimated using KMIR Haldor Topsoe catalyst through non-linear regression. The future results obtained are expected to have high consistency when compared with the data obtained from literature.

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APPENDICES

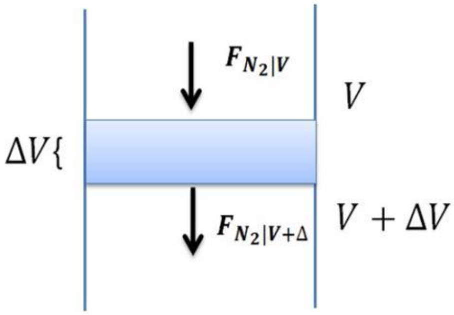
Dr Kennedy and Dr Eberhart in 1995 proposed the original PSO algorithm. (1)

$v_{p,d}{}^{k+1}=wv_{p,d}{}^{k}+c1r1(x_{p,d}{}^{ind}-x_{p,d}{}^{k})+c2r2(x_{d}{}^{glo}-x_{p,d}{}^{k})$ .... (i)
$x_{p,}{}^{+1}=x_{p,d}{}^{k}+v_{p,d}{}^{k+1}$…………………… (ii)

The rate of reaction can be written as the rate of disappearance of nitrogen gas or hydrogen gas and this equal to the rate of formation of ammonia gas (2)

$$\frac{rN2}{-1}=\frac{rH2}{-3}=\frac{rNH3}{2}$$

Mass balance calculation performed across catalyst bed. Volume of ΔV equal to catalyst bed. (3)



$$FN2|V-FN2|V+\Delta V+rN2\eta\Delta V=0$$

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

$$\lim \Delta V\rightarrow 0(\frac{\mathrm{FN2|V+\Delta V-FN2|V}}{\Delta \mathrm{V}})=-rN2\eta$$
$$\frac{-\mathrm{dFN2}}{\mathrm{dV}}=-rN2\eta$$

Then,

$$\frac{\mathrm{dFN2}}{\mathrm{dV}}=-\frac{1}{2}rNH3\eta\mathrm{since}rN2=\frac{-\mathrm{rNH3}}{2}$$

NOMENCLATURES

ai= Activity of the component i (i = N2, H2 and NH3)

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

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

C = Concentration (kmol/m3)

c= Search parameter in DGLCPSO

F_{N2}^{ln} = Initial molar flow rate of nitrogen entering to the reactor (kmol/s)

F_{NH3}^{ln} = Initial molar flow rate of ammonia entering to the reactor (kmol/s)

F_{CH4}^{ln} = Initial molar flow rate of methane entering to the reactor (kmol/s)

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

F_{N2}= 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 (kmol/m3s)

K_a = Equilibrium constant

k_B = Boltzmann's constant (= $1.38065\times10_{-23}$ J/K)

h = Planck constant (= $6.62607\times10_{-34}$ J.s)

M_w = Molecular weight of a molecule

N_A = Avogadro's number (= $6.023\times10_{23}$ mol$_{-1}$)

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

P = Pressure (atm)

Rate of reaction for ammonia (kmol/m3s) =3NHr

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

Absolute translational entropy of a molecule =$otrS$

Tc = 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)

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

ΔV = Change in volume

NLR STATISTICS

```
*********************************************************
       Statistical analysis of the experimental data
*********************************************************
Unweighted statistics

Variable No.                    1
Total points                   32
Degrees of freedom             31
Sum of squares               1449
Variance                    46.74
Standard deviation          6.836

Weighted statistics
Total points                   32
Total degrees of freedom       31
Weighted sum of squares      1449
Weighted variance           46.74
Weighted stand. dev.        6.836


*********************************************************
          Statistical analysis of the regression
*********************************************************

 No.   Parameter    Standard      95% Confidence interval
                    deviation     for the parameters
                                  lower value  upper value
  1    7.4986e-002  4.0050e-003   6.6806e-002  8.3165e-002
  2    3.8174e+004  1.7558e+003   3.4588e+004  4.1759e+004

Degrees of freedom = 30

Total (weighted) sum of squared residuals =      111.8

Combined (weighted) residual variance (s^2) =      3.727

Significance tests


 No.   Parameter    t-calculated   Is parameter significantly
                                      different than zero?
  1    7.4986e-002  1.8723e+001             Yes
  2    3.8174e+004  2.1742e+001             Yes


Confidence limits of regressed variables

 Measured    Degrees of    Residual     95% Confidence limit
 variable    freedom       variance     for each measured variable
    1         30        3.7265e+000        3.9425e+000
```

```
Covariance analysis

Variance-covariance matrix: s^2*Inverse(J transpose J)
 1.6040e-005  1.0312e-001
 1.0312e-001  3.0827e+006



Matrix of correlation coefficients
          1     0.01466
    0.01466           1



Analysis of variance

 Source of           Sum of squares    Degrees of     Variance
 variance                              freedom
 Lack of fit         3.8997e+003          -1          -3.8997e+003

 Experimental error  1.4488e+003          31          4.6735e+001

 Total               1.1180e+002          30          3.7265e+000



Randomness test

 Variable                             1
 Number of positive residuals         1
 Number of negative residuals         0
 Number of runs (changes of sign)     0
 Z =                                    NaN

 Random at 95% level of confidence

**********************************************************
               End of statistical analysis
**********************************************************
```