Kinetic Parameter Estimation in Alkylation of Benzene with 1-Decene through Hybrid Particle Swarm Optimization

by

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

SEPTEMBER 2012

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CERTIFICATION OF APPROVAL

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Approved By,

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(Dr. Periyasamy Balasubmanian)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

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.

(NURUL FARIHAH BINTI MOHD ZULKEFLE)

ABSTRACT

In this project, a kinetic model for alkylation of benzene with 1-decene over acid catalyst is presented. The desirable product from this alkylation process is 2-phenyldecane which is formed via double bond isomerization and aromatic alkylation reaction. 2-phenyldecane is formed by alkylation of benzene with alkylcarbenium ion. Alkylcarbenium ions are produced from protonation and deprotonation reaction of 1-decene isomers. In this reaction, kinetic constants follow Arhenius equation. Pre-exponantial factors of the elementary step were calculated from first principle. Activation energies of elementary steps were estimated by using Hybrid Particle Swarm Optimization (HPSO) algorithm. Parameter estimation was performed by varying the initial guess of PSO algorithm which will conduct global search of the parameters. Afterwards, the solution obtained using PSO algorithm is given as initial guesses to the Levenberg–Marquardt algorithm to determine the improved optimal solution. Parameter estimation was carried out using simulated data and the activation energies are constant with the assumed values.

ACKNOWLEDGEMENTS

First, I praise to the Almighty God for giving me the strength and His blessing to complete this project within the given time frame. I also would like to specially thanks my supervisor, Dr Periyasamy Balasubramaniam for his willingness and understanding while supervising me throughout these two semester period of the project completion. They have given me many useful insight and information that help me complete this project accordingly. Last but not least, my utmost thanks to my parents and friends for their constant support and motivation they gave me while completing this project.

Thank you.

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CHAPTER 1

INTRODUCTION

1.1 PROJECT BACKGROUND

Alkylation process is the transfer of an alkyl group from one molecule to another. The alkyl group can be transferred as an alkyl carbocation, a free radical, a carboanion or a carbene (or their equivalent). There are many application related to alkylation process such as detergent, pharmaceutical and agrochemical industries. However, this project will focuses on detergent industries where alkylation of benzene with certain olefin is used. Linear alkylbenzene (LAB) has emerged as the dominant detergent intermediate since the early 1960s driven by the environmental need to produce biodegradable detergent. In a study, linear and branched alkylbenzenes are said to be the key surfactant intermediate with nearly 3.7 million tons per year of global capacity. The declination of branched alkylbenzene since 2004 has increase the consumption of linear alkylbenzene. There are competitions of other surfactants as well; however the alkylbenzene consumption is still in demand. Traditionally, LAB was produced by using Friedel-Craft alkylation by using homogenous acid catalyst. This catalyst brings many drawbacks towards environment and the process itself but it still used in the industries. However, in recent years, researches have been done to overcome these drawbacks and also give a better solution to increase the production rate.

1.2 Problem Statement

Linear Alkylbenzene (LAB) is an extremely important intermediate in detergent industries. They were prepared by using Friedel-Craft method using homogenous acid catalyst such as $AlCl_3$ and HF. These catalysts were many drawbacks to the process and environment.

Solid acid catalysts such as Y-zeolite are preferred to avoid the usage of corrosive $AlCl_3$ catalyst. In the alkylation process, C_{11} – C_{14} are used to prepare phenyl-alkanes isomers as the feedstock to the detergent industries. In order to understand the kinetics of the process, C_{10} olefin is chosen as a model compound. Earlier, the kinetic model of alkylation of benzene with 1-decene over solid catalyst was developed from the first principle which relies on mass and energy balance. Now, we would like to develop the parameter optimization method to estimate activation energies of the elementary steps through Hybrid Particle Swarm Optimization (HPSO).

1.3 Objectives

- To estimate the activation energies of the elementary steps in alkylation of benzene with 1-decene through particle swarm optimization.
- To estimate the activation energies of the elementary steps in alkylation of benzene with 1-decene through hybrid particle swarm optimization.

1.4 Scope of Study

This project will be focus on organic chemistry and reaction engineering as the reaction mechanism in this project will be develop using both of these branches. Besides, knowledge of material and energy balance will be applied as well. The first step of this project is getting an introduction of topic itself. In this process, any books, research paper, journal and website related towards the topic need to be read in order to have better understanding on the reaction mechanism and method of optimization. In this project, we are using MATLAB software to do the optimization of parameter estimation and the calculation method need to be translated into computer codes. The process of understanding the reaction, kinetic model itself takes time about 3 weeks. Another one week available to had recap on the MATLAB software. As for the model, it will develop and the respective calculation will be calculated using the software in sequence. Mixture of C_{11} – C_{14} are used to prepare phenyl-alkanes isomers as the feedstock to the detergent industries. Earlier, the kinetic model of alkylation of benzene with 1-decene over solid catalyst was developed from the first principle. In the present work, it is proposed to develop the parameter optimization method to estimate activation energies of the elementary steps through Hybrid Particle Swarm Optimization (HPSO) method

CHAPTER 2

LITERATURE REVIEW

Linear Alkylbenzenes (LAB) is an important intermediate in production of detergent since early 1960s. It usually obtained by acid catalyzed alkylation of the aromatic ring. Traditionally, these compounds were produced by Friedel-Craft reaction (C. DeCastro, et al., 2000) using homogeneous acid catalyst. Homogeneous catalyst such as $AlCl_3$ and HF are used extensively in the detergent industry for the production of alkylbenzene even though they suffer from a series of technical and environmental drawbacks. They are highly corrosive, hazardous, consumption of high amount of catalyst, separation and disposal of spent catalyst, and lower selectivity towards 2-phenylalkanes.

Heterogeneous acid catalyst offers a many advantages and in last four decades, there are significant progress had been made towards to improve the development of industrial alkylation processes. Several numbers of materials such as homogeneous catalysts immobilized on solid supports, silica–aluminas, clays, heteropolyacids, and metal oxides. A special class of materials that were found to perform particularly well in alkylation is constituted by zeolites and modified zeolites such us beta, Y, MCM-22, and mordenite have been tested as catalyst in this alkylation process. A major breakthrough in the industrial production of ethylbenzene with a solid acid catalystwas achieved by Mobil-Badger in 1976 using a ZSM-5 zeolite in a gas phase fixed-bed reactor. Other companies followed and developed or improved their own technologies for the production of ethylbenzene using solid catalysts. Besides ZSM-5, Y zeolite and MCM-22 are reported to be the most successful solid acid catalysts for the gas phase alkylation of benzene with ethylene. Therefore, in this work, we choose Y-zeolite as the heterogeneous acid catalyst to overcome drawbacks in traditional Friedel Craft reaction.

The elementary reaction involved in an alkylation of bezene is (i) Double bond isomerization and (ii) Aromatic Alkylation. Isomerization is the process whereby the chemical process by which a compound is transformed into any of its isomeric form having the same chemical composition but with different structure or configuration and, hence, generally with different physical and chemical properties. In double bond isomerization, there are two main processes involving protonation and deprotonation. Protonation is a process of adding proton, H^+ to a molecule; meanwhile deprotonation is process of removing the proton from a molecule.

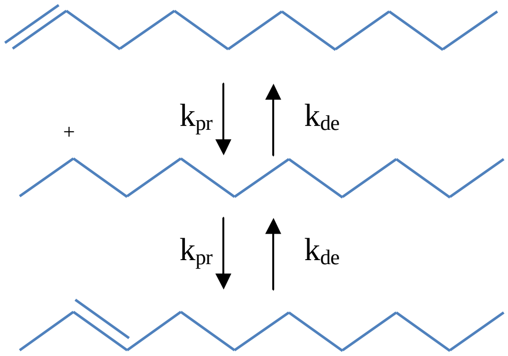
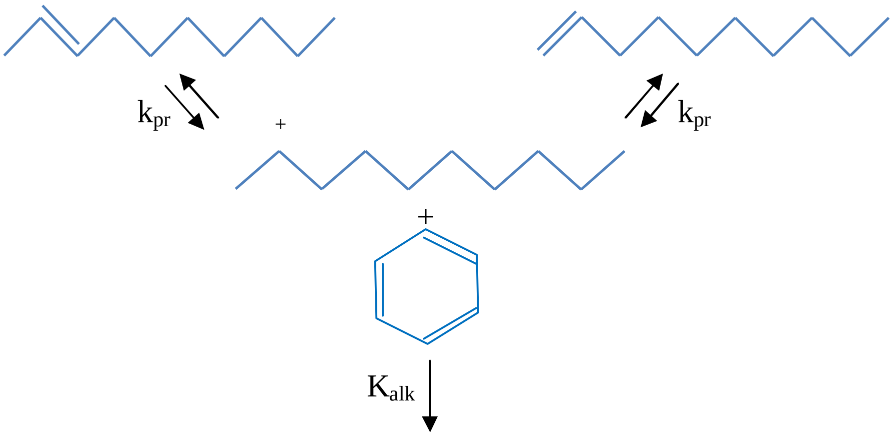


Figure 1: Isomerazation reaction

Alkylation process, the transfer of an alkyl group from one molecule to another occurs between protonated isomer and benzene ring to form phenyl isomer in this project.



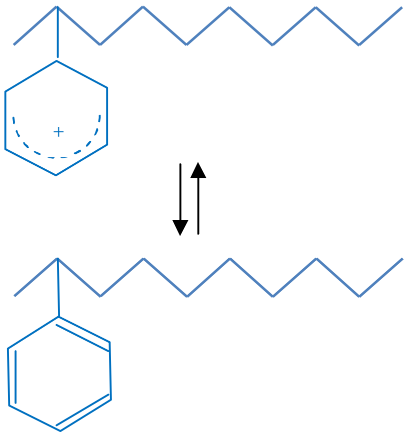


Figure 2: Primary Reaction Network

Mixture of C_9-C_{14} linear alkylbenzenes are the raw materials for the manufacture of biodegradable surfactant in a detergent industry. These alkylbenzenes are produced via aromatic alkylation with C_9-C_{14} α-alkenes. Kinetic modeling of alkylation of benzene with long chain linear α-alkenes over solid acid catalysts is from first principles is develop by Nevashini P., Periyasamy B. (2012). Pre-exponential factors of the elementary steps were calculated based on transition state history and stastical thermodynamics.

In this project, Particle Swarm Optimization (PSO) and Hybrid Particle Swarm Optimization are used in estimation of activation energy, E_a in alkylation of benzene and 1-decene. PSO technique was originally proposed by Kennedy and Eberhart (1995) based on social behavior of collection of swarm. Each of swarm represent particle, move along the search space and exchange information with other particle (M. Schwaab, et al., 2008)

$$v^{k+1}_{p,d} = wv^{k}_{p,d} + c_1r_1\,(x^{\mathrm{ind}}_{p,d} - x^{k}_{p,d}) + c_2r_2(x^{\mathrm{glo}}_{d} - x^{k}_{p,d}) \qquad (1)$$

$$x^{k+1}_{p,d} = x^{k}_{p,d} + v^{k+1}_{p,d}\,. \qquad (2)$$

In Eqs. (1)-(2), p denotes the particle, d is the search 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} represent 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 [0, 1]. w, c_1 and c_2 are search parameters. The parameters 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 methods are not very sensitive to initial guesses of model parameters, which makes its use appealing when large number of unknown parameters are present in the model (M. Schwaab, et al., 2008).

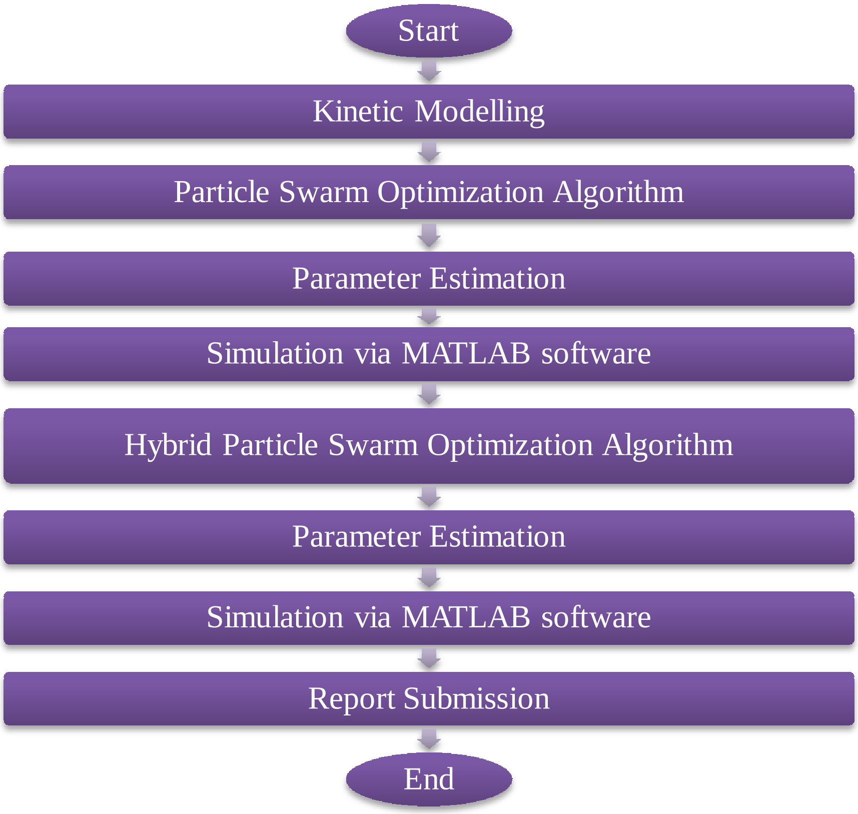
Apart from PSO method, Hybrid Particle Swarm Optimization (HPSO) method is another method used in the parameter estimation. HPSO is the combination of PSO method followed by Levenberg-Marquardt algorithm. Initial guesses will randomly generate by using PSO and the particle conduct a global search over the parameter 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 PSO algorithm is given as initial guesses to the Levenberg–Marquardt algorithm to determine the improved optimal values (P. Balasubramanian, 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 (Manolis, 2005). 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.

CHAPTER 3

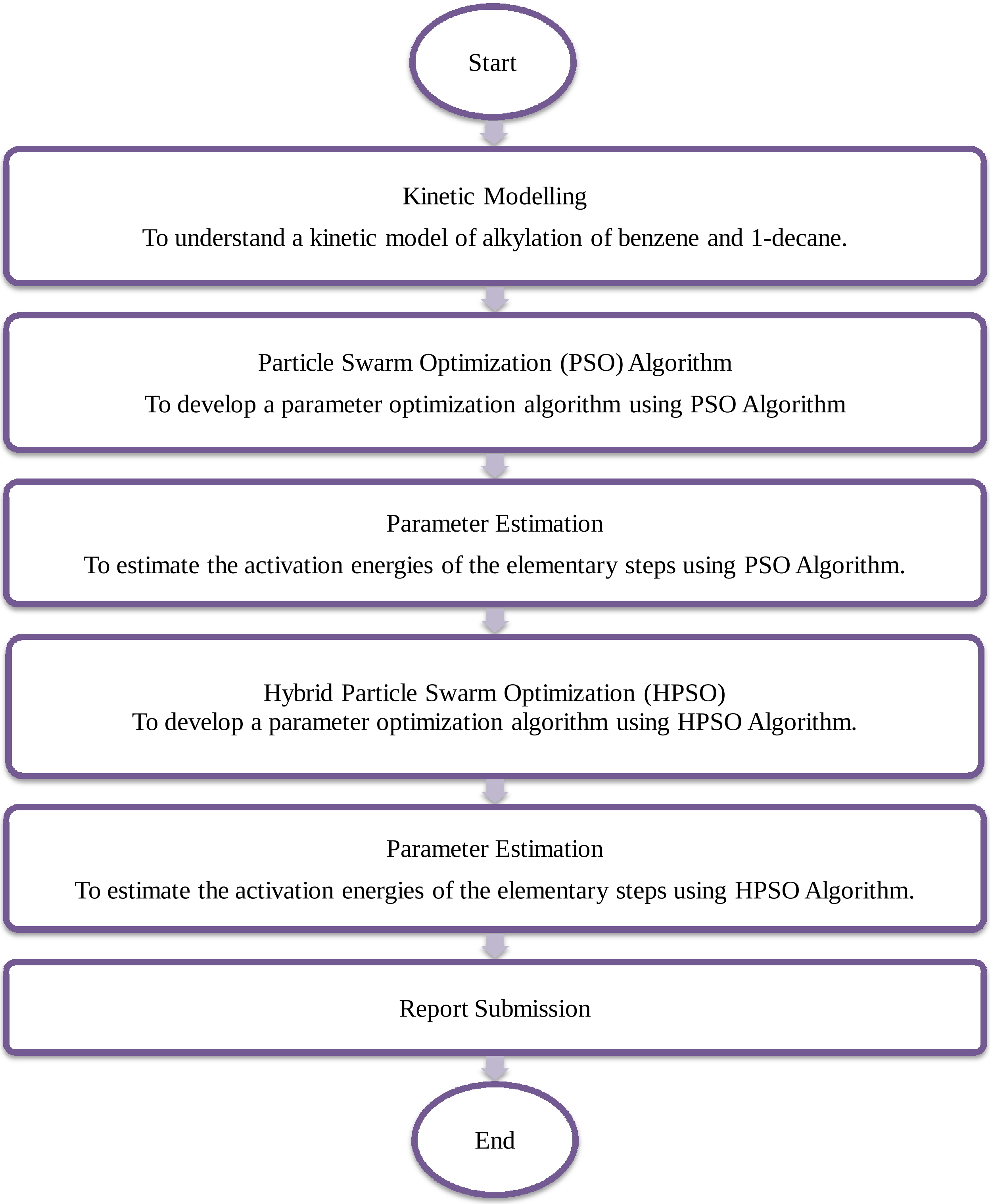
METHODOLOGY

3.1 Project Methodology

Below is the process flow diagram throughout Final Year Project1 (FYP1). This diagram summarizes the project flow and describes the activities or task that have been done and scheduled for the Final Year Project period. In order to ensure the project is on the correct path and also identify the work need to be done in future, the process flow is done.



3.2 Project Flow



Start

Kinetic Modelling

To understand a kinetic model of alkylation of benzene and 1-decane.

Particle Swarm Optimization (PSO) Algorithm

To develop a parameter optimization algorithm using PSO Algorithm

Parameter Estimation

To estimate the activation energies of the elementary steps using PSO Algorithm.

Hybrid Particle Swarm Optimization (HPSO)

To develop a parameter optimization algorithm using HPSO Algorithm.

Parameter Estimation

To estimate the activation energies of the elementary steps using HPSO Algorithm.

Report Submission

End

This final year project is a simulation project which is conducted by using the modeling software basis, MATLAB. The first part of the project is conduction proper research to understand the molecular level mechanism of the reaction that occurs. Full understanding on the alkylation process of benzene and 1-decene over solid acid catalysts gives an insight of the overall project. Journals and technical papers were a good and reliable source to gather information. Compared to traditional method Friedal-Craft alkylation, there are differences and advantages of alkylation over solid acid catalyst. Besides solid acid catalysts and also 1-decene, there are few researches done by manipulating those catalysts and olefins. This provides a good comparison for the project outcome later. In this project, we are going to estimate activation energy, E_a of the alkylation of benzene and 1-decene. There are two different method used in parameter estimation which are;

1. Particle Swarm Optimization PSO algorithm
2. Levenberg-Marquardt (LM) algorithm

In order to estimate the activation energy, there are several factor such as pre-exponential factor, critical temperature, pressure, volume, acentric factor, molar volume and translational entropy are calculated to be able to finally calculate the activation energy value.

3.3 Project Activities

In this project, there are several activities will be conducted. They are;

i. To write a MATLAB Program for PSO algorithm.
ii. To estimate Activation Energy, E_a of the alkylation model using PSO algorithm
iii. To write a MATLAB Program for HPSO algorithm.
iv. To estimate Activation Energy, E_a of the alkylation model using HPSO algorithm
v. To analyze the results.
vi. To perform the simulation of the parameter estimation.

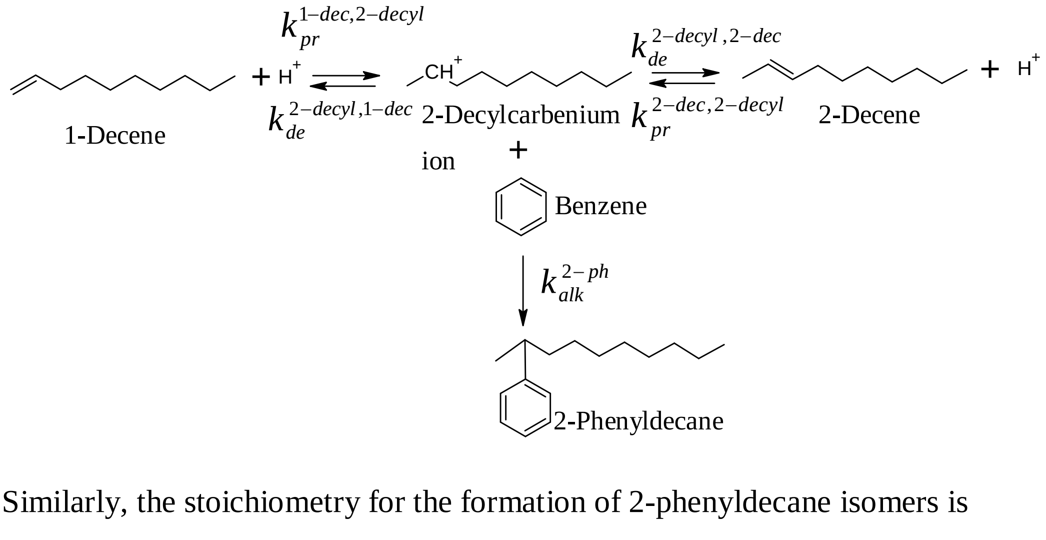
3.4 Kinetic Modeling

Kinetic modeling of alkylation of benzene with long chain linear α-alkenes over solid acid catalysts is from first principles is develop by Nevashini, and Periyasamy B. (2012).

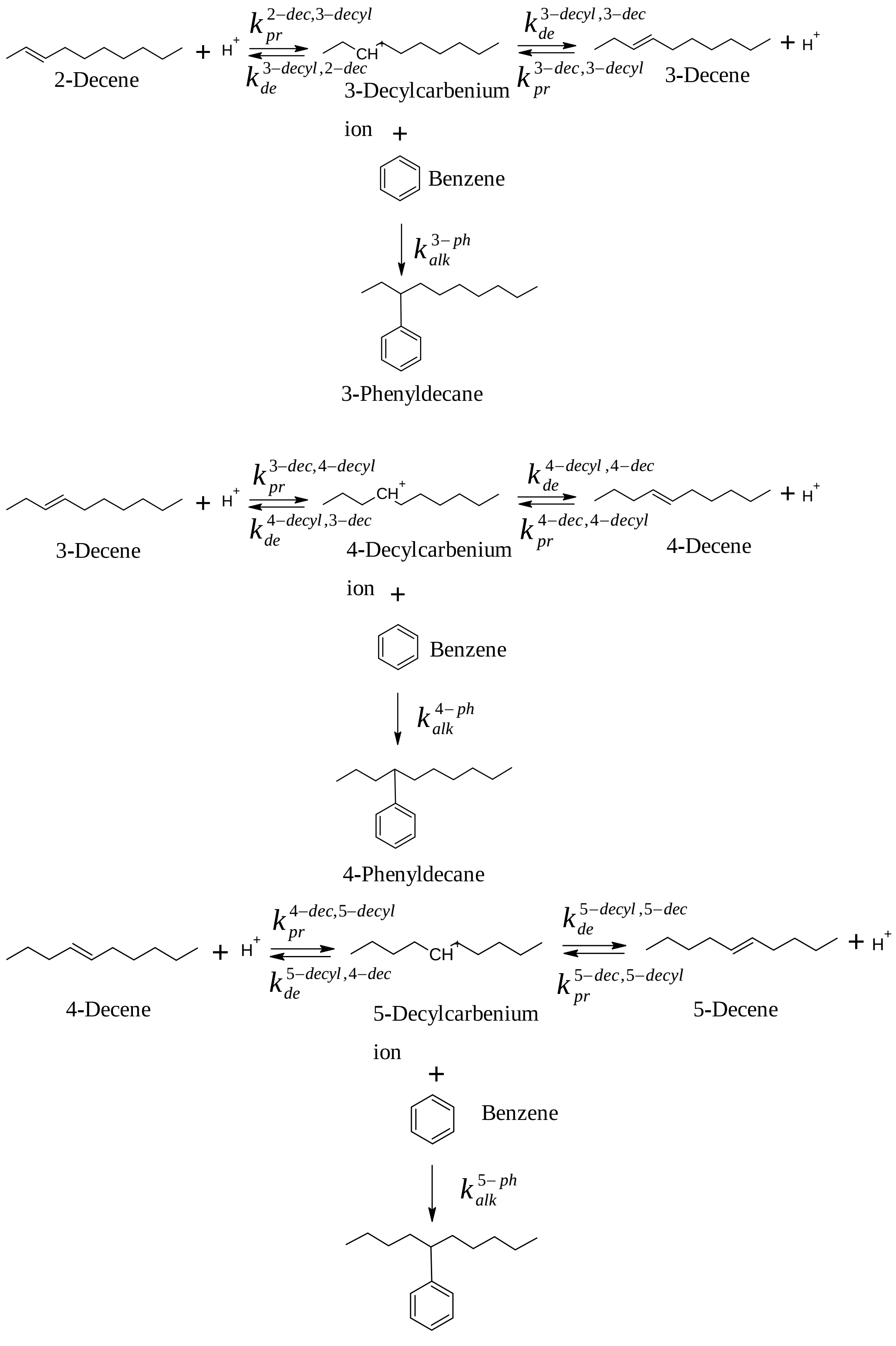
The reactions for alkylation of benzene with 1-decene occur over solid acid catalysts in two steps mechanisms, namely, (i) double bond isomerization, and (ii) benzene alkylation. In the former, 1-decene isomers are formed via protonation and deprotonation reactions on acid sites of solid acid catalysts. Protonation of 1-decene isomers yield alkylcarbenium ions and react with benzene to form phenyldecane isomers. In the following, the derivation of kinetic equations for alkylation of benzene with 1-decene is presented.

3.4.1 Stoichiometry

The stoichiometry for the formation of 2-phenyldecane from 1-decene and 2-decene via double isomerization and aromatic alkylation is given by



Similarly, the stoichiometry for the formation of 2-phenyldecane isomers is


2-Decene
+ H$^+$
$k_{pr}^{2-dec,3-decyl}$
$k_{de}^{3-decyl,2-dec}$
CH$^+$
3-Decylcarbenium ion
$k_{de}^{3-decyl,3-dec}$
$k_{pr}^{3-dec,3-decyl}$
3-Decene
+ H$^+$
+
Benzene
k_{alk}^{3-ph}
3-Phenyldecane
3-Decene
+ H$^+$
$k_{pr}^{3-dec,4-decyl}$
$k_{de}^{4-decyl,3-dec}$
CH$^+$
4-Decylcarbenium ion
$k_{de}^{4-decyl,4-dec}$
$k_{pr}^{4-dec,4-decyl}$
4-Decene
+ H$^+$
+
Benzene
k_{alk}^{4-ph}
4-Phenyldecane
4-Decene
+ H$^+$
$k_{pr}^{4-dec,5-decyl}$
$k_{de}^{5-decyl,4-dec}$
CH$^+$
5-Decylcarbenium ion
$k_{de}^{5-decyl,5-dec}$
$k_{pr}^{5-dec,5-decyl}$
5-Decene
+ H$^+$
+
Benzene
k_{alk}^{5-ph}
5-Phenyldecane

(3)

Here, 1-decene isomers such as 2-decene, 3-decene, 4-decene, and 5-decene are formed via double isomerization reactions, and 2-phenyldecane isomers such as 3-phenyldecane, 4-phenyldecane, and 5-phenyldecane are produced via alkylation of benzene with the corresponding alkylcarbenium ions.

3.4.2 Rate Coefficent

The rate coefficients of the elementary reactions are derived through transition state theory and single event concept. The rate coefficients can be represented as;

$$k' = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{o,\neq}}{R}\right) \exp\left(-\frac{\Delta H^{o,\neq}}{RT}\right) \tag{4}$$

The standard entropy of the transition state of the chemical species contains translational, vibrational and rotational degrees of freedom. The rotational entropy comprises the external as well as the internal rotation of the reacting species and is related to the symmetry number of the molecule. The formula for the calculation of standard entropy from reactant to transition state is given by

$$\Delta S_{sys}^{o,\neq} = \Delta S^{o,\neq} + R \ln \frac{\sigma_{gl}^{r}}{\sigma_{gl}^{\neq}} \tag{5}$$

The global symmetry of the molecule is defined as

$$\sigma_{gl} = \frac{\sigma_{ext}\sigma_{\text{int}}}{2^n} \tag{6}$$

Substituting eq.(5) in eq. (4) results the following expression.

$$k' = n_e \frac{k_B T}{h} \exp\left(\frac{\Delta S^{o,\neq}}{R}\right) \exp\left(-\frac{\Delta H^{o,\neq}}{RT}\right) \tag{7}$$

The formula for the calculation of number of single event n_e is given by

$$n_e = \frac{\sigma_{gl}^{r}}{\sigma_{gl}^{\neq}} \tag{8}$$

The rate coefficient expression can be further simplified as

$$k' = n_e A \exp\left(-\frac{E_{act}}{RT}\right) \tag{9}$$

3.4.3 Rate Equations

The rate of reaction for 1-decene over solid acid catalyst can be represented as

$$r_{1-dec} = -n_e k_{pr}^{1-dec,2-decyl} c_{1-dec} c_{H^+} + n_e k_{de}^{2-decyl,1-dec} c_{R_2^+} \tag{10}$$

Similarly, the rate of equation for 2, 3, and 4-decene are

$$r_{i-dec} = n_e k_{de}^{i-decyl,i-dec} c_{R_i^+} + n_e k_{de}^{(i+1)-decyl,i-dec} c_{R_{(i+1)}^+} - \Big(n_e k_{pr}^{i-dec,i-decyl} + n_e k_{pr}^{,i-dec,(i+1)-decyl}\Big) c_{i-dec} c_{H^+} \; , for\ i = 2\ to\ 4 \tag{11}$$

The rate expression for 5-decene is given by

$$r_{5-dec} = n_e k_{de}^{5-decyl,5-dec} c_{R_5^+} - n_e k_{pr}^{5-dec,5-decyl} c_{5-dec} c_{H^+} \tag{12}$$

The rate expression for formation of 2-phenyldecane isomer can be represented as

$$r_{i-ph} = n_e k_{alk}^{i-ph} c_{R_i^+} c_B \; , for\ i = 2\ to\ 5 \tag{13}$$

The alkylcarbenium ions formed during double isomerization are surface intermediates. Therefore, pseudo steady state approximation can be applied to calculate the molar concentration of alkylcarbenium ion is

$$r_{R_2^+} = n_e k_{pr}^{1-dec,2-decyl} c_{1-dec} c_{H^+} + n_e k_{pr}^{2-dec,2-decyl} c_{2-dec} c_{H^+} - \Big(n_e k_{de}^{2-decyl,1-dec} + n_e k_{de}^{2-decyl,2-dec} + n_e k_{alk}^{2-ph} c_B\Big) c_{R_2^+} = 0 \tag{14}$$

Thus, the rate of expression for the molar concentration for 2, 3, 4, and 5-decylcarbenium ion can be written as

$$c_{R_2^+} = \frac{\Big(n_e k_{pr}^{(i-1)-dec,i-decyl} c_{(i-1)-dec} + n_e k_{pr}^{i-dec,i-decyl} c_{i-dec}\Big) c_{H^+}}{n_e k_{de}^{i-decyl,(i-1)-dec} + n_e k_{de}^{i-decyl,i-dec} + n_e k_{alk}^{i-ph} c_B} \; , for\ i = 2 to\ 5 \tag{15}$$

The total acid balance is required to calculate the molar concentration of hydrogen ion, and is given by

$$c_t = c_H^+ + \sum_{i=2} c_{R_i}^+$$

(16)

3.4.4 Activation Energy, E_a Estimation

The activation energy, E_a was estimated by using the following formula

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

In the following formula, to determine the pre-exponential factor of the elementary steps is

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

(17)

The change in standard entropy from the reactant to transition state comprises three contributions namely, translational, rotational, and vibrational degrees of freedom. In this paper, the translational entropy of the molecule is considered to calculate the change in standard entropy of the reacting system. The translational entropy of the molecule is calculated using Sackur-Tetrode equation and is given by

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

(18)

The critical properties of molecules are essential in the calculation of acentric factor, molar volume, and entropy of molecules. The critical temperature, critical pressure, critical volume of the molecules is calculated using Marrero and Pardillo group contribution method (1999). The acentric factor and molar volume of the molecule is calculated using Edmister correlatation and Yamada and Gunn (1973) correlation, respectively. The calculated pre-exponential factor for the elementary steps was performed by Nevashini P. (2012) is shown in *Table 1*.

Table 1: Calculated pre-exponential factor

Elementary step	value
Protonation (m^3/mol-s)	1.6665×10^8
Deprotonation (s^{-1})	1.5782×10^{15}
Alkylation (m^3/mol-s)	5.2835×10^8

3.4.4 Reactor Balance

The limiting reactant for the alkylation process is 1-decene, and kinetic equations were developed for this process by considering that the reaction took place in a CSTR.

The conversion of 1-decene is

$$x = \frac{c_{0,1dec} - c_{1-dec}}{c_{0,1-dec}} \tag{19}$$

The kinetic equation for 1-decene is

$$0 = x + r_{1-dec}\frac{\mathrm{W_{cat}}}{F_{0,1-dec}} \tag{20}$$

Similarly the kinetic equation for 2, 3, 4, and 5-decene are

$$0 = -y_{i-dec} + r_{i-dec}\frac{W_{cat}}{F_{0,1-dec}}, \qquad for\ i = 2\ to\ 5 \tag{21}$$

Furthermore, the kinetic equation for 2, 3, 4, and 5-phnyldecene are

$$0 = -y_{i-dec} + r_{i-ph}\frac{W_{cat}}{F_{0,1-dec}}, \qquad for\ i = 2\ to\ 5 \tag{22}$$

3.4.5 Parameter Estimation

In the present work, Hybrid Particle Swarm Optimization (HPSO) will be applied in this project to estimate the activation energies, E_a in alkylation of benzene and 1-decene. HPSO technique is a combination between Particle Swarm Optimization (PSO) and Levenberg-Marquart (LM) algorithm.

<u>Particle Swarm Optimization (PSO)</u>

PSO is based on social behavior of collection of swarm where each of swarm represent particle, move along the search space and exchange information with other particle. The update of particle velocity and position was determined by using [1] and [2]. In the initial iterations, the random character of the search is high and the particle conduct a global search. As the iteration evolves, the particles concentrate around more promising region during exploration stage, which will improve the solutions. The PSO algorithm is presented in detail below;

i. Initialize the search parameter:
    Niter: number of iterations;
    Npt: number of particles;
    Nd: number of searched dimensions;
    x^{MIN} and x^{MAX} : vectors of length Nd with the searching limits;
    c_1, c_2, w_0, w_f :PSO search parameters;
    set k=0 (iteration counter).

ii. Calculate the maximum particle velocities along each direction *d*:

$$v_d^{MAX} = (x_d^{MAX} - x_d^{MIN})/2 \tag{23}$$

iii. Calculate initial particle positions and velocities:

$$x_{p,d}^{k} = x_d^{MIN} + r(x_d^{MAX} - x_d^{MIN}) \tag{24}$$

$$v_{p,d}^{k} = v_d^{MAX}(2r - 1) \tag{25}$$

iv. Evaluate the objective function for each particle.

v. Write the particle position and particle objective functions in a file used for construction of the confidence region.

vi. Update x^{glo}, a vector with dimension Nd that contains the best position found by the whole particle swarm.

vii. When the number of iteration reached maximum (k=Niter), the search is terminated.

viii. Update x_p^{ind}, Npt vectors with dimension Nd that contain the best position found by each particle of the swarm.

ix. Calculate the inertial weight value:

$$w = w_0 + (w_f - w_0)\frac{k}{Niter} \tag{26}$$

x. Update the particle velocities for *p*=1…Npt; *d*=1…Nd:

$$v_{p,d}^{k+1} = wx_{p,d}^{k} + c_1 r_1\left(x_{p.d}^{ind} - x_{p,d}^{k}\right) + c_2 r_2\left(x_d^{glo} - x_{p,d}^{k}\right) \tag{27}$$

xi. If the absolute particle velocity is higher than the maximum permitted value then:

$$v_{p,d}^{k+1} = v_d^{MAX} sign\ (v_{p,d}^{k+1}) \tag{28}$$

xii. Update the particle position

$$x_{p,d}^{k+1} = x_{p,d}^{k} + v_{p,d}^{k} \tag{29}$$

xiii. If the particle position is not inside the searching limits, the particle is placed at the violated searching limit.

xiv. Add an iteration to iteration counter (k=k+1) and return to step iv.

The implementation of PSO algorithm is very easy. However, PSO algorithm is not sensitive to the initial guesses. Therefore in order to overcome this disadvantage, HYPSO method is applied in this project. PSO algorithm will provide the initial guess for Levenberg-Marquart (LM) algorithm will calculate the objective function.

Levenberg-Marquart (LM) algorithm

LM algorithm is an interactive technique that locates the minimum of a multivariate function which express as the sum of squares of non-linear real-valued function. It has become a standard technique for non-linear least-squares problem.

Let f be an assumed functional relation which maps a *parameter vector* $p \in R^m$ to an estimated *measurement vector* $\hat{x} = f(p), \hat{x} \in R^m$. An initial parameter estimate $p_0$and a measured vector x are provided and it is desired to find the vector p^+ that best satisfies the functional relation f, i.e. minimizes the squared distance $\in^T \in$ with $\in = x - \hat{x}$. The basis of the LM algorithm is a linear approximation to f in the neighborhood of p. For a small $\|\delta_p\|$, a Taylor series expansion leads to the approximation

$$f(p + \delta_p) \approx f(p) + \boldsymbol{J}\,\delta_p \tag{30}$$

where $\boldsymbol{J}$ is the Jacobian matrix $\frac{\partial f(p)}{\partial p}$. Like all non-linear optimization methods, LM is iterative: Initiated at the starting point p_0, the method produces a series of $p_{1,}p_2, p_3, \ldots.$ that converge towards a local minimizer p^+ for f. Hence, at each step, it is required to find the δ_p that minimizes the quantity $\|x - f(p + \delta_p)\| \approx \|x - f(p) + \boldsymbol{J}\,\delta_p\| = \|\in - \boldsymbol{J}\delta_p\|$, The sought δ_p is thus the solution to a linear least-squares problem: the minimum is attained when $\boldsymbol{J}\,\delta_p - \in$ is orthogonal to the column space of $\boldsymbol{J}$. This leads to $J^T = (\boldsymbol{J}\,\delta_p - \in) = 0$ which yields δ_p as the solution of the so-called *normal equations* [30]:

$$\boldsymbol{J}^T\boldsymbol{J}\,\delta_p = \boldsymbol{J}^T \in \tag{31}$$

The matrix $\boldsymbol{J}^T\boldsymbol{J}$ in the left hand side of Eq. (28) is the approximate Hessian, i.e. an approximation to the matrix of second order derivatives. The LM method actually solves a slight variation of Eq. (28), known as the *augmented normal equations*

$$N\,\delta_p = J^T \in \tag{32}$$

In LM, the damping term is adjusted at each iteration to assure a reduction in the error $\in$. If the damping is set to a large value, matrix $\boldsymbol{N}$ in Eq. (29) is nearly diagonal and the LM update step δ_p is near the steepest descent direction. Moreover, the magnitude of δ_p is reduced in this case. Damping also handles situations where the Jacobian is rank deficient and $\boldsymbol{J}^T\boldsymbol{J}$ is therefore singular [29]. In this way, LM can defensively navigate a region of the parameter space in which the model is highly nonlinear. If the damping is small, the LM step approximates the exact quadratic step appropriate for a fully linear problem. LM is adaptive because it controls its own damping: it raises the damping if a step fails to reduce $\in$; otherwise it reduces the damping. In this way LM is capable to alternate between a slow descent approach when being far from the minimum and a fast convergence when being at the minimum's neighborhood [29]. The LM algorithm terminates when at least one of the following conditions is met:

- The magnitude of the gradient of $\in^T\in$ in the right hand side of Eq. (29), drops below a threshold $\in_1$;
- The relative change in the magnitude of $\delta_p$drops below a threshold $\in_2$
- The error $\in^T\in$ drops below a threshold $\in_3$
- A maximum number of iterations k_{max} is completed

LM is an optimal compromise between the steepest descent and Gauss-Newton method. LM wills applies steepest descent method when the initial guess is far from minimum and when the initial guess is close to minimum, the Gauss-Newton method will be applied. Therefore, it is essential to provide right value for the initial guess; otherwise this method will fail in providing the right solution.

3.5 Gantt Chart

No	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	🟥	🟥						**Mid Semester Break**							
2	Literature review and survey		🟥	🟥												
3	To understand the Kinetic Model				🟥	🟥	🟥									
4	Submission of Extended Proposal							🟥								
5	Proposal Defense									🟥	🟥					
6	PSO Algorithm										🟥	🟥				
7	Parameter Estimation											🟥	🟥	🟥	🟥 ●	
9	Submission of Interim Draft Report															🟥
10	Submission of Interim Report															🟥

Table 2*: Gantt chart of FYP I*

No	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Parameter Estimation	🟥	🟥	🟥	🟥	🟥	🟥	🟥	**Mid Semester Break**							
2	Progress Report									🟥						
3	Parameter Estimation									🟥	🟥	🟥	🟥			
4	Pre-EDX												🟥			
6	Submission of Draft Dissertation													🟥 ●		
7	Submission of Technical Paper													🟥	🟥	
9	Oral Presentation														🟥	🟥
10	Submission of Project Dissertation															🟥

***Table 3**: Gantt chart of FYP II*

🟥 Expected completion

- Milestone 1 – Parameter Estimation
- Milestone 2 - Submission of Project Dissertation

CHAPTER 4

RESULTS AND DISCUSSIONS

Estimated parameters using HPSO are detailed in this section. Pre exponential factors of the elementary steps were calculated from the statistical thermodynamics. Activation energies of the elementary step were estimated using simulated data.

Table 4: *The estimated model parameters through Hybrid PSO (N_{iter}=10, N_{pt}=20)*

Parameter (kJ/mol)	PSO			HPSO
	Run 1	Run 2	Run 3	
$E_{pr}^{1\text{-dec, 2-decyl}}$	57.26	59.31	52.00	53.90
$E_{de}^{2\text{-decyl,1-dec}}$	116.66	118.37	116.90	113.50
E_{pr}	52.15	57.31	48.28	52.90
E_{de}	106.60	109.49	108.43	109.40
$E_{alk}^{2\text{-ph}}$	90.42	89.67	93.00	91.00
$E_{alk}^{3\text{-ph}}$	99.33	96.97	92.16	94.00
$E_{alk}^{4\text{-ph}}$	99.98	98.71	101.45	96.00
$E_{alk}^{5\text{-ph}}$	98.72	119.61	105.27	99.00
Variance Analysis				
Total Sum of Squares			343486	
Regression Sum of Squares			343486	
Residual Sum of Squares			1.93×10^{-12}	
F Value			1.98×10^{19}	

Observations:

For the first estimated model, 20 particles were considered to estimate 8 model parameter and the number of iteration of 10. It is observed the results obtained by PSO were different due to randomness. The estimated activation energies by PSO are close to each other and also close to value estimated by HPSO.

Table 5: *The estimated model parameters through Hybrid PSO (N_{iter}=10, N_{pt}=40)*

Parameter (kJ/mol)	PSO			HPSO
	Run 1	Run 2	Run 3	
$E_{pr}^{1\text{-dec, 2-decyl}}$	56.41	50.62	58.84	53.90
$E_{de}^{2\text{-decyl,1-dec}}$	113.66	118.38	118.27	113.50
E_{pr}	52.51	49.75	55.35	52.90
E_{de}	106.67	110.74	108.56	109.40
$E_{alk}^{2\text{-ph}}$	90.37	91.93	90.17	91.00
$E_{alk}^{3\text{-ph}}$	99.25	94.43	92.17	94.00
$E_{alk}^{4\text{-ph}}$	93.92	97.16	109.35	96.00
$E_{alk}^{5\text{-ph}}$	102.96	115.95	108.29	99.00

Variance Analysis	
Total Sum of Squares	343486
Regression Sum of Squares	343486
Residual Sum of Squares	$1.93\text{x}10^{-12}$
F Value	$1.98\text{x}10^{19}$

<u>Observations:</u>

The second model was performed by increase the number of particle of 40 to estimate eight parameters of activation energies. The number of iteration was kept constant at 10. The estimated activation energies by PSO are different each time, but closer to each other and also closer to value estimated by HPSO compared to the first model.

***Table 6:** The estimated model parameters through Hybrid PSO (N_{iter}=10, N_{pt}=60)*

Parameter (kJ/mol)	PSO			HPSO
	Run 1	Run 2	Run 3	
$E_{pr}^{1\text{-dec, 2-decyl}}$	59.69	50.61	59.85	53.90
$E_{de}^{2\text{-decyl,1-dec}}$	117.45	114.37	114.87	113.50
E_{pr}	54.49	49.78	58.34	52.90
E_{de}	106.56	109.94	108.85	109.40
$E_{alk}^{2\text{-ph}}$	89.06	91.98	89.86	91.00
$E_{alk}^{3\text{-ph}}$	93.10	96.29	91.30	94.00
$E_{alk}^{4\text{-ph}}$	108.07	94.50	92.33	96.00
$E_{alk}^{5\text{-ph}}$	97.07	104.63	111.32	99.00

Variance Analysis	
Total Sum of Squares	343486
Regression Sum of Squares	343486
Residual Sum of Squares	1.93×10^{-12}
F Value	1.98×10^{19}

Observations:

In the third model, the number of particle of 60 was considered to estimate eight parameters of activation energies and the number of iteration was kept constant at 10. The estimated activation energies by PSO are different each time; however the results are closer to each other and also closer to value estimated by HPSO.

Table 7: *The estimated model parameters through Hybrid PSO (N_{iter}=50, N_{pt}=20)*

Parameter (kJ/mol)	PSO			HPSO
	Run 1	Run 2	Run 3	
$E_{pr}^{1\text{-dec, 2-decyl}}$	58.89	49.44	52.82	53.90
$E_{de}^{2\text{-decyl,1-dec}}$	114.76	114.07	110.33	113.50
E_{pr}	56.61	48.47	54.15	52.90
E_{de}	108.31	109.80	109.53	109.40
$E_{alk}^{2\text{-ph}}$	89.66	91.44	90.75	91.00
$E_{alk}^{3\text{-ph}}$	92.62	94.63	93.48	94.00
$E_{alk}^{4\text{-ph}}$	94.06	102.72	95.83	96.00
$E_{alk}^{5\text{-ph}}$	105.18	98.57	100.21	99.00

Variance Analysis	
Total Sum of Squares	343486
Regression Sum of Squares	343486
Residual Sum of Squares	$1.93\text{x}10^{-12}$
F Value	$1.98\text{x}10^{19}$

Observations:

The number of particle was increased to 50 and the number of particle of 20 was considered for the forth model. Compared to the first model (N_{iter}=10, N_{pt}=20) and the third model (N_{iter}=10, N_{pt}=60), the estimated activation energies by PSO are different each time but closer to each other and also closer to value estimated by HPSO.

Table 8: *The estimated model parameters through Hybrid PSO (N_{iter}=50, N_{pt}=40)*

Parameter (kJ/mol)	PSO			HPSO
	Run 1	Run 2	Run 3	
$E_{pr}^{1\text{-dec, 2-decyl}}$	51.77	56.67	58.96	53.90
$E_{de}^{2\text{-decyl,1-dec}}$	106.32	115.42	114.65	113.50
E_{pr}	56.77	54.65	57.24	52.90
E_{de}	109.48	109.18	108.66	109.40
$E_{alk}^{2\text{-ph}}$	90.02	90.69	89.60	91.00
$E_{alk}^{3\text{-ph}}$	92.71	93.80	91.98	94.00
$E_{alk}^{4\text{-ph}}$	104.48	95.21	103.97	96.00
$E_{alk}^{5\text{-ph}}$	96.77	99.56	117.29	99.00

Variance Analysis	
Total Sum of Squares	343486
Regression Sum of Squares	343486
Residual Sum of Squares	$1.93\text{x}10^{-12}$
F Value	$1.98\text{x}10^{19}$

Observations:

For the fifth model, the number of particle of 40 and number of iteration was maintain at 50 was considered for the forth model. In this model, the estimated activation energies by PSO are different each time but closer to each other and also keep closer to value estimated by HPSO.

Table 9: *The estimated model parameters through Hybrid PSO (N_{iter}=50, N_{pt}=60)*

Parameter (kJ/mol)	PSO Run 1	PSO Run 2	PSO Run 3	HPSO
$E_{pr}^{1\text{-dec, }2\text{-decyl}}$	57.24	49.76	48.63	53.90
$E_{de}^{2\text{-decyl,}1\text{-dec}}$	114.68	113.03	111.71	113.50
E_{pr}	55.41	49.20	48.95	52.90
E_{de}	109.04	109.60	109.62	109.40
$E_{alk}^{2\text{-ph}}$	90.40	91.36	91.38	91.00
$E_{alk}^{3\text{-ph}}$	93.21	94.36	93.93	94.00
$E_{alk}^{4\text{-ph}}$	95.19	96.27	96.89	96.00
$E_{alk}^{5\text{-ph}}$	98.36	100.10	98.77	99.00

Variance Analysis	
Total Sum of Squares	343486
Regression Sum of Squares	343486
Residual Sum of Squares	$1.93\text{x}10^{-12}$
F Value	$1.98\text{x}10^{19}$

Observations:

For the sixth model, the number of particle increased to 60 and number of iteration was maintain at 50 was considered. In this model, the estimated activation energies by PSO are very close to each other and to value estimated by HPSO.

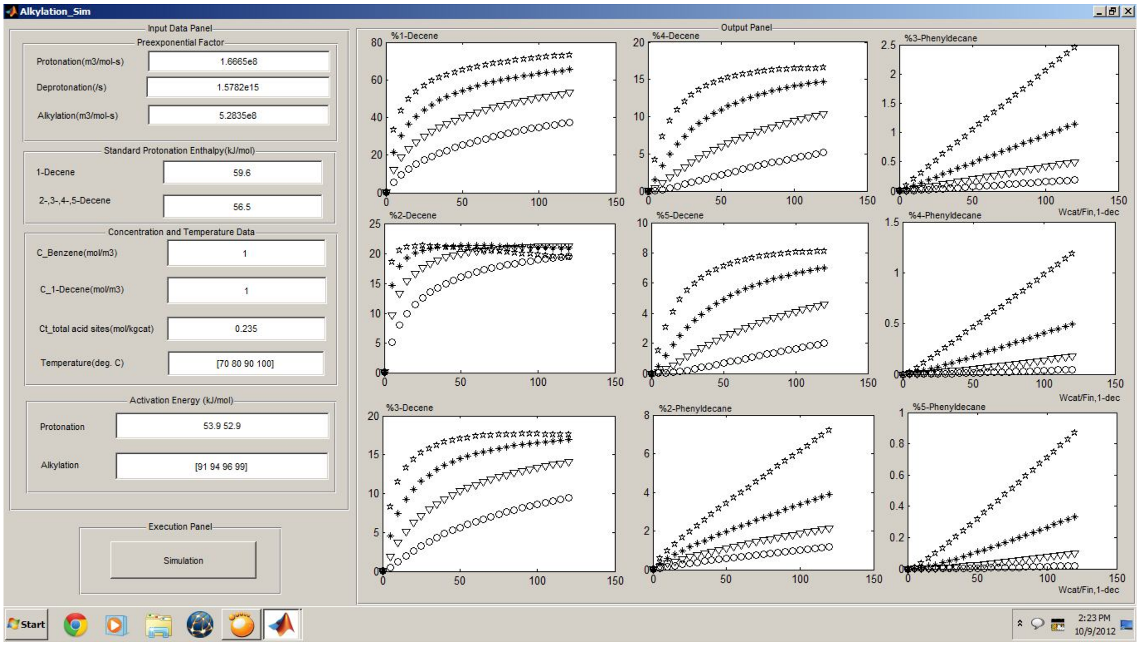
Discussions

The parameter estimation had been performed by varying the number of particles and number of iteration and it was repeated for three times. It was observed that the results obtained by PSO algorithm are different each time because of randomness; the parameters were nearer to the estimated values of HPSO. The higher number of particles and iteration in the PSO facilitates the good initial guess for the local optimize (gradient based method). However, higher number of iteration and particle required longer simulation time. Therefore, for HPSO method, only a small number of particle and iteration required since the estimated activation energies are constant.

Graphical User Interface (GUI)

A MATLAB based graphical user interface (GUI) was develop for alkylation of benzene with 1-decene over solid acid catalysts. The GUI consists of two parts namely, (i) simulation, and (ii) parameter estimation. The GUI for the simulation program is depicted in Figure 3. It consists of the panels namely, (i) Input data panel, (ii) execution panel, (iii) output panel. The pre-exponential factors, activation energies, concentration, and temperature are the end-users input data. The MATLAB software stores these data as a string in the callback program and simulation can be performed by clicking the pushbutton shown in the execution panel. After execution, the plot for percent formation of 1-decene and 2-phenyldecane isomers will automatically displayed in the output panel.

Figure 4 shows the GUI for the parameter estimation and consists of three panels, namely, (i) input data panel, (ii) execution panel, (iii) output panel. The pre-exponential factors, concentration, temperature, PSO algorithm parameters, lower and upper limits of parameters are the end-users input data. The data for the space time and percentage yield of reacting species must loaded as file_name.dat in the MATLAB working directory. The model parameters using PSO and HPSO will be automatically tabulated in the output panel. The GUI displays the statically analysis of parameter estimates such as variance analysis, 95% confident intervals, and the correlation in the output panel. In addition, it shows the parity diagram, percent conversion of 1-decene, and the percent yield of 2-phenyldecane diagram.



Input Data Panel

Preexponential Factor

Protonation(m3/mol-s): 1.6665e8
Deprotonation(/s): 1.5782e15
Alkylation(m3/mol-s): 5.2835e8

Standard Protonation Enthalpy(kJ/mol)

1-Decene: 59.6
2-,3-,4-,5-Decene: 56.5

Concentration and Temperature Data

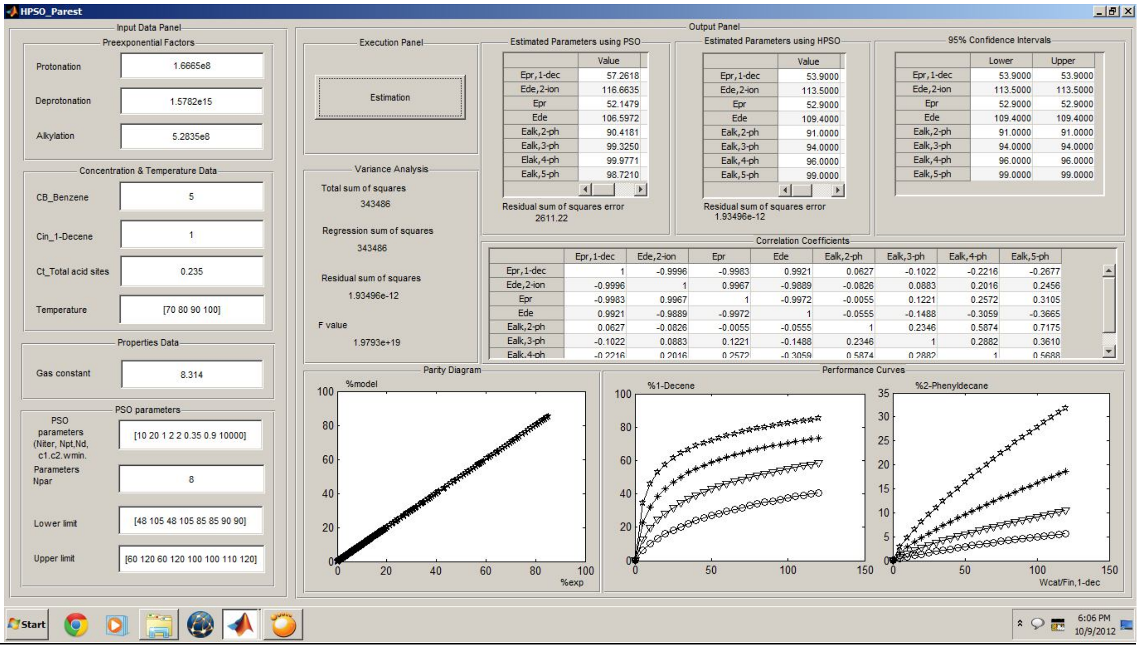
C_Benzene(mol/m3): 1
C_1-Decene(mol/m3): 1
Ct_total acid sites(mol/kgcat): 0.235
Temperature(deg. C): [70 80 90 100]

Activation Energy (kJ/mol)

Protonation: 53.9 52.9
Alkylation: [91 94 96 99]

Execution Panel

Figure 3: *MATLAB GUI for the simulation of benzene with 1-decene*



Input Data Panel

Preexponential Factors

Protonation: 1.6665e8
Deprotonation: 1.5782e15
Alkylation: 5.2835e8

Concentration & Temperature Data

CB_Benzene: 5
Cin_1-Decene: 1
Ct_Total acid sites: 0.235
Temperature: [70 80 90 100]

Properties Data

Gas constant: 8.314

PSO parameters

PSO parameters (Niter, Npt,Nd, c1.c2.wmin.: [10 20 1 2 2 0.35 0.9 10000]
Parameters Npar: 8
Lower limit: [48 105 48 105 85 85 90 90]
Upper limit: [60 120 60 120 100 100 110 120]

Execution Panel

Variance Analysis

Total sum of squares
343486

Regression sum of squares
343486

Residual sum of squares
1.93496e-12

F value
1.9793e+19

Output Panel

Estimated Parameters using PSO

	Value
Epr,1-dec	57.2618
Ede,2-ion	116.6635
Epr	52.1479
Ede	106.5972
Ealk,2-ph	90.4181
Ealk,3-ph	99.3250
Elak,4-ph	99.9771
Ealk,5-ph	98.7210

Residual sum of squares error
2611.22

Estimated Parameters using HPSO

	Value
Epr,1-dec	53.9000
Ede,2-ion	113.5000
Epr	52.9000
Ede	109.4000
Ealk,2-ph	91.0000
Ealk,3-ph	94.0000
Ealk,4-ph	96.0000
Ealk,5-ph	99.0000

Residual sum of squares error
1.93496e-12

95% Confidence Intervals

	Lower	Upper
Epr,1-dec	53.9000	53.9000
Ede,2-ion	113.5000	113.5000
Epr	52.9000	52.9000
Ede	109.4000	109.4000
Ealk,2-ph	91.0000	91.0000
Ealk,3-ph	94.0000	94.0000
Ealk,4-ph	96.0000	96.0000
Ealk,5-ph	99.0000	99.0000

Correlation Coefficients

	Epr,1-dec	Ede,2-ion	Epr	Ede	Ealk,2-ph	Ealk,3-ph	Ealk,4-ph	Ealk,5-ph
Epr,1-dec	1	-0.9996	-0.9983	0.9921	0.0627	-0.1022	-0.2216	-0.2677
Ede,2-ion	-0.9996	1	0.9967	-0.9889	-0.0826	0.0883	0.2016	0.2456
Epr	-0.9983	0.9967	1	-0.9972	-0.0055	0.1221	0.2572	0.3105
Ede	0.9921	-0.9889	-0.9972	1	-0.0555	-0.1488	-0.3059	-0.3665
Ealk,2-ph	0.0627	-0.0826	-0.0055	-0.0555	1	0.2346	0.5874	0.7175
Ealk,3-ph	-0.1022	0.0883	0.1221	-0.1488	0.2346	1	0.2882	0.3610
Ealk,4-ph	-0.2216	0.2016	0.2572	-0.3059	0.5874	0.2882	1	0.5688

Figure 4: *MATLAB GUI for parameter estimation in alkylation of benzene with 1-decene*

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

A kinetic model for liquid phase alkylation of benzene with 1-decene over acid catalyst is presented by using single event kinetics. The elementary reaction involve in the production of linear alkylbenzene are double bond isomerization and alkylation. Pre-exponantial factors of these reactions were calculated from first principle. Activation energies of the alkylation reaction were estimated using Hybrid Particle Swarm Optimization (HPSO). The estimated parameters by PSO algorithm are varying for each simulation. However, higher number of iteration and particle will give closer values. Meanwhile, for HPSO algorithm, the estimated activation energies are constant. Therefore, only small number of iteration and particles is required for the simulation.

5.2 Recommendation

In this work, the experimental work for alkylation of benzene with 1-decene is not carried out. This work will be the future scope of the present work. Besides, the model must be validated using actual experimental data.

ACKNOWLEDGEMENT

The financial support from Universiti Teknologi PETRONAS, Malaysia under STIRF-grant (4/2012) is gratefully acknowledged

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