

**Kinetic Modelling of In situ Catalytic Adsorptive Gasification Unit Utilizing
Palm Kernel Shell (PKS) for Hydrogen Production**

By :

Hasnor Bin Abdullah (15531)

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

Supervisor :

Dr. Periyasamy Balasubramanian

MAY 2014

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Kinetic Modelling of In situ Catalytic Adsorptive Gasification Unit Utilizing Palm
Kernel Shell (PKS) for Hydrogen Production

By :

Hasnor Bin Abdullah (15531)

A project dissertation submitted to
Chemical Engineering Program
University Technology PETRONAS
in partial fulfilment of the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Approved by :

.....
Dr. Periyasamy Balasubramanian

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

(HASNOR BIN ABDULLAH)

ACKNOWLEDGEMENT

First and foremost I would like to express his appreciation and gratefulness to Allah the Almighty, that has given me the strength to complete this final year project within the given time frame.

Special thanks to my supervisor Dr. Periyasamy Balasubramanian for his continuous support, guidance and dedication in ensuring me to fully understand the whole project. He has providing me sufficient knowledge about the project and has given me useful insight and information that helps me to complete this project within the specific time.

Last but not least, my special thanks also goes to my lovely wife Pn. Fadillah Bte Muda who always supporting me in term of moral and taking care of my childrens during the project activities.

Thank you.

ABSTRACT

Hydrogen production from the biomass has become more popular nowadays. This is because of its advantages of lower in sulphur and nitrogen content which would prevent the formation of SO_x and NO_x emission that is harmful to the environment. Because of its greener and environmentally friendly fuel, the demand for the study of the Hydrogen production from this biomass has increased in the last few years. There are a few methods identified to extract the hydrogen out from the biomass. One of them is through steam gasification process. There were many studies done through experimental analysis as to determine the amount of hydrogen production from the biomass. This has incurred with cost to build the model, time spent for the analysis and the safety of the personal who involved in the experiment and many others. Due to these reasons, the requirement of developing the kinetic model for estimating the hydrogen production from the biomass has escalate for the last few years. Despite its lower cost and lesser time spend, the safety of the personal is also protected.

Therefore, in this study, understanding of the key critical parameters that influence the gasification process which could affect the hydrogen and other gases production have been identified through literatures studies and the experimental data that have been done by the post graduate students in the laboratory of University Technology of Petronas (UTP). Through these data, kinetic models for the Palm Kernel Shell (PKS) have been developed base on estimation values that have been validated using Hybrid Particle Swarm Optimization (HPSO) and Levenberg-Marquat (LM) method.

TABLE OF CONTENT

CHAPTER 1 : INTRODUCTION	1
1.1. Background of study	1
1.2. Problem Statement	2
1.3. Objective	2
1.4. Scope of Study	3
CHAPTER 2 : LITERATURE REVIEW	4
2.0. Introduction	4
2.1. Experimental studies of biomass gasification.	5
2.2. Modelling and simulation of biomass gasification.	8
CHAPTER 3: METHODOLOGY	10
3.1. Project flowchart	10
3.2. Gantt chart and key milestone	11
3.3. Methodology	12
3.4. Reaction kinetic modelling of PKS	13
3.5. Reaction stoichiometry	15
3.6. Rate of equation	15
3.7. Material balance	17
3.8. Reaction Kinetic modelling flow chart	18
CHAPTER 4: RESULT AND DISCUSSION (PART-1)	19
4.1 Introduction	19
4.2. Kinetic modelling reaction of Palm Kernel Shell (PKS)..	19
4.3. Model validation with experimental data	20
4.3.1. Effect on temperature	20
4.3.2. Effect on steam biomass ratio	23
4.3.3. Effect on adsorbent to biomass ratio	25

4.4.	Overall model validation for each gas of all three parameters using parity diagram	27
4.4.1.	Effect on Hydrogen concentration	27
4.4.2.	Effect on Methane concentration	28
4.4.3.	Effect on Carbon Monoxide concentration	30
4.4.4.	Effect on Carbon Dioxide concentration	30
CHAPTER 5 : CONCLUSION AND RECOMMENDTIONS		31
5.1	Conclusion	31
5.2	Recommendations	31
REFERENCES		32

LIST OF FIGURE

Figure 1	Experimental result of the effect on temperature. . . .	8
Figure 2	Effect on temperature to H ₂ production	21
Figure 3	Effect on temperature to CO, CO ₂ and CH ₄ production. . .	22
Figure 4	Effect on steam to biomass ratio to H ₂ production . . .	23
Figure 5	Effect on steam to biomass ratio to CO, CO ₂ and CH ₄ production	24
Figure 6	Effect on adsorbent to biomass ratio to H ₂ production . . .	25
Figure 7	Effect on adsorbent to biomass ratio to CO, CO ₂ and CH ₄ production	26
Figure 8	Parity diagram for H ₂ production between model and experimental Data	27
Figure 9	Parity diagram for CH ₄ production between model and experimental data.	28
Figure 10	Parity diagram for CO ₂ production between model and experimental data.. . . .	29
Figure 11	Parity diagram for CO production between model and experimental data.	30

LIST OF TABLES

Table 1	Experimental result under effect of temperature	7
Table 2	Experimental result of different steam to biomass ratio . . .	7
Table 3	Gantt chart and key milestone for FYP-1	11
Table 4	Gantt chart and key milestone for FYP-1	12
Table 5	Material balance equations	17
Table 6	Pre exponential factor and Activation energy obtained from PKS model.	20

CHAPTER 1

INTRODUCTION

1.0 INTRODUCTION

1.1 Background of study

Current dependent of the world's energy on fossil fuel has increased tremendously. Due to the rapid development of technology, the demand for energy has increased significantly during last few decades. This has result to the global warming effects and energy supplies issues around the world [1]. This alarming situation has drawn an attention to the world to find other alternative renewable energy which is greener and environmental friendly. Beside that, the dependency to the solely fossil fuel energy has result to uncontrolled price of fuel due to the higher demand hence increase the cost of leaving for many developing countries. The price is expected will continue to be increased since the supply and demand is not in balance due to the depleting of the fossil fuel supply. Because of these reason the urgency to find the alternative fuel is really essential and need to be expedited for the benefit of the future generation.

Renewable energy such as from solar, hydro power, wind energy, biomass energy and many other have attracted many scientists to conduct the detail study. For country like Malaysia, biomass energy is more favours than others renewable energy. This is because Malaysia has abundant supply of biomass from the palm oil trees. Almost 85.5% of biomass waste is contributed from the palm oil [2]. Therefore, in this project it will focus on the hydrogen production from one of the biomass waste produced from the palm oil which is palm kernel shell (PKS). The project is related to the kinetic modelling of catalytic adsorptive gasification of the hydrogen production using the palm kernel shell.

1.2 Problem statement

Due to the high demand of renewable energy from the world, it has attracted many researcher to focus on the alternative energy especially from the biomass. Palm Kernel Shell (PKS) is one of them where it has the capacity to produce sufficient hydrogen gas through gasification process. In order to obtain this hydrogen gas, it requires a lot of effort, money and time that need to be spent in the laboratory as to run series of experiments for collecting the data. Each of the data needs to be validated as to ensure the consistency and accuracy of the result. It is crucial for all data to be validated before the plant model for commercialize can be developed into a big scale. Failure to get the sufficient data from the study will cause the plant model that will be built base on the available data will be not delivered the amount of Hydrogen as per target. Therefore, in order to provide sufficient data for analysis, another alternative source of data need to be used other than from the experiment. With these sufficient data for study it can provide better understanding and can predict the hydrogen production base on the identified parameters. Besides that, the kinetic model for the PKS is hard to find. Unlike other type of biomass, there are many model that have been developed. So, it is important for this study to find the kinetic model for the PKS so that it can be used for future estimation.

1.3 Objectives

There are two main objectives of this study.

- i. To estimate the kinetic parameters estimation through hybrid particle swarm optimization method, gradient based method and Levenberg-Marquart method.
- ii. To validate the proposed kinetic model by comparing with the experimental data which have been obtained previously in UTP

1.4 Scope of study

This current project will focus more on the kinetic parameter estimation for the gasification process of the Palm Kernel Shell based on the three parameters that could influence the Hydrogen production. Those identified parameters are the effect of the temperature, the effect of the steam to biomass ratio and the effect of the adsorbent Calcium Oxide (CaO) to the biomass ratio. Therefore, the main area of this study is mainly more on the finding of the kinetic parameter that is fit for all six reactions through MATLAB program. The initial guess values will be accessed using the Hybrid Particle Swarm Optimization (HPSO) and Levenberg-Marquardt (LM) algorithm that will be developed in the MATLAB program. From the values obtained from these two algorithms, it will be validated using the Residual Sum of Square Error (RSSE) until it shows the lowest possible error. Finally, the data obtained from this model will be compared with the experimental data as to ensure the consistency between these two results.

CHAPTER 2

LITERATURE REVIEW

2. Introduction

Hydrogen is a kind of clear energy with good applications prospects [4]. It can be obtained from various type of biomass available in this world. Palm kernel shell (PKS) is one of them. According to Yusuf et al [3], there are about 40 palm kernel crashing plants in Malaysia with a total capacity of 5.46 million tonnes. This palm kernel shell have good prospects to be utilized in biomass gasification process due to the high calorific value (20.40 MJ kg^{-1}), considerable mass composition of fixed carbon (14.78%), volatile matter (81.03%), ash (4.10%) and moisture content (17.50%). One of the well-known methods to get the hydrogen from this PKS is through steam gasification process. Steam gasification is an effective way to extract or carry out the hydrogen production from the biomass [4]. To create steam gasification model requires understanding of the gasification process, the design, feedstock and operating parameters that will influence the production of the hydrogen.

This chapter comprises the review on the experimental and the modelling of the catalytic adsorptive gasification of palm kernel shell for hydrogen production published in the journals and other source of information. There are several gasification methods available in the previous studies. Those methods such as air, oxygen, steam or combination of these agents as gasifying agent have been used in many biomass gasification studies. Among these methods, steam gasification is being identified as a potential process to produce more and clean hydrogen. It has many advantages compare with other methods [3]

To investigate the gasification process, some of the related information from the previous experimental studies for the catalytic adsorptive steam gasification will be described in this part. Besides that, the model studies for the development of the kinetic parameters and equilibrium model for the hydrogen production also will be reviewed.

2.1 Experimental studies of biomass gasification

There were many studies done via experimental work. This is to understand the issues and problem of the gasification process before it can be commercialized. Through these studies, understanding of the process behaviour through various factors can be identified for further study. There are many gasification agents have been used in gasification process. Those agents such as air, N₂, pure O₂, steam, CO₂ and mixtures are the known agents used in biomass gasification [5]. However, steam agents is more popular due to its value. As mentioned by Behdad [6], in his literature review, reveals that steam gasification is the most widely accepted agent for the production of hydrogen mainly due to the quantity of the product gas and the high yield of hydrogen. The main reactions of biomass gasification considered in the gasifier are as follow [7];

i. Water gasification



ii. Boudouard reaction



iii. Steam/ Methane reforming



iv. Water gas shift reaction



v. Methanation



2.1.1. Effect of controlling parameters

The primary emphasis of biomass gasification is to maximize the yield of the hydrogen production. There are many factors that influence the performance of the biomass gasification process. As stated by Ahmed [5] in his energy review, at least 20 operating parameters that could affect the gasification performance. This are the challenges that the researcher need to overcome in order to get the optimum output from this process.

In the experiment work conducted by Yusuf [3], they have considered 5 process variables on 2 output response which is Hydrogen composition (In percent volume fraction, %) and hydrogen yield (in term of g kg⁻¹ of biomass) in their studies. Those 5 process variables are :

- i. gasification temperatures (X₁)
- ii. Steam to biomass ratio (X₂)
- iii. Superficial velocity (X₃)
- iv. CaO adsorbent to biomass ratio (X₄)
- v. Biomass particle size (X₅)

According from their result, the highest hydrogen yield (150.99 g kg⁻¹) was obtained at the temperature of 750 °C. However, the percentage composition of the hydrogen is only at 68.16 %. Compare to the gasification temperature at 675 °C, the hydrogen composition has achieved to 84.62% with the yield only at 91.11 g kg⁻¹.

From their experiment, the final model equation for the hydrogen composition with significant variables represent the second ordered polynomial regression model.

$$\begin{aligned} \text{H}_2 \text{ composition (\%)} = & 75.53 - 2.70X_1 + 6.07X_4 - 335X_5 + 6.94 X_1X_3 \\ & - 6.33X_1X_4 - 8.51X_2X_4 + 8.72X_3X_5 \end{aligned} \quad (6)$$

For the hydrogen yield, the mathematical relationship of the regression model with significant process variables are as follow:

$$\begin{aligned} \text{H}_2 \text{ (g kg}^{-1} \text{ of biomass)} = & 73.31 - 32.72X_1 + 19.01X_2 + 16.17X_4 + 8.35X_5 \\ & + 11.88X_1X_3 + 9.59X_1X_5 - 8.25X_2X_4 + 12.17X_3X_5 \end{aligned} \quad (7)$$

According to the study done by Zakir [2], the high temperature and higher steam to biomass ratio favoured for higher hydrogen yield, gas yield, gasification and carbon conversion efficiency but did not favour the lower heating value of gas. However, for the steam to biomass ratio, the effect was not significant if the ratio more than 2. Below table 1 and 2 shows the effect of the temperature and the steam to biomass ratio.

Table 1 : Experimental results under effect of temperature [2]

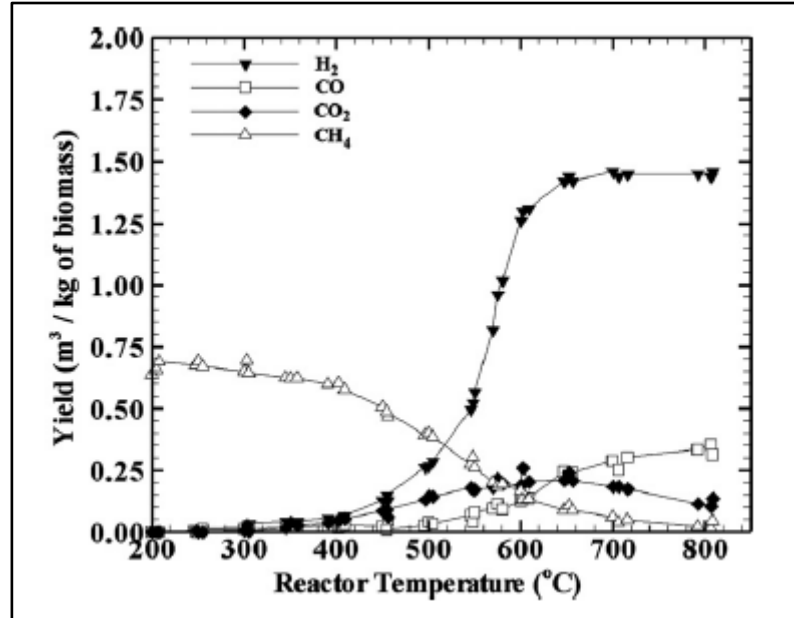
Table 3 – Experimental results under effect of temperature.			
Temperature (°C)	600	675	750
Biomass feed rate (kg/h)	1.35	1.35	1.35
Steam/biomass (wt/wt)	2.0	2.0	2.0
Gas composition (vol%, Dry N ₂ free)			
H ₂	78.00	82.10	67.40
CO	8.78	6.45	14.33
CO ₂	0.00	0.00	7.57
CH ₄	13.22	11.43	10.70
H ₂ yield (g/kg biomass)	31.80	80.39	150.99
Gas yield (m ³ /kg biomass)	0.49	1.19	2.69
Char yield (g/kg biomass)	32.68	27.33	21.00
Gasification efficiency (%)	12.41	25.66	111.98
Carbon conversion efficiency (%)	11.06	20.06	87.01
Lower heating value (MJ/Nm ³)	14.27	13.78	12.88

Table 2 : Experimental results of different steam to biomass ratio [2]

Table 4 – Experimental results of different steam to biomass ratio.			
Temperature (°C)	675	675	675
Biomass feed rate (kg/h)	1.80	1.35	1.10
Steam/biomass (wt/wt)	1.50	2.00	2.50
Gas composition (vol%, Dry N ₂ free)			
H ₂	80.87	82.10	82.61
CO	10.49	6.45	5.45
CO ₂	0.00	0.00	7.99
CH ₄	8.63	11.43	3.95
H ₂ yield (g/kg biomass)	28.69	80.39	97.93
Gas yield (m ³ /kg biomass)	0.43	1.19	1.44
Char yield (g/kg biomass)	32.55	27.33	26.08
Gasification efficiency (%)	10.34	25.66	43.08
Carbon conversion efficiency (%)	8.03	20.96	24.66
Lower heating value (MJ/Nm ³)	13.14	13.78	11.02

Another study done by Behdad [6], as shown in figure 1 below, its reveal that, at lower temperatures, the selectivity of the gasification reactions shift toward methane production with little amount of H₂, CO and CO₂. However, with increasing in temperature (Between 600 – 900 °C), the selectivity shifted toward the H₂ production. This situation occurs because of at higher temperature, methane gas produced from the first reaction will be reacted with the steam and produce H₂ and CO.

Figure 1: Experimental results of the effect on temperature



2.1.2. Catalytic steam gasification

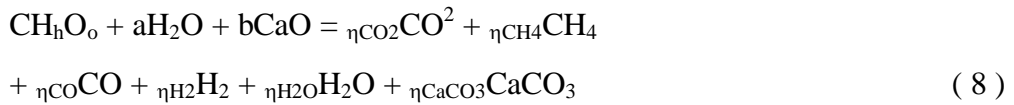
Despite the tremendous research effort on the catalytic steam gasification of biomass, the process under the condition of low temperature (< 750 °C) is still not fully understood. According to the Moghtaderi [6], in his experiments, reveals that at low temperatures, the selectivity of the gasification reaction will shift toward methane production with little H₂, CO and CO₂. With increasing in temperature, the selectivity will shift toward more H₂ production primarily. The controlling parameters such as steam to biomass ratio, catalyst weight to biomass flow rate ratio, heating rate and reaction temperature have been used in his research. According to Zakir [2] the use of catalyst in biomass steam gasification has improved the hydrogen production significantly. It has enhance the reaction rate at lower reaction temperature and improve the gas quality through reducing the tar content in the product gas. The catalyst activity in the biomass gasification has increased the hydrogen content to 60 vol% [2].

2.2. Modelling and simulation of biomass gasification

Biomass gasification is a proven technology to produce satisfactory yield of hydrogen. It has been identified as the most efficient and economical route for hydrogen production. Many studies have been performed to increase the hydrogen yield. Due to the extensive range of investigations, mathematical and computational approaches have been applied to conduct the studies [5].

2.2.1. Thermodynamic equilibrium model for steam gasification in presence of CaO

According to the Acharya [3], kinetic of hydrogen enriched gas production from biomass in presence of CaO was studied by Guoin and Hao in a fixed bed reactor. They found the optimum operating conditions to be steam to biomass ratio (S/B) = 0.9, calcium to carbon molar ratio (Ca/C) = 0.5 and reaction temperature at 495 °C/ 923 K. The overall reaction for steam gasification in presence of CaO can be written as:



To identify the composition η_{CO_2} , η_{CH_4} , η_{CO} , η_{H_2} , $\eta_{\text{H}_2\text{O}}$ and η_{CaCO_3} for different values of a and b and temperature, equilibrium model is used. At equilibrium, the total Gibbs free energy is at minimum. The total Gibbs free energy is given by:

$$G^t = \sum_{i=1}^N n_i \mu_i \quad (9)$$

n_i = number of moles of species i

μ_i = Chemical potential of species I given by,

Chemical potential μ_i can be written in terms of pressure as:

$$\mu_i = G_i^0 + RT \ln \left(\frac{\phi_i P_i}{P^0} \right) \quad (10)$$

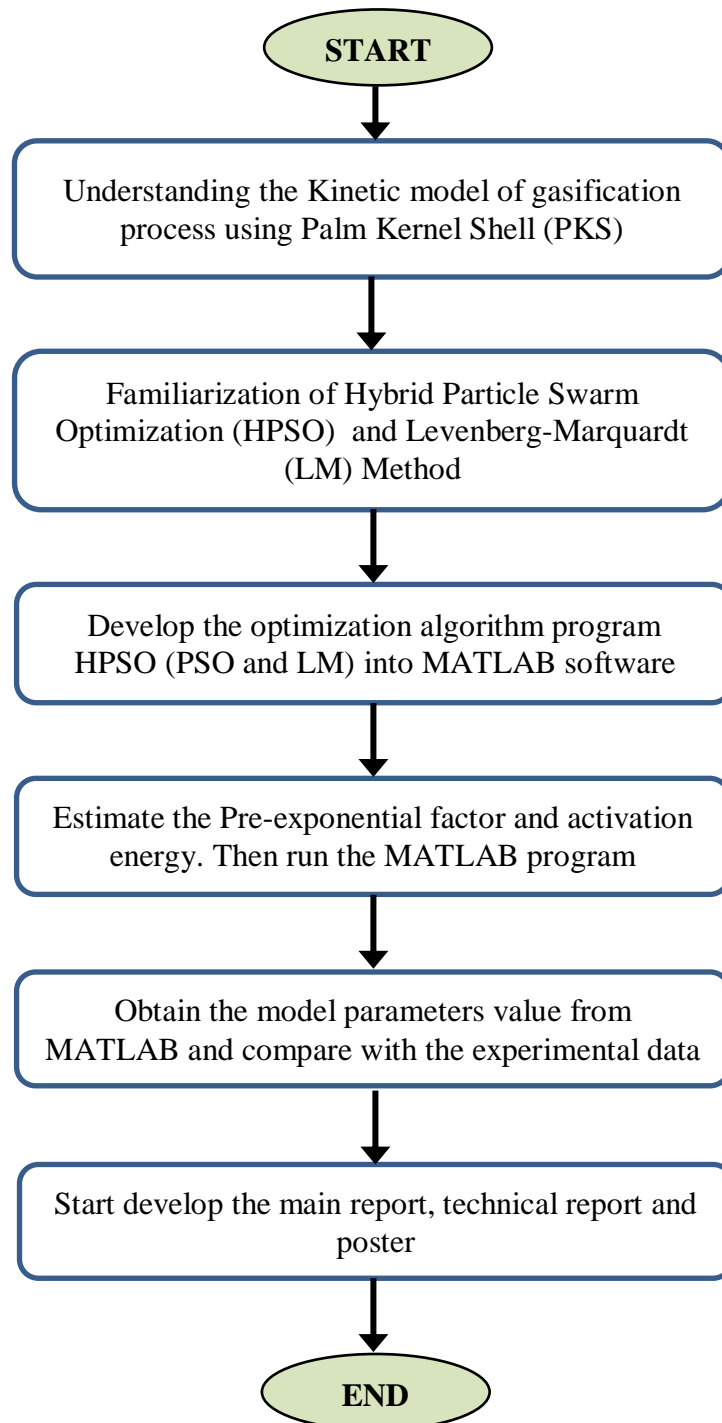
G_i^0 = Standard Gibbs free energy and standard fugacity of species I,

ϕ = Fugacity coefficient

CHAPTER 3

METHODOLOGY

3.1 Project Flow Chart



NO	DETAIL WORK (FYP - 2)	WEEKS															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
1	Literature review of the particle swarm Optimization algorithm	█	█	█													
2	Continue develop the methodology		█	█													
3	Start implement the energy and mass balance of PKS into MATLAB				█	█	█	█									
4	Data analysis , documentation and start develop the reports and the poster					█	█	█	█	█	█						
5	Submission of progress report								█								
6	Pre-EDX											█					
7	Submission of draft report												█				
8	Submission of dessertation (Soft bound)													█			
9	Submission of technical paper														█		
10	Oral presentation															█	
11	Submission of project dessertation (Hard bound)																█

Table 4 : Gantt Chart and key milestone for FYP-2

3.3 Methodology

In this study, the kinetic model data will be obtained based on three identified parameters that will influence the hydrogen gas production. Those identified parameters that will be used for data comparison with the experimental work are;

- Effect on Gassifier operating temperature.
- Effect on the steam to biomass ratio.
- Effect on the adsorbent to Biomass ratio

In order to achieve the objective of this study, the work will be divided into several parts. Those parts are mathematical model development and validation of the experimental work from various models available in the current research. The mathematical model will be developed using the MATLAB software. It consist of rate of equation, mass balance equations, Hybrid particle swarm Optimization (HPSO), Arhenius equation, Modified Arhenius equation and residual sump of error calculation.. Inside the model, the reaction kinetics also implemented in the model to simulate the rate of consumptions of reactants and the rate of gas production. MATLAB software is used since its ability to solve the ordinary differential equation (ODE) that able to solve the energy balance equations with short period of time. A kinetic model parameters need to be developed to estimate the pre-exponential factor and activation energy of Arrhenius equation for all 6 reactions that takes place in the steam gasification process for palm kernel shell.

3.4 Parameter Estimation

For this kinetic model, hybrid particle swam optimization (HPSO) method will be used as to estimate the activation energies E_i and the pre-exponential Factor A_i for all reactions. HPSO is combination method of Particle Swarm Optimization (PSO) and Levenberg-Marquat (LM) algoritm.

PSO method has some drawback. It is not considerate much on the initial guest value. Therefore, in order to overcome this issues, HPSO method is applied where the PSO algorithm will be provide the initial guest value for the Levenberg-MARquat (LM) algorithm to calculate the objective function. LM algorithm is an interactive

technique that locates the minimum of a multivariable function which express as the sum of squares of non-linear real value function.

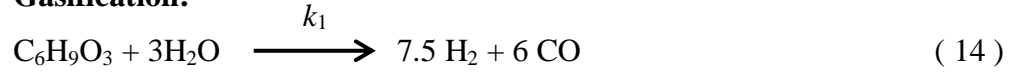
This value later will be evaluated using the Residual Sump of Square Error (RSSE). The kinetic parameters from the experimental data that is gained from the experimental work done in gasification unit in UTP will be used to validate the model prediction profiles. The PKS model will be tested with several case studies to demonstrate the accuracy of the model with the experimental work and other comparable model. The model will be simulated using different values of set parameters.

3.5 Reaction Stoichiometry

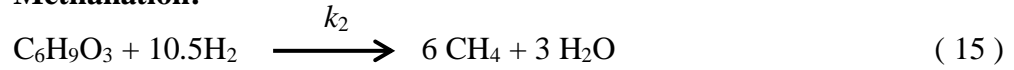
There are six chemical reactions identified for the gasification process in this study.

The reaction stoichiometry for each of the chemical reactions are as below :

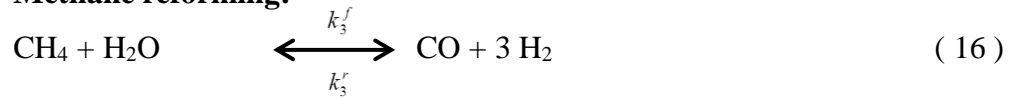
i. Gasification:



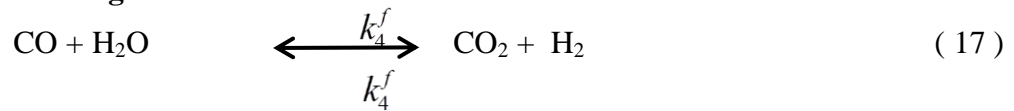
ii. Methanation:



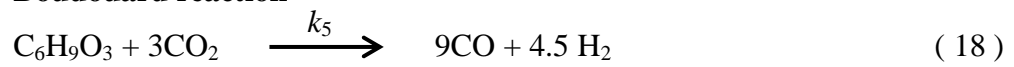
iii. Methane reforming:



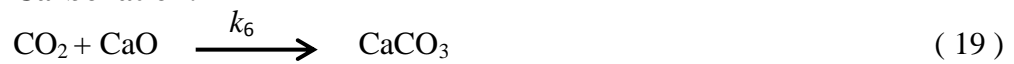
iv. Water gas shift reaction:



v. Boudouard reaction:



vi. Carbonation:



3.6 Rate equations

From the above chemical reactions, the rate of equations are as follow:

$$r_1 = -k_1 C_{\text{PKS}} C_{\text{S}} \quad (20)$$

$$r_2 = -k_2 C_{\text{PKS}} C_{\text{H}} \quad (21)$$

$$r_3 = -k_3^f C_{\text{M}} C_{\text{S}} + k_3^r C_{\text{CO}} C_{\text{H}} \quad (22)$$

$$r_4 = -k_4^f C_{\text{CO}} C_{\text{S}} + k_4^r C_{\text{CO}_2} C_{\text{H}} \quad (23)$$

$$r_5 = -k_5 C_{\text{PKS}} C_{\text{CO}_2} \quad (24)$$

$$r_6 = -k_6 C_{\text{CO}_2} C_{\text{CaO}} \quad (25)$$

The rate of reaction for each reaction is very much depending on the reaction constant and the concentration of the reactant. The reaction constant is defined by Arrhenius equation as below :

$$k_i = A_i e^{E_i / RT_i} \quad (26)$$

Where ;

A_i is the pre-exponential factor

E_i is the activation energy

T_i is the gasifier temperature

R is the ideal gas constant

In order to have best estimate of the rate of the reaction, a reference pre-exponential factor will be used. This involved with modification of the original Arrhenius equation as below :

$$k_i = A_{ref} e^{(-E/R(1/T-1/T_{av}))} \quad (27)$$

Where : $A_{ref} = A e^{(-E/RT_{av})}$

Where: T_{av} is the temperature average

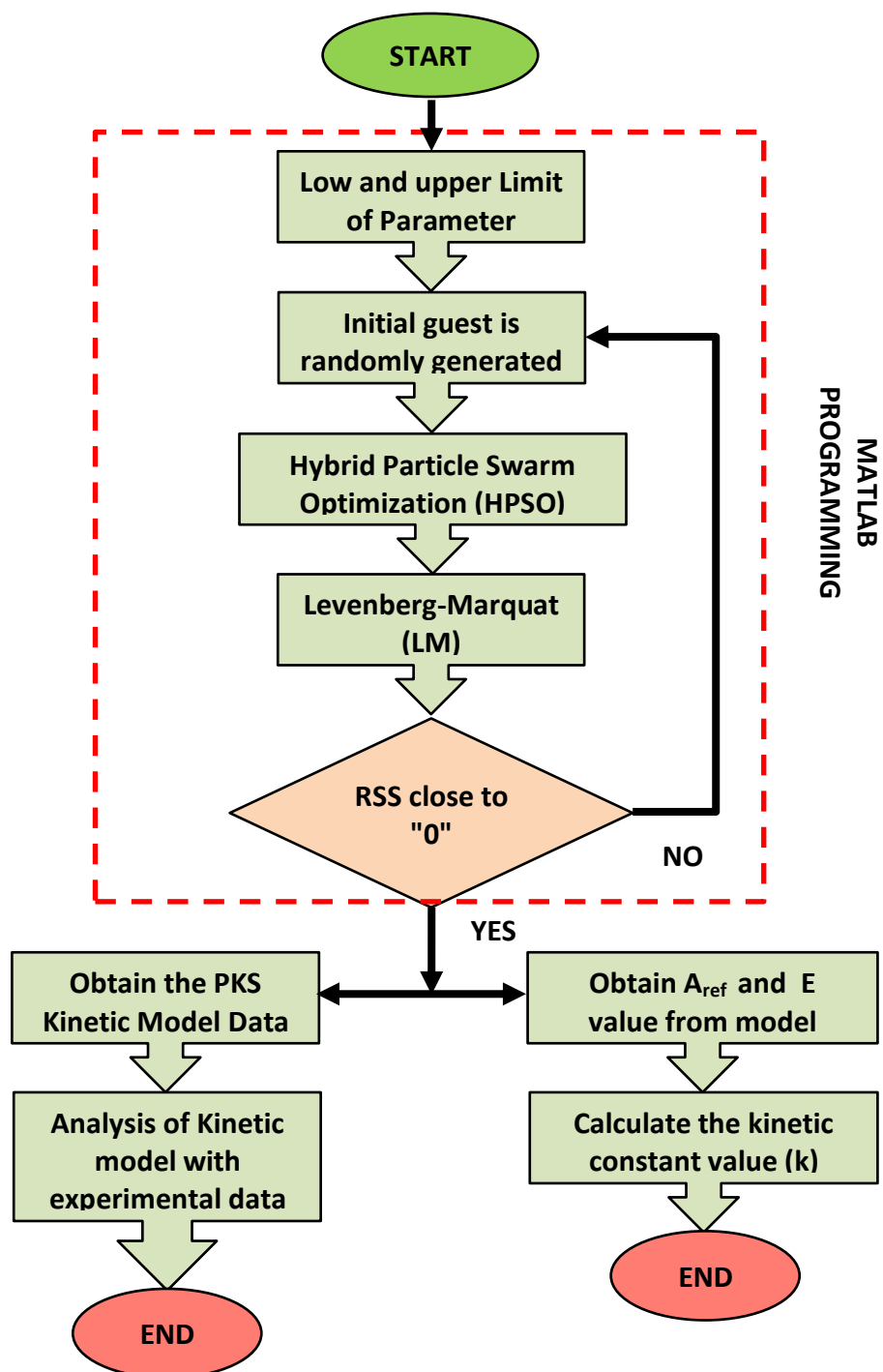
3.7 Material balance equation

Unsteady state mass balance in a batch reactor is identical to steady state mass balance in ideal Plug Flow reactor. Gasification is modelled as ideal plug flow reactor. Below table 5 are the material balance equations for all components:

Table 5 : Material balance equations

Component	Material balance Equations	
PKS	$\frac{dC_{PKS}}{dt} = (r_1 + r_2 + r_5)$	(28)
Steam	$\frac{dC_S}{dt} = (3r_1 - 3r_2 + r_3 + r_4)$	(29)
Hydrogen	$\frac{dC_H}{dt} = (-7.5r_1 + 10.5r_2 - 3r_3 - r_4 - 4.5r_5)$	(30)
Carbon Monoxide	$\frac{dC_{CO}}{dt} = (-6r_1 - r_3 + r_4 - 9r_5)$	(31)
Carbon Dioxide	$\frac{dC_{CO_2}}{dt} = (-r_4 + 3r_5 + r_6)$	(32)
Methane	$\frac{dC_{CH_4}}{dt} = (-6r_2 + r_3)$	(33)
CaO	$\frac{dC_{CaO}}{dt} = r_6$	(34)

3.8 Reaction Kinetic Modelling flow chart



CHAPTER 4

RESULT AND DISCUSSION

4.0 Result and Discussion

4.1. Introduction

This chapter presents the results of the reaction kinetic model obtained from the Hybrid Particle Swarm Optimization (HPSO) method base on the three identified parameters. Each of the parameters has been set up according to the experimental work set up. From the experimental data, the work set up as per below:

- Effect on temperature set for 600 °C , 675 °C and 750 °C.
- Effect on Steam to biomass ratio set for 1.5, 2.0 and 2.5
- Effect on the adsorbent to biomass ratio for 0.5, 1.0 and 1.5

The result from the experimental data obtained from the previous studies in UTP will be used to validate the data that will be obtained from the kinetic model. The main focus is more towards the H₂ production and some other gases such as CO₂, CO and CH₄.

4.2. Kinetic Modelling reaction of the Palm Kernel Shell (PKS)

Base on the result obtained from the Hybrid Particle Swarm Optimization (HPSO) and the Levenberg Marquat (LM) algorithm, the kinetic values obtained are as per table 6 below. The minimum RSSE obtained from the initial guess value is 5.32×10^3 and F-value at 1.43×10^2 . In order to get the best fit data, the RSSE vale should be as low as possible while the F-value should be as high as possible. This involved with more than 50 times initial guess values with 150 iterations (Maximum).

NO	Reaction Process	Pre-exponential Factor (A)	Activation Energy (E _a)
1	PKS Gasification	7.22 x 10	5.59 x 10 ⁴
2	Methanation	1.05 x 10 ³	1.37 x 10 ⁵
3	Methane Reforming (Forward)	7.52 x 10 ⁹	1.78 x 10 ⁵
4	Methane Reforming (Reverse)	2.34 x 10 ⁵	1.6 x 10 ⁵
5	Water Gas Shift (Forward)	6.13 x 10 ¹⁰	1.71 x 10 ⁵
6	Water Gas Shift (Reverse)	9.49 x 10 ⁹	1.69 x 10 ⁵
7	Bourdard	1.18 x 10	8.52 x 10 ⁴
8	Carbonation	9.98 x 10 ⁷	1.18 x 10 ⁵

Table 6 : Pre exponential factor and Activation energy obtained from PKS model

4.3. Model validation with the experimental data

4.3.1. Effect on Temperatures

Below figure-2, shows the effect of three different operating temperatures; 873 K, 948 K and 1023 K on the hydrogen products concentration between the kinetic model and the experimental work. The three lines represent the model data while the three symbols (Triangle, diamond and square) represent the experimental data. Based on these trending, both data shows almost similar pattern of the H₂ production. Except that for the first 10 minutes, the experimental data shows higher value than the model. This because the experimental work was carried out under batch process. This will result to sudden spike of hydrogen concentration at the beginning before it start to follow the model data. The mean error between these two data will be discussed later. Base on the model trending, the H₂ production has the higher concentration at the temperature of 873 K. However, based on the experimental data the highest H₂ concentration was detected at the temperature of 948 K. The different between these two data was not so significant. The different between 873 K and 948 K is less than 5 mol/m³.

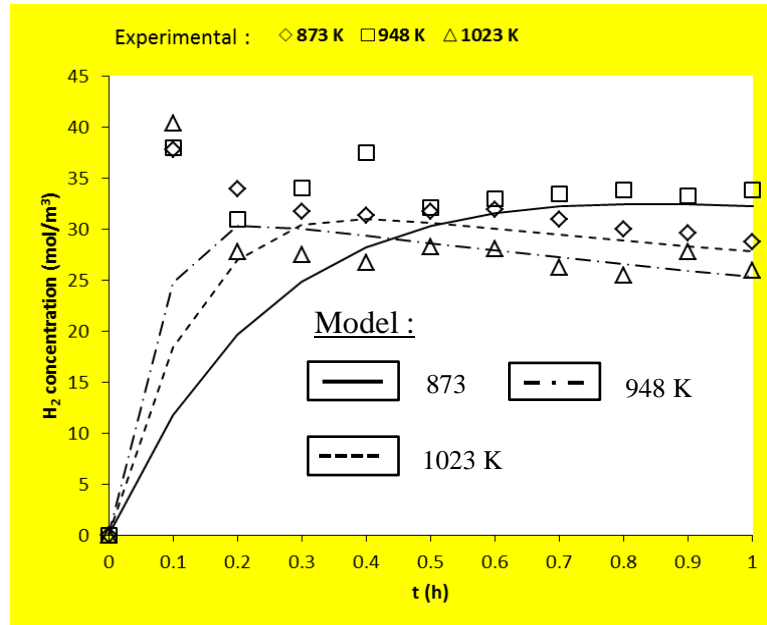


Figure 2 : Effect on temperatures to Hydrogen production

Below figure 3 shows for other gases production such as CO, CO₂ and CH₄ that also will be produced in this gasification reaction based on the effect of various temperatures between the experimental data and the model.

Based on these three trending, especially the CO₂ concentration, the experimental data does not detect any CO₂ gas during the experiment except at temp 1023 K.. Compare with the model data, the CO₂ concentration increased slowly. This discrepancy is due to the amount of the CaO (adsorbent) used for the experiment is not as per model prediction. The CO₂ produced during the water gas shift reaction have been converted to CaCO₃ by the present of the absorbent CaO. However, for the CO, the experimental data shows almost similar pattern with model data. Base on the identified reaction, CO₂ gas will be produced from the water gas shift reaction where it has reversible reaction. There are two reactions occurred in the gasifier that will produce the CO. Those reactions are gasification reaction and Methane reforming reaction.

For the CH₄ gas, the trending shows slow increment of gas from 0 to a range of 1.8 to 10 for all three ratios. CH₄ is produced in the gasifier from the reaction of the PKS

and the H₂. Based on these two models, both data shows that the CH₄ production is more favours at higher temperature. This can be seen when the CH₄ is detected at 9 with the temperature at 1023 K. Similarly with the model data, where it shows higher CH₄ concentration at the temperature 1023 K.

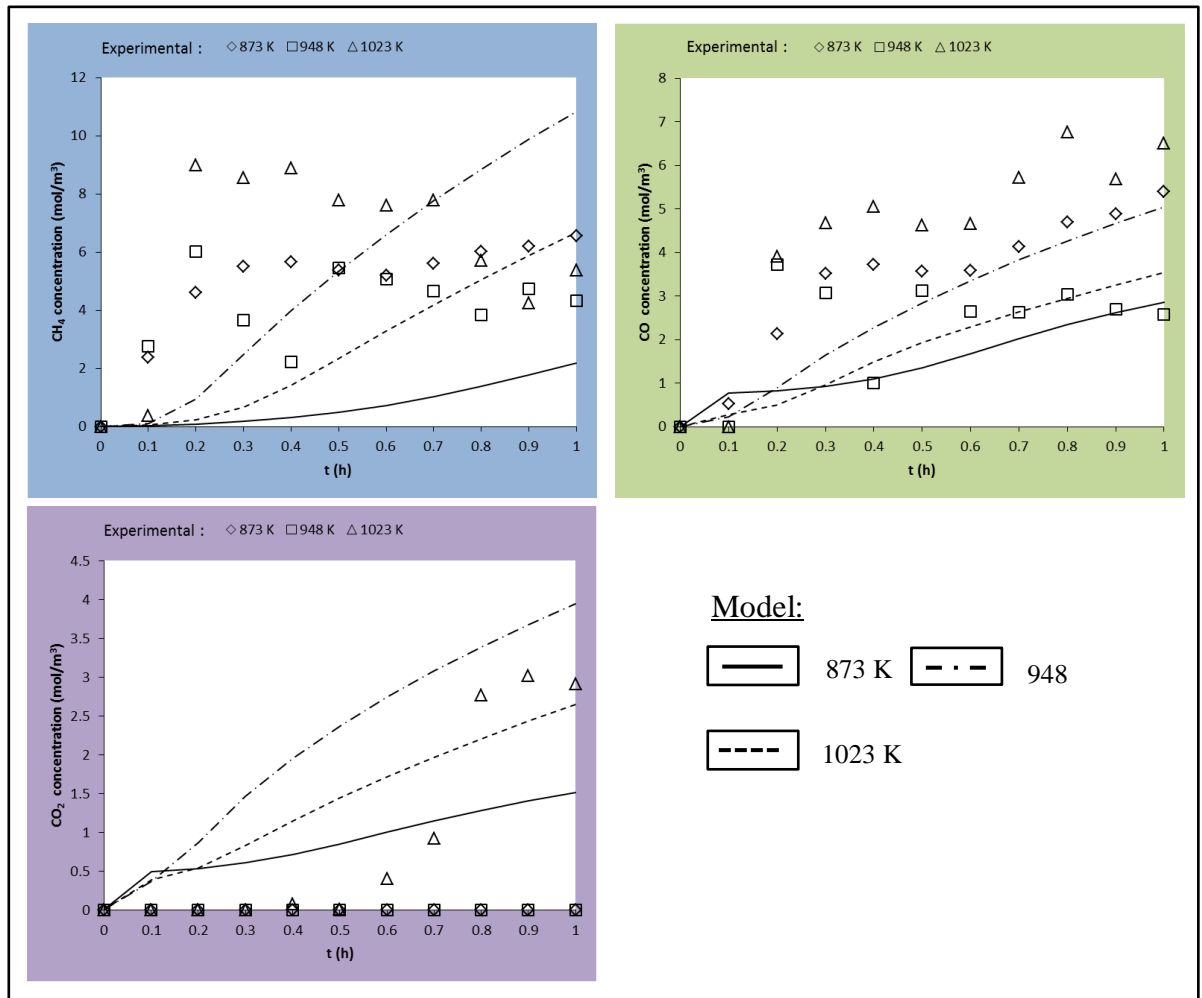


Figure 3 : Effect on temperatures to CO,CO₂ and CH₄ production

4.3.2. Experimental data for Effect on Steam to Biomass ratio

Below figure 4, shows the effect of three different ratios of steam to biomass; 1.5, 2.0 and 2.5 on the hydrogen products concentration between the kinetic model and the experimental work. The three lines represent the model data while the three symbols (Diamond, square and triangle) represent the experimental data. Based on these trending, both data shows almost similar pattern of the H₂ production. However, the experimental data shows a bit higher value than the model. Through the model data, the highest H₂ concentration detected at the ratio of 2.0. similarly with the experimental data where the highest H₂ concentration detected was at 2.0.

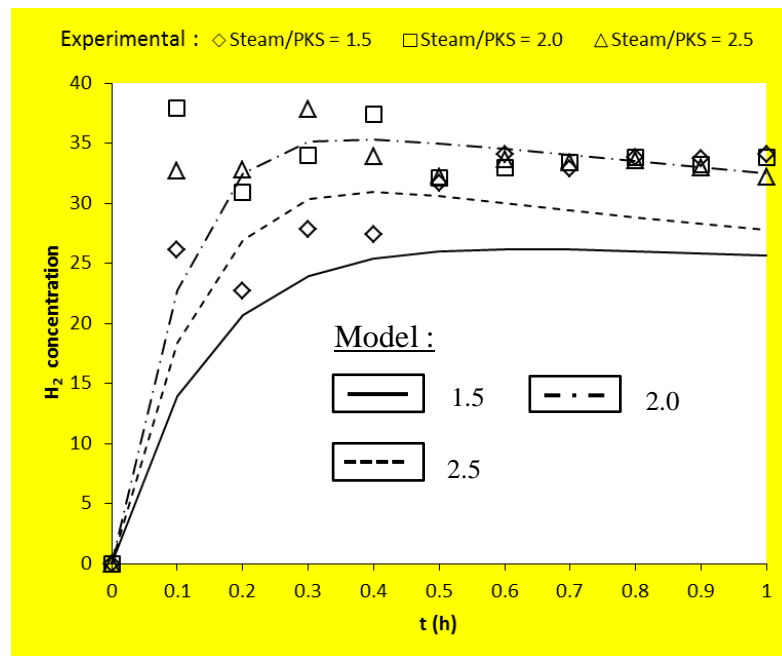


Figure 4 : Effect on Steam to Biomass ratio to H₂ Production

For the effect on the other gases such as CO, CO₂ and CH₄ to steam biomass ratio, below figure 5, shows some discrepancy for the CO and CH₄. This is similar with the effect on temperature, where the gases concentration detected high for the first 10 to 20 minutes. This is similar with the H₂ concentration, where its detected higher concentration for the first 10 minutes. As highlighted earlier this is due to the batch reaction process where the H₂ concentration will sudden increase since the PKS still has more H₂ in it until the gasifier reaction continue and reduce the H₂ concentration in the PKS. Unlike the model data, the unsteady state mass balance in a batch reactor

is consider identical to the steady state mass balance in an ideal plug flow reactor. The gasifier in the model is considered as ideal plug flow reactor. Therefore, the model data shows slow increment of the CH₄ and CO throughout the 60 minutes operation. For the CO₂ gas, both data shows similar trend where both does not detected any CO₂ at the steam to biomass ratio of 1.5. This is because at lower ratio, the CO produced from the gasification and methane reforming reaction does not have enough steam to react with the H₂O in order to produce CO₂. Through the model, the CO₂ was detected at higher ratio of 2.5 and similarly with the experimental data. However, at the ratio of 2.0 the experimental data does not indicates any CO₂ gas. Unlike the model data, the CO₂ was detected from a range of 0 to 2.8. This is because, the model is in ideal condition while the experimental work is on the real condition.

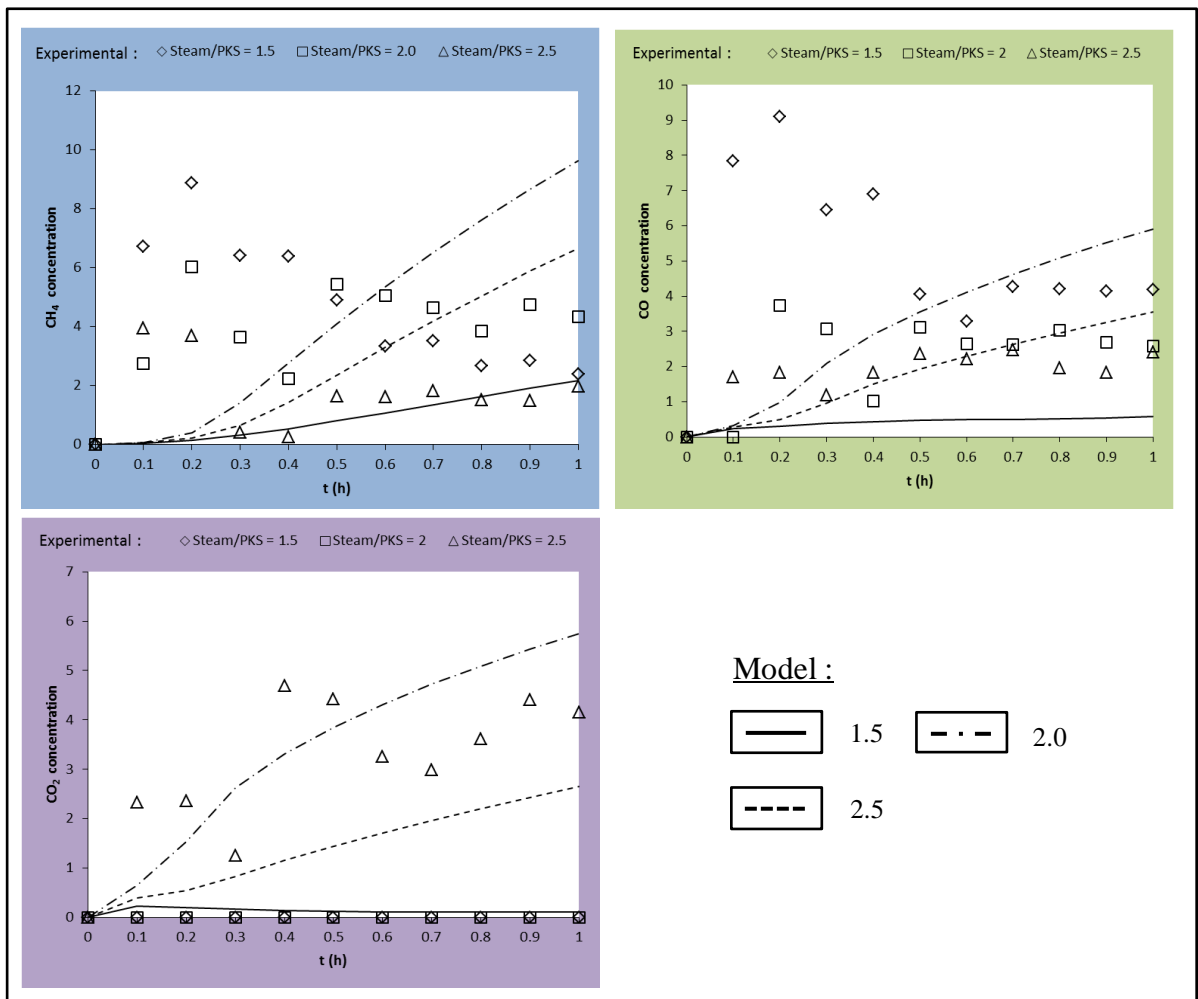


Figure 5 : Effect on steam to biomass ratio to CO,CO₂ and CH₄ production

4.3.3. Effect on the Adsorbent to the Biomass ratio

Below figure-6, shows the effect of three different ratios of adsorbent to biomass; 0.5, 1.0 and 1.5 on the hydrogen products concentration between the kinetic model and the experimental work. The three lines represent the model data while the three symbols (Diamond, square and triangle) represent the experimental data. Based on these trending, both data shows almost similar pattern of the H₂ production for all three ratios. However, the experimental data values shows a bit lower value than the model data. Generally, H₂ concentration is directly proportional with the adsorbent to biomass ratio. The higher ratio, H₂ concentration will be higher. Base on the trending below, both have an agreement on that statement.

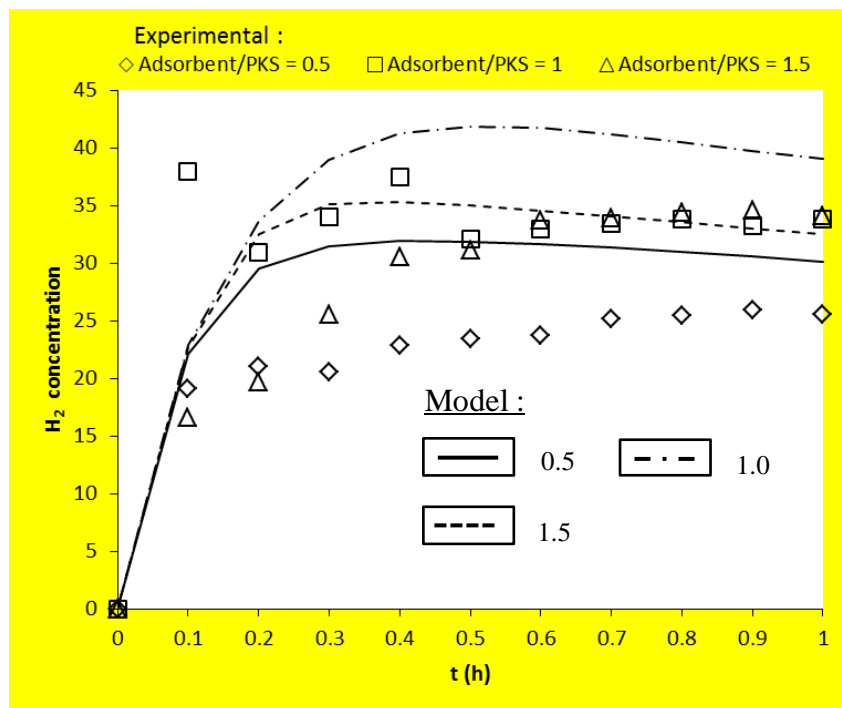


Figure 6 : Effect on Adsorbent to Biomass ratio for H₂ Production

Below figure 7 shows the effect on the other gases such as CO, CO₂ and CH₄ to adsorbent to biomass ratio. For the CH₄ gas, the model and the experimental data does not fit much. The model shows the CH₄ concentration is higher at the lower ratio (0.5). Unlike the experimental data, the highest CH₄ concentration was detected at the ratio of 1.5. Similar with the CO gas concentration, the model data and the experimental data does not have a good agreement. For the CO₂ gas, both data shows almost similar pattern. The CH₄ value is high at the lower ratio. However, the value for the experimental data is lower than the prediction data. For the ratio of 1.0 and 1.5, the experimental and model data have an agreement. This is because the higher amount of CaO in the gasifier, the lower CO₂ gas will be produced. The carbonation reaction between CO₂ and CaO will be occurred and produced CaCO₃. That is the reason why the CO₂ is not detected at the higher ratio.

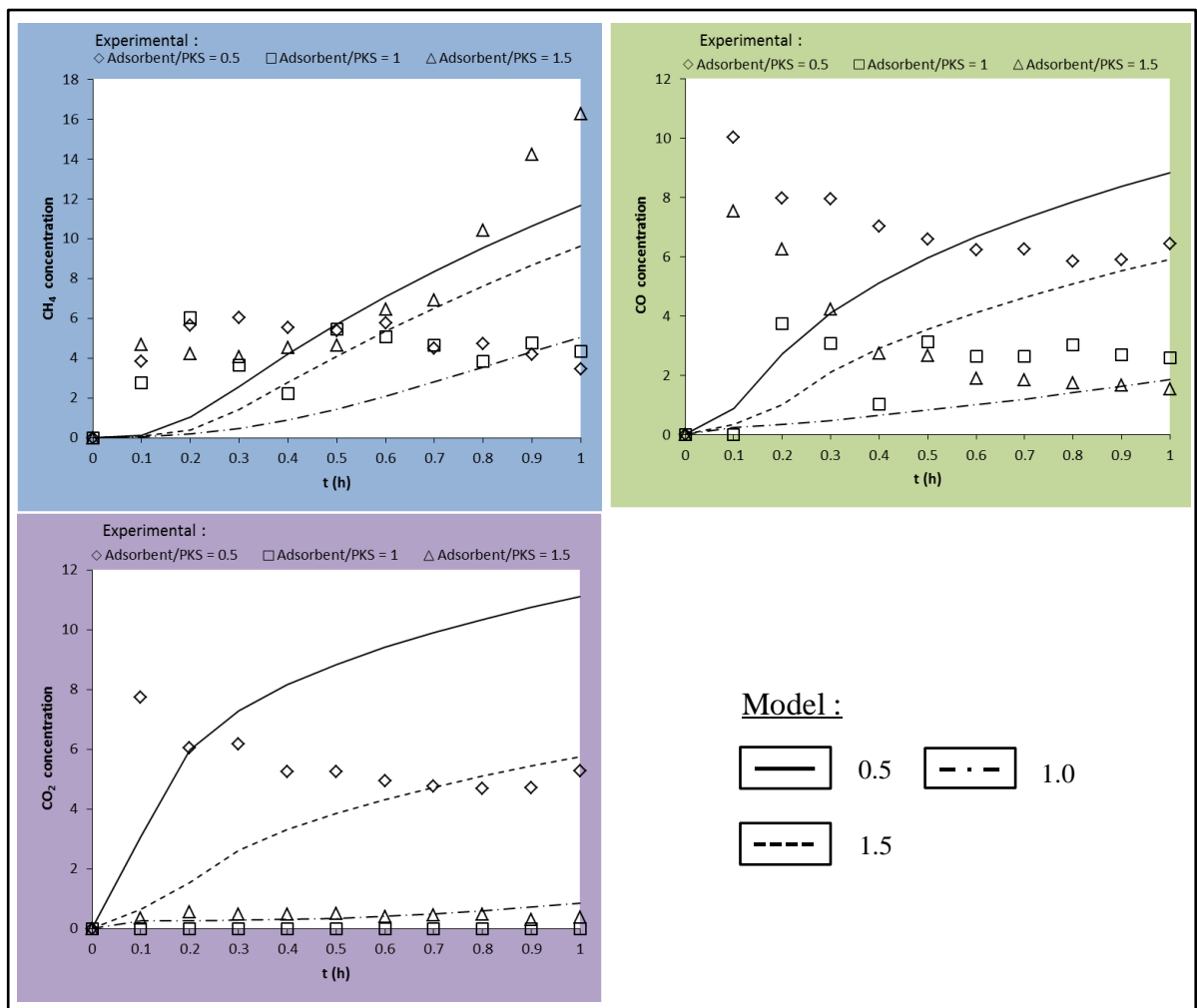


Figure 7 : Effect on Adsorbent to biomass ratio to CO,CO₂ and CH₄ production

4.4. Overall model validation for each gas of all three parameters using parity diagram

In order to validate the overall model data accuracy, all the parameters such as effect on temperature, steam to biomass ratio and adsorbent to biomass ratio, have been collected into single diagram called parity diagram. Through this diagram, the overall data fitting can be seen and the overall fitting accuracy can be obtained using R^2 method. R^2 value is unitless. The fraction of this R^2 is between 0 to 1. At zero R^2 value, it shows the data does not help each other and no linear relationship. However, at one R^2 value, it means all points lie exactly on a straight line with no scatter. It help and fit each other.

4.4.1. Effect on Hydrogen concentration

Refer to the below figure 8, almost 60% of the experimental data and the model data are lies together. It means the model prediction for H_2 production base on all three parameters; temperatures, steam to biomass ratio and adsorbent to biomass ratio, have 60% agreement.

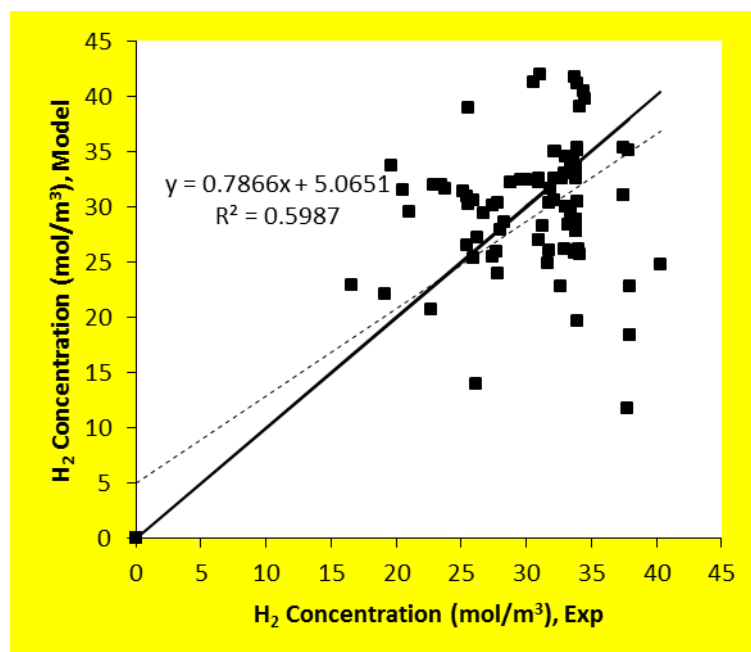


Figure 8 : Parity diagram for H_2 concentration between model and experimental data

4.4.2. Effect on Methane concentration

For the Methane gas (CH_4) in the below figure-9, it has only 10.9 % agreement between these two data. The reason of this poor agreement is due to the condition of the gasifier process between the model and the experiment. In the model, the reaction is considered under continuous process whereas for the experimental data, it is a batch process. In batch process, the H_2 production is higher at the first few minutes and start to reduce toward the one hour experiment. This result to both data does not lies each other. Besides that, the model operation is works under steady state process where it does not involve with any fluctuations.. Unlike the experimental work, it involve with many factors that could lead to poor result. For example, the sample preservation, sampling technique, time interval for sample collection and many others disturbances.

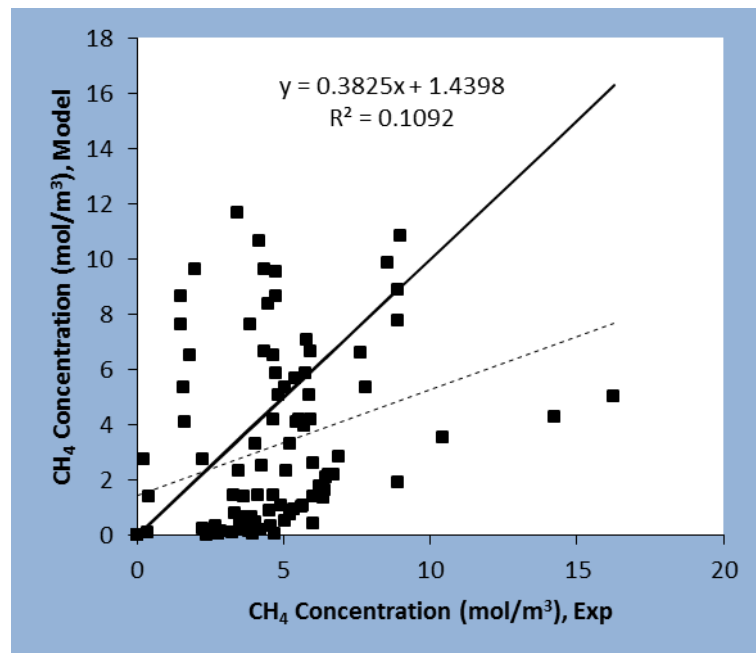


Figure 9 : Parity diagram for CH_4 concentration between model and experimental data

4.4.3. Effect on Carbon Dioxide concentration

Refer to the figure 10 below, the CO₂ production by the model prediction data and the experimental data shows almost 60% agreement for all three different parameters; effect on temperature, steam to biomass ratio and adsorbent to biomass ratio. Under the lower ratio of adsorbent and steam to biomass ratio, both model detected well the CO₂ gas whereas under higher ratio, both model does not detect any CO₂ gas. This is considered good agreement as there are many factors that could affect the result especially from the experimental work.

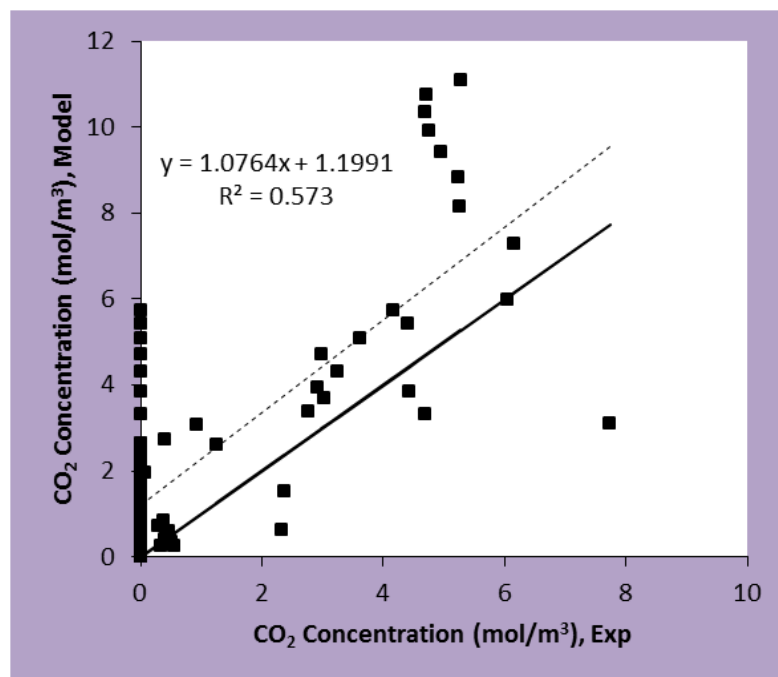


Figure 10 : Parity diagram for CO₂ concentration between model and experimental data

4.4.4. Effect on Carbon Monoxide concentration

For the CO gas, below figure 11 shows the CO production by the model prediction data and the experimental data shows only 10% agreement for all three different parameters; effect on temperature, steam to biomass ratio and adsorbent to biomass ratio. CO can be produced from the gasification reaction and the methane reforming reaction. These are the only source of CO producer in the gasifier. In the model prediction data, the reversible reaction for the methane reforming has been considered. Whereas under the dynamic process of the experimental work, this reversible reaction is unknown. This has result to the poor agreement.

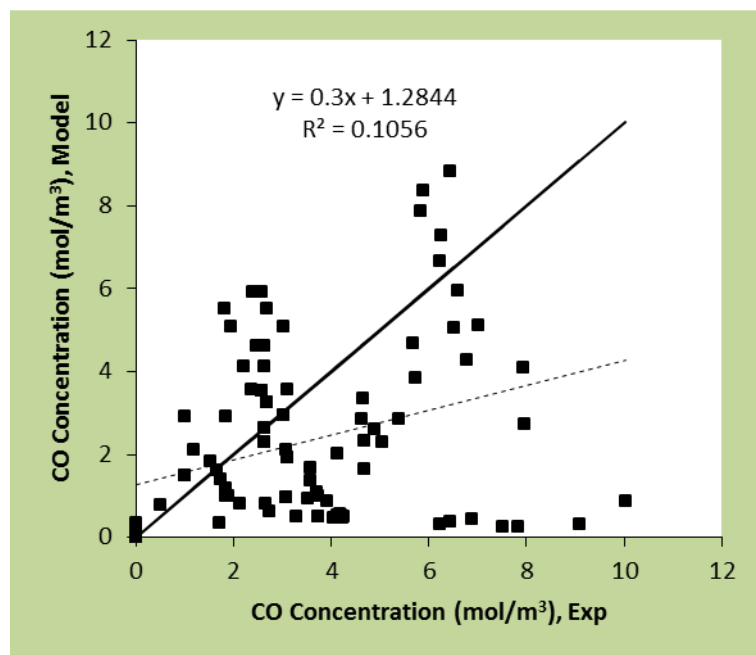


Figure 11 : Parity diagram for CO concentration between model and experimental data

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the first order of the reaction kinetic model that have been developed for the prediction of the product gas composition, the data was validated with the experimental data that have been conducted in UTP by the previous students. in the current study the kinetic constant values have been validated using the HPSO method which have reduced the error to the minimum possible. With the estimated value obtained from this model, it can be concluded that, the model and the experimental data are almost in correspond each other. Even though the two data are not 100 % linear to each other, but it is still can be accepted. This is because the model is under steady state condition while the experiment work is a real condition where it involve with many disturbances during the experiment.

Therefore, with the kinetic model development it will ease the future study for the researchers to further explore the technique so that it could help them to validate the experimental data and improve the result.

5.2 Recommendation

In order to have a better and accurate prediction, the experimental data need to be validated with several experiments. This is to ensure the consistency of the data before it can be used to validate the data from the model prediction. Besides that, the time interval for the sampling also need to be revised. This is because to provide ample time for the operator who run the experiment to collect the sample at the right time.

REFERENCES

- [1] Chang A, Chang H, Lin F, Lin K, Chen C., 2011, "Biomass gasification for hydrogen production," *International Journal of Hydrogen Energy* 36: 14252-14260
- [2] Khan Z, Yusup S, Ahmad M, Rashidi., 2013, "Integrated catalytic adsorption (ICA) steam gasification system for enhance hydrogen production using palm kernel shell," *International Journal of Hydrogen Energy* 39: 3286-3293
- [3] Yusuf S, Khan Z, Ahmad M, Rashidi N., 2014, "Optimization of hydrogen production in in-situ catalytic adsorption (ICA) steam gasification based on response surface methodology," *Biomass and Bioenergy* 60: 98-107.
- [4] Wang L, Dun Y, Xiang X, Jio Z, Zhang T., 2011, "Thermodynamic research on hydrogen production from biomass and coal co-gasification with catalyst," *International Journal of Hydrogen Energy* 36: 11676-11683
- [5] Ahmed T, Ahmad M, Yusup S, Inayat A, Khan Z., 2012, "Mathematical and computational approaches for design of biomass gasification for hydrogen production: A review," *Renewable and Sustainable Energy Reviews* 16(2012)2304-2315
- [6] Moghtaderi B., 2007, "Effects of controlling parameters on production of hydrogen by catalytic steam gasification of biomass at low temperature," *Fuel* 86: 2422-2430
- [7] Shen L, Gao Y, Xiao J., 2007, "Simulation of hydrogen production from biomass gasification in interconnected fluidized beds," *Biomass and Bioenergy* 32: 120-127
- [8] Acharya B, Dutta A, Basu P., 2009, "An investigation into steam gasification of biomass for hydrogen enriched gas production in present of CaO," *International Journal of Hydrogen Energy* 35: 1582-1589
- [9] Yan F, Zhang L, Hu Z, Cheng G, Jiang C, Zhang Y, Xu T, He P, Luo S, Xiao B., 2010, "Hydrogen rich gas production by steam gasification of char

derived from cyanobacterial blooms (CDCB) in a fix bed reactor: influence of particle size and residence time on gas yield and syngas composition,” *International Journal of Hydrogen Energy* 35: 10212-10217.

- [10] Wei H.L, Nor Ashidi M.I, 2013, Teaching peer learning particlece swarm optimization, *Applied soft computing*, 18: 30-58
- [11] Schwaab, M., Biscaia, E. C., Monteiro, J. J., & Pinto, J. C. 2007, Nonlinear Parameter estimation through particle swarm optimization, *Chemical Engineering Science*, 63, 1541-1552.
- [12] Rex.T.L, Ng, Douglas H.S, Wan Azlina.W. K.G, Denny K.S.2013, Modelling and optimization of biomass fluidised bed gasifier, *Applied Thermal Engineering*, 61: 98-105
- [13] Andres Z. Mendiburu, Joao A. Carvalho, Christian J.R. Coronado, 2014, Thermochemical equilibrium modeling of biomass downdraft gasifier: Sthoichiometric models, *Energy*, 66: 189-201
- [14] Schwaab, M., Kelly Yong, T. L., Lee, K. T., Mohamed, A. R., & Bhatia, S. Potential of Hydrogen from oil palm biomass as a source of renewable energy worldwide. *Energy Policy*, 35, 5692-5701
- [15] Parthasarathy, P., Narayan, K., & Lee, K. T. Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yeild- A review. *Renewable Energy*, 570-579.
- [16] Kennedy, J., Eberhart, R.,(1995). Particl Swarm Optimization. *In: Proceedings of IEEE International Conference on neural Network. Vol. 4*, pp.1942-1948
- [17] Kumar, V., Balasubramanian, P., (2009) Kinetic parameter estimation in hydrocracking using hynrid particle swarm optimization. *Fuel* 88 2171-2180