Simulating of Biofuel Production from Rice Husks

by

TRAN THI THU HANG

Dissertation submitted

in partial fulfillment of the requirements for the

Bachelor of Engineering (Hons)

Chemical Engineering

SEPTEMBER 2012

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Simulating of Biofuel Production from Rice Husks

by

TRAN THI THU HANG

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Murni Melati Ahmad)

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.

_____

TRAN THI THU HANG

ACKNOWLEDGEMENT

I would like to take this opportunity to thank Chemical Engineering Department, Universiti Teknologi PETRONAS to offer a great platform for me to enhance my technical knowledge. I'm also deeply thankful to Dr. Murni Melati Ahmad, my supervisor who has introduced me to a new field of knowledge on biomass and optimization. Thank to her, I have now entered to a wider world of chemical engineering.

Besides, I want to express my great gratitude to my parents and my friends who have always been beside me, encouraged me to keep the good motivation untill the end of this university chapter. The end of this chapter is just the beginning of a whole new life. In order to show my greatest thank to all of my instructors in life, I will continue to keep the learning attitude and contribute back to the society.

ABSTRACT

In the context of energy crisis and environmental damage due to rapid depletion and overuse of fossil fuel, alternative renewable energy resources such as biomass have been being significantly studied recently. In Southeast Asia countries like Malaysia, one of the abundant biomass feed stocks is rice husk which is a residue from rice production process. Rice husk can be transformed into gasoline through a series of fast pyrolysis and catalytic cracking processes. However, there is limited work on simulating the whole process. The objective of this project is to develop a mathematical simulation for the production of gasoline from rice husk using MATLAB. From the developed model, parametric studies have been conducted to identify the operating conditions which give the highest yield of product. The mathematic model was based on kinetic equations for the two main processes together with basic mass and energy balance for other sub-processes in the flowsheet. As a result, the model has shown that from 1000kg of rice husk, 191 liters of gasoline would be obtained. Within the studied range, the operating conditions at temperature of 783K and residence time of 5s for pyrolysis and at 723K in 1.25h for catalytic cracking are proposed to get the highest gasoline yield. The developed model can be considered as a basis for further research on simulating the production process of biofuel from rice husk.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1   Global Energy Crisis

Nowadays, the modern world is run significantly on fossil fuel. According to BP's "Statistical Review of World Energy" up to 2010, it can be seen that the world oil consumption has exceeded current production capacity and it is on the increasing trend. Figure 1.1.1 shows that the total production in 2010 was about 81millions barrels/day while the total consumed oil reached more than 90millions barrels/day. In detail, the intensively increased consumption belongs to the Asia-Pacific area, where there is fast-growing demand for transportation and construction. Moreover, it is not only the matter of insufficient supply but also the depletion of this conventional energy resource together with its negative effect on the environment. The need of replacement for fossil oil has come to the peak of concern lately.
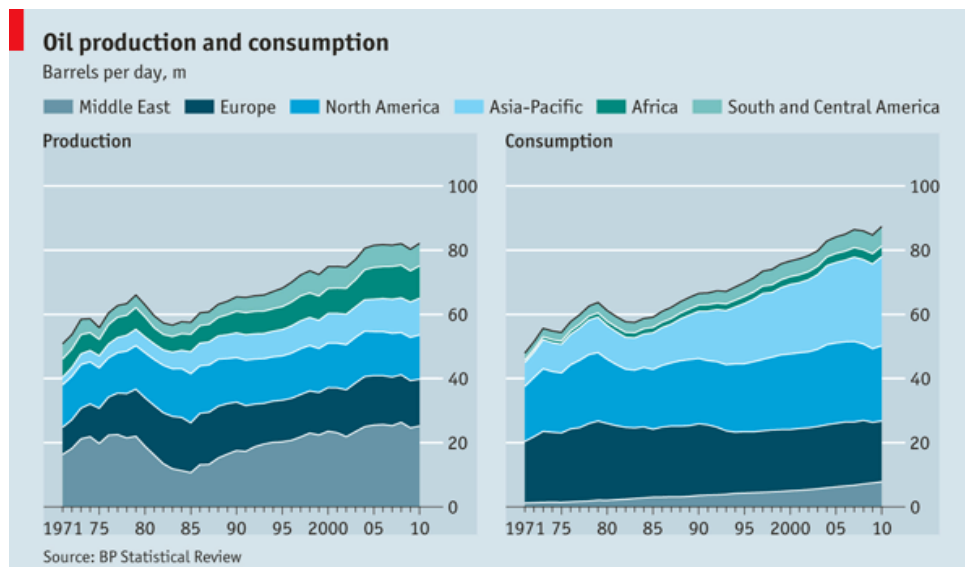

Figure 1.1.1: BP's Statistical Review of World Energy (Adopted from The Economist online, 2011)

1.1.2 Biomass as alternative fuel

There are some available choices for alternative resources, such as hydropower, wind power, solar energy, geothermal power and biomass. Generally, all these types of renewable energy are harnessed for direct heating or running turbines to produce electricity but not yet replacing fuel to run our daily transportation (GreenENERGYCHOICE, 2012). However, biomass is attractive in producing a form of liquid biofuel which is similar to fossil fuel. Biofuel is considered neutral in CO_2 emission because it is claimed that the amount of CO_2 produced by biofuel is equal to the amount that the biomass consumed in their growing stages (BIOMASS Energy Centre, 2012). For that, biomass has become a promising resource for energy demand.

1.1.3 Biomass sustainability

Biomass is derived from any living or recently living organisms. In the energy resource view, biomass usually refers to virgin wood, energy crops, agricultural wastes, etc (BIOMASS Energy Centre, 2012). In Brazil, sugar cane and corn has been used to produce bioethanol, a form of biofuel, since 1920s. As more and more biomass from crops became the feedstock to produce biofuel, it has raised a controversial issue on the threat against food supplies (Abbas and Ansumali, 2010). New technology in biomass area has started to change the focus into agricultural waste such as sugar cane residue, rice husk, poultry residue, etc. Among those materials, rice husk is considered as a promising abundant source, especially in Southeast Asia, to generate bio-oil and further upgrading to biofuel. Abbas and Ansumali (2010) reported on potential of rice husk in producing bioethanol. Many researchers have done experimental studies on rice husk thermal treatment to produce bio-oil such as Tsai (2005), Zheng (2006), Guo (2011).

In Malaysia, rice is one of the main foods in daily life. According to Akinbile (2011), the area of paddy fields in Malaysia was about 0.7 million hectares. The average rice production of Malaysia from 2005 to 2012 was 2.3 million tons/year (FAO, 2012). With a husk to paddy ratio of 0.2 (Abbas and Ansumali, 2010), it can be seen that rice husk is a good resource to be utilized to produce biofuel in large scale.

1.1.4 Biomass conversion technology

The technologies to exploit energy potential from biomass include gasification, pyrolysis, transesterification and hydrolysis (Centi and Santen, 2007).

Gasification is a heating process with controlled amount of oxygen at more than 1000^oC which will decompose the chemicals in biomass into CO and H_2. This product mixture is call syn-gas which then is used to produce CH_4, H_2 and other useful hydrocarbon.

Transesterification process produces biodiesel from triglyceride in a catalytic reaction. The triglyceride can be derived from different biomass such as peanut, soy bean, palm, etc.

In the purpose to produce biofuel, hydrolysis accompanied by fermentation has been practiced in mass production with sugar cane and corn as in Brazil. In another view, with the trend of using agricultural waste as feedstock, pyrolysis process, especially fast pyrolysis is currently being studied to transfer biomass into bio-oils. Fast pyrolysis is a thermal decomposition process without the presence of oxygen at high heat transfer rate and short residence time. The products of this process are char, oil (bio-oil) and gas. Bio-oil is a dark brownish viscous liquid that has some similar properties to fossil crude oil (Sadaka and Boateng, 2012). The advantage of bio-oil is that it contains only small amount of nitrogen, metals and sulfur. However, due to the high oxygen content, heating value of bio-oil is considerably low compared to fossil oil. Therefore, bio-oil needs to be further upgraded to more useful form called biofuel through catalytic cracking process.

1.2 PROBLEM STATEMENT

Although the possibility of producing gasoline from rice husk has been proven, there is still limited kinetic simulation via mathematical approach to represent the two processes of rice husk pyrolysis and bio-oil upgrading.

1.3 OBJECTIVES

Objectives of this study are:

- To develop a mathematical model for simulating the production of gasoline from rice husk.
- To perform parametric study on the effect of temperature and reaction time on gasoline yield.

1.4 SCOPE OF STUDY

The scope of this study is about pyrolysis process of rice husk to produce bio-oil and upgrading bio-oil to gasoline. A flowsheet is designed to represent the whole production process. The two main reaction processes are modeled based on kinetic equations while simplified mass and energy balance equations are employed to represent the sub-processes. In this study, the mathematical equations are established using MATLAB. The developed model is the medium for performing parametric study on the process. As a result, recommended operating conditions are identified.

CHAPTER 2

LITERATURE REVIEW

2.1 STATISTIC STUDY ON RICE HUSK TO BIOETHANOL

Abbas and Ansumali (2010) are the two researchers from Australia and India who have studied about the potential of rice husk as a feed stock for bioethanol. They claimed that the increasing production trend of rice was correlated with the world's increasing population. From that, rice husk is an attractive waste material for producing bioethanol. Table 1 shows their summary on chemical content in rice husk according to three main components which are cellulose, hemicellulose and lignin. In their study, only cellulose and hemicellulose are reacted and transformed into ethanol. Although the final product of this research is not gasoline, the authors have provided the chemical content of rice husk and proved the high potential of utilizing rice husk as an abundant source of biomass to produce biofuel.

Table 2.1: Composition of main constituents of rice husk (Abbas and Ansumali, 2010)

Constituents	Average Composition (%)
Cellulose	33.43
Hemicellulose	20.99
Lignin	18.25
Ash/silica	17.45

2.2 INTRODUCTION TO PYROLYSIS AND BIO-OIL

According to Sadaka and Boateng (2012), pyrolysis is a process of heating biomass without the presence of oxygen to produce bio-oil and bio-char coal. The required condition for this process is high temperature which is more than $220^{o}C$. The products of this process are charcoal (carbon and ash), condensable vapors called pyrolysis oil or

bio-oil, and non-condensable gases called synthesis gas. Typical properties of pyrolysis oil are summarized in Table 2. From that, we can see that bio-oil consists of large amounts of oxygenated components. It leads to high polarity characteristic, thus bio-oil does not mix well with hydrocarbon and has lower heating value. Sadaka and Boateng also claimed that recently, the fast pyrolysis has been studied more because it maximizes liquid production in condition of rapid heating rate (more that $204^{o}C$ per second) and high temperature (more than $538^{o}C$). The authors also discussed about types of reactor suitable for pyrolysis process. Overall, the work of Sadaka and Boateng provides basic knowledge on pyrolysis and bio-oil production technology.

Table 2.2: Properties of Pyrolysis Oil (Sadaka and Boateng, 2012)

Physical Property	Typical Value
Moisture content	15% - 30%
pH	2.8 - 4.0
Specific gravity	1.1 - 1.2
Elemental analysis	
C	55% - 64%
H	5% - 8%
O	27% - 40%
N	0.05% - 1.0%
Ash	0.03% - 0.30%
High heat value	6,878 - 11.175 Btu/lb

2.3 EXPERIMENTAL WORK ON RICE HUSK PYROLYSIS

There are a number of experimental studies on rice husk pyrolysis which are mostly from China. The main objective is to observe the bio-oil yield at different operating conditions, from which identifies the optimum. The difference is also in terms of equipment set-up and analysis method. Nevertheless, we can see the agreement in their result of operating temperature and oil yield. Table 3 displayed the findings of four recent studies. These data will provide the reference for comparison with the calculated result from mathematical model subsequently.

Table 2.3: Experimental findings on rice husk pyrolysis

Content/Author	Tsai (2005)	Zheng (2006)	Zhu (2008)	Guo (2011)
Objectives	• Perform parametric study on operating conditions of pyrolysis process	• Analyze properties of bio-oil from rice husk • Improve former pyrolysis systems	• Study biomass fast pyrolysis • Perform upgrading bio-oil to useful chemical by catalytic steam reforming	• Study the composition and properties of pyrolysis oil from rice husk
Reactor type	Fixed bed	Fluidized bed	Fluidized bed	Fluidized bed
Operating temperature	400-500°C	420-540°C	450-550°C	440-550°C
Holding time	1-8mins	-	Less than 1s	2s
Maximum oil yield	40wt% at 500°C	56wt% at 465°C	51wt%	46.36wt%

2.4 KINETIC MODELING OF PYROLYSIS PROCESS

Prakash and Karunanithi (2008) did an extensive study to give a review on kinetic modeling in biomass pyrolysis. They concluded that the mechanism for pyrolysis of biomass so far followed a general approach that the raw feed was virgin biomass and the end products are gas/volatiles, tar and char. Due to the complex reactions in the pyrolysis route, there have been several attempts to develop kinetic model representing the process. Five typical models were summarized according to the extent of complexity. Prakash and Karunanithi declared the extended Koufopanos model studied by Srivastava et al. (1996) as the most widely used scheme. This scheme proposed the secondary tar cracking of the primary pyrolysis products which caused a modified final product distribution. The scheme was claimed to be able to cover most of the possible aspects of pyrolysis reactions and provide reasonably accurate product distributions at wide heating rate and temperature range. Their process mechanism will be discussed further in the result and discussion.

2.5 INTRODUCTION TO CATALYTIC CRACKING

In the urge of studying on upgrading wood-oils to fuels and chemicals through catalytic conversion methods, Adjaye (1993) compared the two main routes which were using hydrogenating catalyst such as Co-Mo and Ni-Mo and using zeolites as catalyst. The author declared that the upgrading method which used hydrogenating catalyst involved high pressure operation and the catalysts would be severely coked and sometime poisoned. On the other hand, using zeolites as catalyst, the operating process was performed in atmospheric condition. The main advantage of this route was the zeolite shape selectivity. This property resulted in a definite product distribution which could not be seen in hydrotreating catalysts. Moreover, the problem of sulfiding the hydrogenating catalyst was also avoided. Lastly, unlikely with hydrotreating catalyst, zeolites catalyst did not face a threat from water vapour which was a main product in cracking reactions. To summarize, Adjaye proposed to upgrade wood-oil through catalytic conversion using zeolites catalysts.

The study of Sharma and Bakhshi (1992) also showed an agreement with Adjaye (1993) that although the hydrotreating catalyst such as $Co-Mo/Al_2O_3$ resulted in a higher hydrocarbon yield than zeolite HZSM-5, they were only active at high temperature and required hydrogen. In contrast, HZSM-5 specifically assisted the formation of C_5-C_{10} hydrocarbon (fuel compounds) and less formation of coke. Moreover, HZSM-5 catalytic cracking required only atmospheric pressure and no hydrogen addition.

2.6 EXPERIMENTAL WORK ON UPGRADING BIO-OIL PROCESS

In 2010, Hew et al reported their result from experimental work on catalytic cracking of bio-oil from empty fruit bunch to explore the potential of this bio-oil to gasoline and organic liquid product (OLP). The maximum temperature was set at 450^oC and Zeolite catalyst, ZSM-5 was employed. The authors concluded that the yield of OLP and gasoline depended significantly on temperature. The optimum operating conditions for OLP and gasoline were at 350^oC and 400^oC respectively. With that, the optimum yields were 91.20% for OLP and 46.67% for gasoline. This study provides a detail experimental method to upgrade bio-oil to gasoline. Although the feedstock is not from

rice husk, the optimum conditions in the result may be used as a based case to compare with the future mathematical model.

Twaiq et al. (2003) studied about the kinetic of catalytic cracking of palm oil with HZSM-5 as catalyst. Their model showed an agreement with their experimental data that the optimum gasoline yield is 40.5% in the temperature range of $400^{o}C – 450^{o}C$.

2.7 KINETIC MODELING OF BIO-OIL UPGRADING

Ancheyta and Sotelo (2002) did a study on kinetic modeling for catalytic cracking of vacuum gas oil with 6 lumps. It represented the most important products of fluid catalytic cracking process which were gasoline (C5), C3's (propane and propylene), C4's (butane, i-butane and butenes), dry gas (H2, C1-C2), coke and lastly, unconverted vacuum gas oil. In this model, gasoline yield was reported to be about 85% which showed an agreement with the industrial value.

In 2003, Twaiq et al. performed a kinetic study of palm oil catalytic cracking into liquid hydrocarbon using HZSM-5 zeolite. The kinetics was defined by using lumped parameter models containing three steps of 3-lump, 4-lump and 6-lump models. The reaction route consisted of multiple cracking reactions of palm oil to diesel, kerosene, gas, gasoline and coke, together with further cracking of diesel, kerosene and gasoline to gas and coke. They declared that coke was mainly formed from the cracking of the gasoline and diesel fractions. Twaiq et.al. also stressed on the deactivation of the catalyst during the reaction. As a result, the developed kinetic equation was described as a function of catalyst activity.

Recently, Mortensen et al. (2011) completed a study on reviewing the catalytic upgrading of bio-oil to engine fuels. In the study, the authors discussed about two main routes of bio-oil upgrading which are hydrodeoxygenation and zeolite craking. Each of the upgrading routes was analyzed in terms of stoichiometric equation, catalyst and reaction mechanism, kinetic model and deactivation. The discussion is a valuable reference for kinetic model development.

2.8 MATHEMATICAL APPROACH FOR MODEL VALIDATION

Inayat et al. (2011) completed a process model of hydrogen production from oil palm empty fruit bunch (EFB) using MATLAB for parametric study. Their study employed first-order reaction kinetics calculation together mass and energy balance calculations for modeling the process. The developed model was used to examine the effect of temperature and steam/biomass ratio on the hydrogen purity, yield and efficiency. Inayat et al. applied the Minimization Squared Differences method between experimental and model values to validate their model. The authors also included the economic modeling and optimization in their work. As a result, the work of Inayat et al. (2011) is a good reference for applying MATLAB software in modeling a chemical production process.

2.9 RESEARCH GAP

From the reviewed literature, it can be concluded that a considerable amount of bio-oil (maximum yield of 40-50%) can be produced from rice husk through fast pyrolysis process, and the bio-oil from biomass can be further upgraded into biofuel, for which gasoline is the main interest at the yield of 40-45%. However, there is limited report on the whole production process from biomass to biofuel, especially from rice husk. Therefore, there is a need to study the production of biofuel from rice husk in a continuous process. The current project is carried out to fulfill the research need using mathematical modeling approach. A simple yet adequate model can provide an effective medium for performing parametric study on the production process.

CHAPTER 3

METHODOLOGY

3.1 RESEARCH FLOW

The activities required in achieving the objectives of this project are summarized in Figure 3.1.
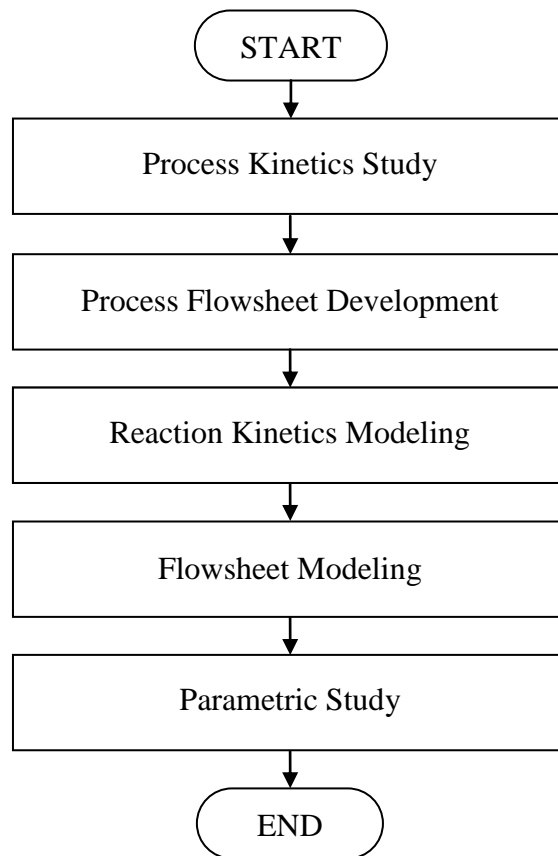

Figure 3.1: Project research flow

3.1.1 Process Kinetics Study:

This step is to identify the details on reaction route, kinetic equations of the process.

3.1.1.1 Pyrolysis process:

Koufopanos et al. (1989) described the pyrolysis of biomass in two stages which are primary and secondary interaction as in Figure 3.1.1.1
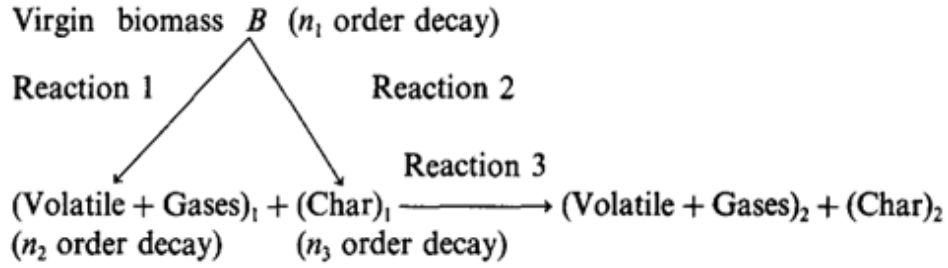

Figure 3.1.1.1: Fast pyrolysis process scheme (Koufopanos et.al., 1989)

The detail kinetic is illustrated in equations (3.1) to (3.5):

$$\frac{dC_B}{dt} = -k_1 C_B^{n_1} - k_2 C_B^{n_1} \tag{3.1}$$

$$\frac{dC_{G_1}}{dt} = k_1 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{3.2}$$

$$\frac{dC_{C_1}}{dt} = k_2 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{3.3}$$

$$\frac{dC_{G_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{3.4}$$

$$\frac{dC_{C_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{3.5}$$

where C_B, C_{G1}, C_{C1}, C_{G2}, C_{C2} are the concentration of biomass, gases 1, char 1, gases 2 and char 2 respectively calculated as:

$$C_{product} = \frac{m_{product}}{m_{initial\ biomass}}$$

and n_1, n_2 and n_3 are the reaction order with $n_1=0$, $n_2=n_3=1.5$ (Prakash and Karunanithi, 2008).

The kinetic constants are formulated as in equations (3.6) to (3.8):

$$k_1 = A_1 exp\left[(D_1/T) + (L_1/T^2)\right] \tag{3.6}$$

$$k_2 = A_2 exp\left[(D_2/T) + (L_2/T^2)\right] \tag{3.7}$$

$$k_3 = A_3 exp\left[(-E_3/R_cT)\right] \tag{3.8}$$

where T is the operating temperature in K and the other parameters are constants with values as $A_1 = 9.973$ x 10^{-5}, $A_2 = 1.068$ x 10^{-3}, $A_3 = 5.7$ x 10^5, $D_1 = 17254$ K, $D_2 = 10224$ K, $L_1 = -9061227$ K^2, $L_2 = -6123081$ K^2, $E_3 = 81$ (Prakash and Karunanithi, 2008).

3.1.1.2 Bio-oil upgrading process:

In this project, the kinetic of catalytic cracking bio-oil from rice husk is assumed to be similar as that of palm oil. Hence, the 6-lump kinetic of palm oil catalytic cracking by Twaiq et.al. (2003) is applied with the reaction route presented in Figure 3.1.1.2
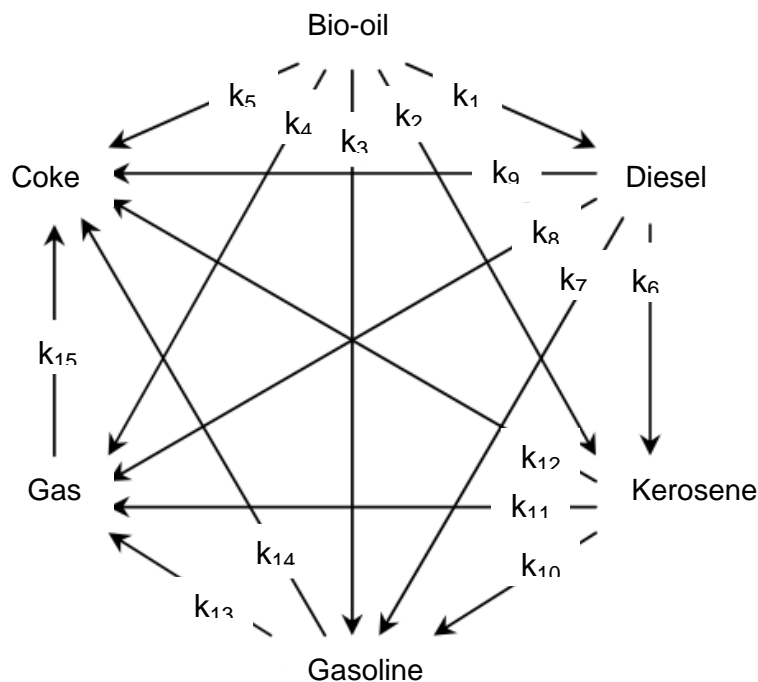

Figure 3.1.1.2: Catalytic cracking process scheme (Twaiq, 2003)

The detail kinetic is illustrated in equations (3.9) to (3.15) (Twaiq, 2003)

$$\emptyset(t) = 0.59k_d t^{-0.59} \tag{3.9}$$

$$k_d = 0.777e^{-17000/RT} \tag{3.10}$$

$$\frac{dC_{Diesel}}{dt} = \emptyset(k_1 C_{Oil}^n - (k_6 + k_7 + k_8 + k_9)C_{Diesel}^n) \tag{3.11}$$

$$\frac{dC_{Kerosense}}{dt} = \emptyset(k_2 C_{Oil}^n + k_6 C_{Diesel}^n - (k_{10} + k_{11} + k_{12})C_{Kerosene}^n) \tag{3.12}$$

$$\frac{dC_{Gasoline}}{dt} = \emptyset(k_3 C_{Oil}^n + k_7 C_{Diesel}^n + k_{10} C_{Kerosene}^n - (k_{13} + k_{14})C_{Gasoline}^n) \tag{3.13}$$

$$\frac{dC_{Gas}}{dt} = \emptyset(k_4 C_{Oil}^n + k_8 C_{Diesel}^n + k_{11} C_{Kerosene}^n + k_{13} C_{Gasoline}^n - k_{15} C_{Gas}^n) \tag{3.14}$$

$$\frac{dC_{Coke}}{dt} = \emptyset(k_5 C_{Oil}^n + k_9 C_{Diesel}^n + k_{12} C_{Kerosene}^n + k_{14} C_{Gasoline}^n + k_{15} C_{Gas}^n) \tag{3.15}$$

where $\emptyset(t)$ is the catalyst activity incorporated with the kinetic model, n is the reaction model which is found to be 1; C_{Oil}, C_{Diesel}, $C_{Kerosene}$, $C_{Gasoline}$, C_{Gas} and C_{Coke} are the concentration of bio-oil, diesel, kerosene, gasoline and gas respectively calculated as:

$$C_{product} = \frac{m_{product}}{m_{initial\ bio-oil}}$$

The reaction constants (from k_1 to k_{15}) are summarized in Table 3.1.1.2.

Table 3.1.1.2: Reaction constants for 6-lump catalytic cracking model in the temperature range of (673 − 723K) (Twaiq, 2003)

Reaction	Rate Constant			
	Parameter	673K	698K	723K
Bio-oil → diesel	k_1	0.2000	0.3000	1.5220
Bio-oil → kerosene	k_2	0.0700	0.1000	0.6250
Bio-oil → gasoline	k_3	0.1000	0.1000	0.9388
Bio-oil → gas	k_4	0.0072	0.0500	0.2500
Bio-oil → coke	k_5	0.0226	0.0690	0.1150
Diesel → kerosene	k_6	0.0260	0.0790	0.1328
Diesel → gasoline	k_7	0.3200	0.6000	1.5220
Diesel → gas	k_8	0.1000	0.5460	0.9105
Diesel → coke	k_9	0.0400	0.0800	0.3600
Kerosene → gasoline	k_{10}	0.0000	0.0000	0.0000
Kerosene → gas	k_{11}	0.0000	0.0000	0.0000
Kerosene → coke	k_{12}	0.0000	0.0000	0.0000
Gasoline → gas	k_{13}	0.0000	0.0000	0.0000
Gasoline → coke	k_{14}	0.0045	0.0100	0.2000
Gas → coke	k_{15}	0.2500	0.0840	0.0606

3.1.2 Process Flowsheet Development

The process modeling is based on following assumptions:

- The reactions occur isothermally (Zheng, 2006 and Twaiq, 2003).
- The operating temperature ranges for pyrolysis and catalytic cracking are 673-783K (Zheng, 2006) and 673-723K (Twaiq, 2003) respectively.
- Rice husk is fed in small particles with the size of 2-3mm which is suitable for pyrolysis reaction (Bridgwater, 1999).
- The efficiency of solid collection of cyclone is 98% for particles size within the range of 10-100μm (McCabe et.al., 2005).
- The efficiency of fractionator is 100%.

The process flow diagram has been constructed in Visio which represents the sequencing of sub-procedures in the two major processes which are fast pyrolysis and catalytic cracking.

Figure 3.1.2 shows the process diagram of the production process for two-step production which consists of biomass pyrolysis and bio-oil catalytic cracking. The moisture content of rice husk is less than 10%, thus it can be directly used for pyrolysis without pre-drying as other biomass feedstock (Zheng, 2006). The pyrolysis reactor uses N_2 as heating medium. Products from pyrolysis reaction are then carried to the cyclone which is designed to separate the char from the gas and volatiles product. After separated, gas and volatiles products are fed into a spray condenser to condense and separate the bio-oil from the incondensable gas. The catalytic cracking process starts with bio-oil being fed into the reactor. The cracking products are then separated in a fractionator into gas, gasoline, diesel, kerosene and coke in which gasoline is the interested final product.

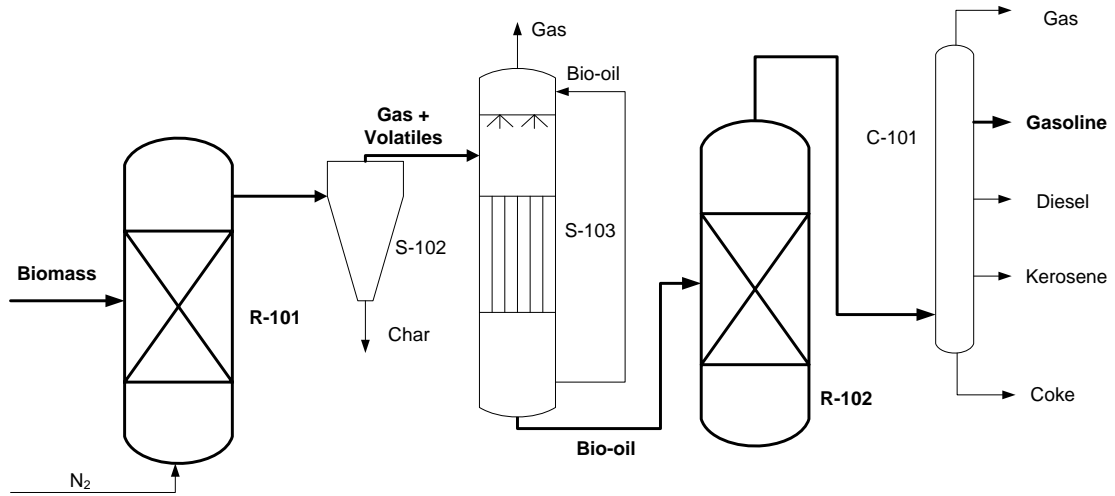| R-101	S-101	S-102	R-102	C-101
Pyrolysis Reactor	Cyclone	Spray Condensor	Catalytic Cracking Reactor	Fractionator

Figure 3.1.2: Process Flow Diagram

3.1.3 Reaction Kinetics Modeling

In this step, all of the kinetic equations are written in mathematical functions in Matlab. The final result of this step will be the complete model representing the production process. All of the kinetic equations are then solved using **ode45 solver** for differential equations.

3.1.4 Flowsheet modeling

Simple mass and heat balance is adopted to model the sub-processes in cyclone, spray condenser and fractionators.

3.1.4.1 Cyclone:

The mass balance in cyclone is assumed to be based on the efficiency of solid collection (McCabe, 2005) which is represented by equation (3.16) and (3.17).

$$m_{solid,o} = m_{solid,i} \times ef \qquad (3.16)$$

$$m_{gas,o} = m_{gas,i} + (m_{solid,i} - m_{solid,o}) \qquad (3.17)$$

where $m_{j,o}$ is the outlet mass flowrate of component j in kg/hr, $m_{j,i}$ is the inlet mass flowrate of component j in kg/hr and ef is the efficiency of solid collection.

3.1.4.2 Spray Condenser:

Spray condenser is a basic direct contact condensation equipment. The theory of this type of condenser is simply based on the exchange between latent of condensing vapor and sensible heat of sprayed liquid displayed in equation (3.18).

$$m_{vapor} \times \lambda = m_{liquid} \times Cp_l \times \Delta T \tag{3.18}$$

where m_j is the mass flowrate of substance j in kg/hr, λ is the latent heat of the vapor in kJ/kg, Cp_l is the heat capacity of the liquid in kJ/kg.K and ΔT is the temperature difference in K.

However, due to the complex components of bio-oil with inconsistent value for latent heat value, the amount of condensed oil and incondensable gases are calculated based on the experimental result from Zheng (2006) on rice husk pyrolysis. Table 3.1.4.2 displays the ratio of gas/oil produced from the experimental study.

Table 3.1.4.2: Production profile from rice husk pyrolysis (Zheng, 2007)

Temperature, K	Gas, wt%	Charcoal, wt%	Bio-oil, wt%	Gas/Oil ratio
693	12	35	53	0.23
723	15	29	56	0.27
753	20	24	56	0.36
783	26	21	53	0.49

3.1.4.3 Fractionator:

It is assumed to represent the performance of fractionators in total mass conservation of component at 100% efficiency. For which, each component in the inlet stream is totally separated in the outlet stream.

3.1.5 Parameter Study

Using the developed model, two parameters which are temperature and residence time are varied to study the effect on the product yield. The product yield is calculated as

$$yield = \frac{mass\ of\ product}{mass\ of\ feed} \times 100\%$$

3.2 GANTT CHART

Table 3.2: Project Gantt chart

No	Detail/Month	May 2012	June 2012	July 2012	August 2012	September 2012	October 2012	November 2012	December 2012
3.1.1	Process Kinetics Study	███	███	███	**(1)**				
3.1.2	Process Flow Sheet Development				███	**(2)**			
3.1.3	Reaction Kinetics Modeling					███	███		
3.1.4	Flowsheet Modeling							**(3)**	███
3.1.5	Parametric Study							███	**(4)**

MILESTONES: **(1)** Reaction Kinetic Model

                                  (2) Process Flow Diagram

                                  (3) Flowsheet mass balance model

                                  (4) Optimum operating conditions

CHAPTER 4

RESULT AND DISCUSSION

4.1 FAST PYROLYSIS

The developed model has been used to generate the concentration of biomass and products which are Gas1, Char1, Gas2 and Char2 at different temperature and residence time for analyzing the effect of these two parameters on the yield of bio-oil which depends on the total amount of gas product from pyrolysis process.

According to Bridgwater et al. (1999), the residence time for fast pyrolysis of biomass should be less than 2s. However, based on the generated data from the current model, at 2s, the yield of Gas1 and Gas2 which would be condensed afterward to bio-oil were less than 25%. Therefore, it is decided to observer the pyrolysis process up to 5s. The studied temperature range of pyrolysis is proposed based on the general range of experimental studies (Tsai, 2005; Zheng, 2006; Zhu, 2008; Guo, 2011).

As the bio-oil is the main product which will be furthered cracking to the final product, gasoline, the focus for parametric study in this step is bio-oil yield.

4.1.1 Effect of residence time on bio-oil yield

The results are observed at different temperature within the studied range and it shows the same trend for all. Figure 4.1.1 displays a typical generated data at 783K.

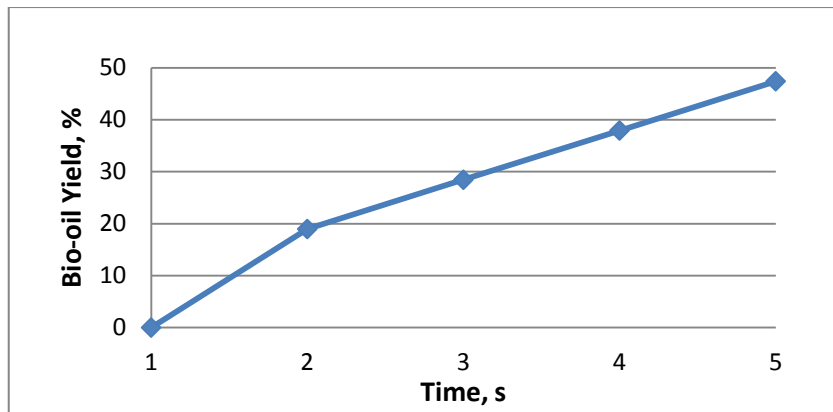It can be seen that the longer the time, the higher of bio-oil yield.

Figure 4.1.1: Effect of residence time on bio-oil yield

4.1.2 Effect of temperature on bio-oil yield

Figure 4.1.2 shows that bio-yield increased linearly respecting with temperature. This result is different from experimental work of Zheng (2006) on rice husk pyrolysis which claimed that the bio-oil yield increased to a maximum value at 753K then decreased at higher temperature. It may due to the simplification in simulating the condenser which has not sufficiently represented the change in the incondensable gas formation. However, the highest yield of bio-oil within the studied range which is 47.41% at 783K is within the range of 40-50% from experimental results by different researchers from literature review.
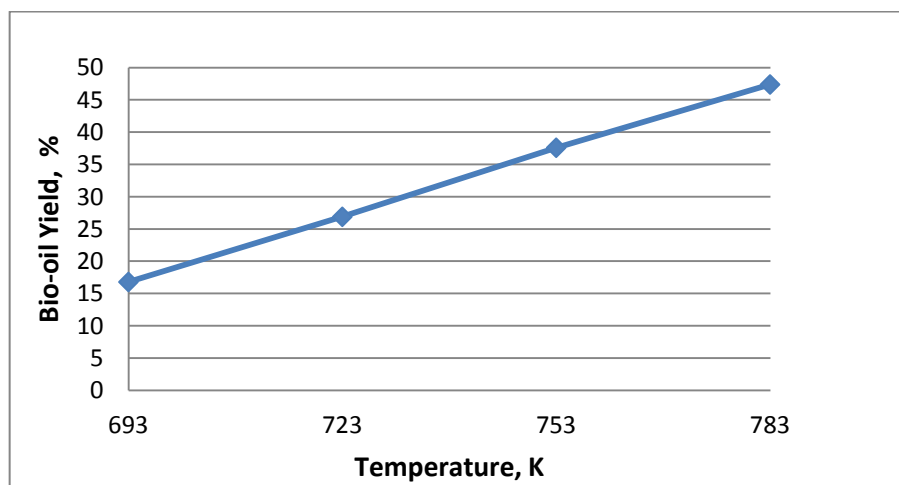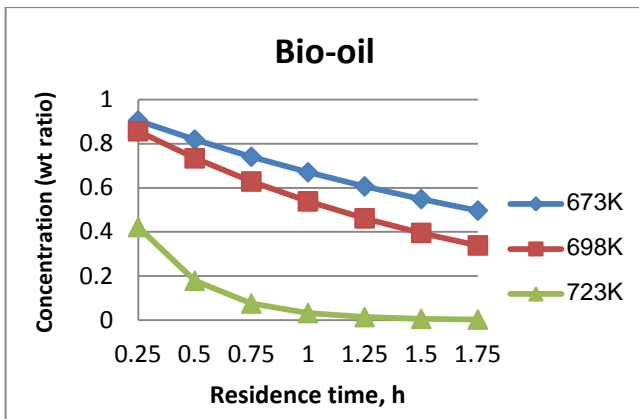

Figure 4.1.2: Effect of temperature on bio-oil yield
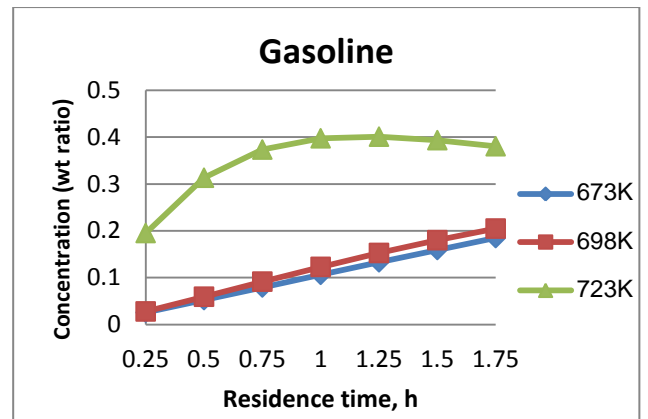
4.2 CATALYTIC CRACKING

The catalytic cracking of bio-oil was observed in the temperature range of 673 – 723K. The operating condition was adopted from Twaiq et al. (2003) for matching the kinetic parameter of the process. Moreover, this temperature range also falls into the study range of other research such as Sharma and Bakhshi (1992) and Hew et al. (2010) on catalytic cracking of different type of bio-oil. Based on the suggested reaction time of Twaiq et al. (2003), the developed model performs extended reaction time to 1.75h to observe the change of the production profile.

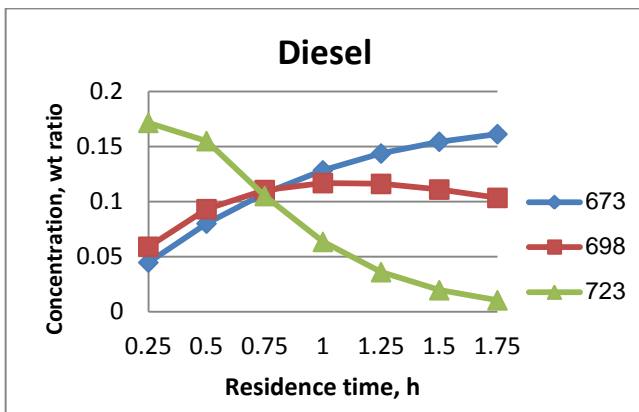### 4.2.1 Effect of residence time on catalytic cracking products

Figure 4.2 demonstrates the concentration of bio-oil and products according to residence time at different temperature. Overall, the bio-oil concentration decreased and concentration of the products increased with time. However, it can be seen that the change patterns are different at different temperature. We can see that at lower temperature (673K, 698K), the concentration changed linearly except for diesel. Whilst, at higher temperature (723K), only coke still increased linearly with time, the other product concentration changed significantly within the first 0.75h then slower as time increased. Especially, concentration of gasoline has reached a maximum value of 40% after 1.25h then decreased and the amount of diesel decreased with time. The reduction of diesel is due to the high rate of secondary cracking to other lighter components such as kerosene, gasoline, etc.
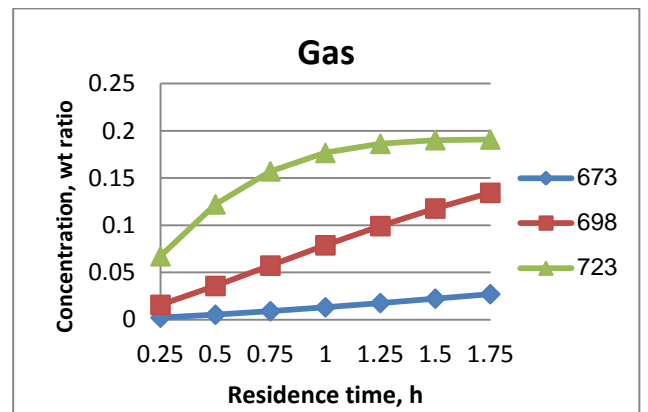
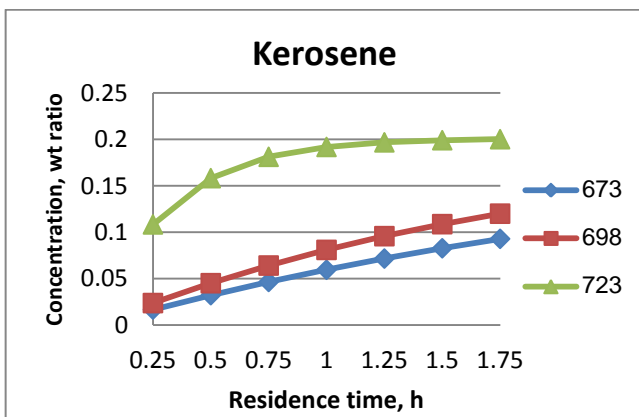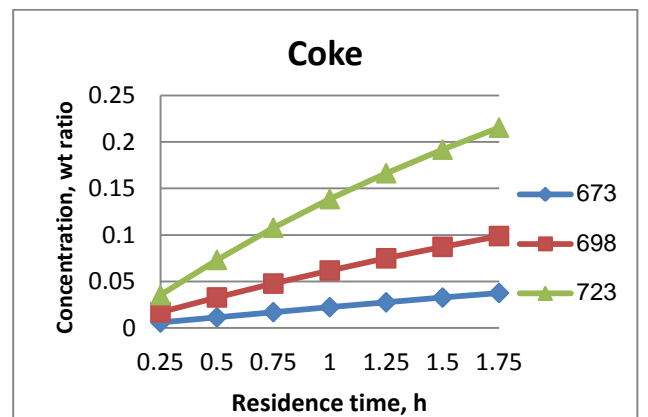Figure 4.2.1: Effect of residence time on cracking products: (a) Bio-oil, (b) Diesel, (c) Kerosene, (d) Gasoline, (e) Gas, (f) Coke

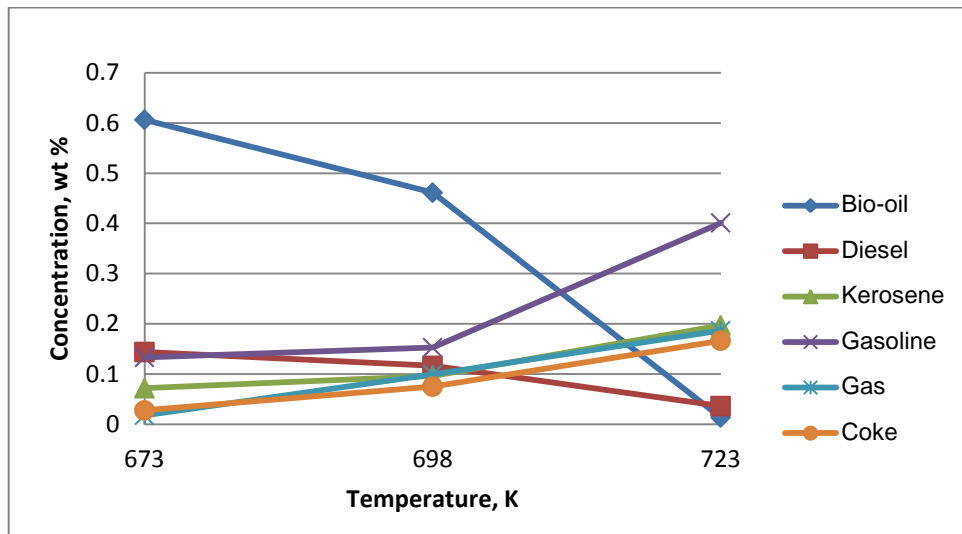**4.2.2   Effect of temperature on catalytic cracking products**

Figure 4.2.2: Effect of temperature on cracking products

From figure 4.2.2, it is observed that overall, the concentration of bio-oil and diesel decreased while other products increased as temperature increased. It can be seen that from 698K to 723K, when the bio-oil concentration decreased significantly, the concentration of gasoline increased also significantly while other products still kept the steady change. It implies that as the temperature increased from 698K, the cracking process favored the production of gasoline than other products.

4.3 FLOWSHEET CALCULATION

The flowsheet calculation is performed at recommended conditions for pyrolysis (783K, 5s) and catalyst cracking process (723K, 1.25h) with basis of 1000kg rice husk input. The result is demonstrated in Figure 4.3

Gas,
$m_{gas} = 238.2$ kg

Gasoline,
$m_{gasoline} = 190.63$kg

Rice husk
$m_{RH} = 1000$

| Fast pyrolys | Solid separati | Bio-oil condensati | Catalytic cracking | Fractionator |

Char,
$m_{char} = 287.66$kg
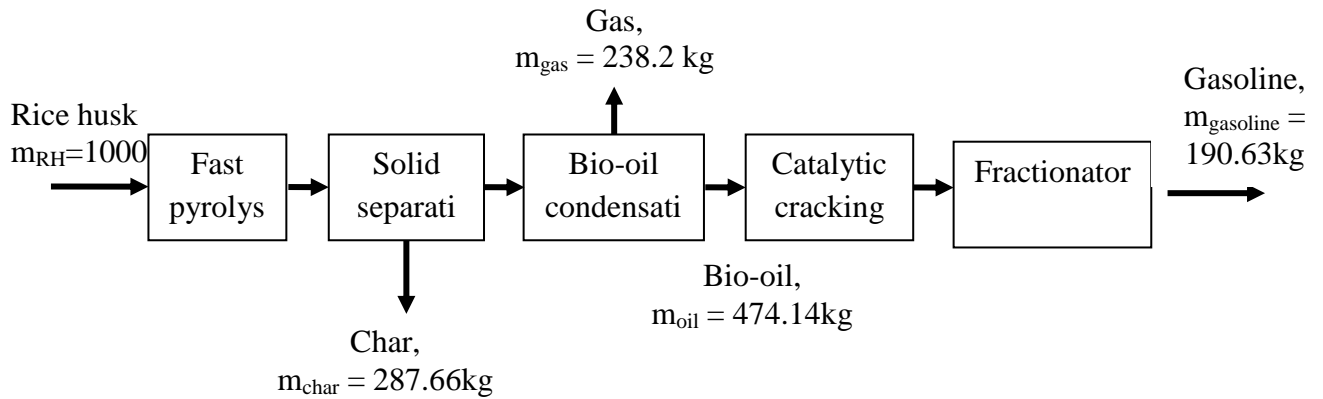
Bio-oil,
$m_{oil} = 474.14$kg

Figure 4.3: Flowsheet calculation

In order words, 1000kg of rice husk would produce 191kg gasoline which approximately equals to 258 liters or about 1.5 US barrel. This is a promise amount of fuel for production from rice husk. The result can be used as a reference for further research with more detailed parameter consideration.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

1. CONCLUSION

In summary, a mathematical model has been developed to simulate the production of gasoline from rice husk through fast pyrolysis and catalytic cracking using MATLAB. From the model, it is observed that the increment of time and temperature resulted in the steady change in pyrolysis process while the cracking products changed significantly at temperature higher than 698K. The generated production profile proposes the maximum amount of 258 liters gasoline would be produced from 1000kg of rice husk within the studied range. The corresponding production conditions are 5s pyrolysis of rice husk at 783K and 1.25h catalytic cracking of bio-oil at 723K. The result from this study shows that it is considerable to produce gasoline from rice husk. This result can be used as a starting reference for further study on the production process afterward with higher accuracy on kinetic modeling.

2. RECOMMENDATION

The project is conducted merely based on the mathematical model for assumed kinetic mechanism only. For the time constrain, there was no experimental work for collecting validation data for specific rice husk as feedstock. As a result, the kinetic parameters of overall biomass pyrolysis and palm oil cracking have been utilized to complete the mathematical model. Therefore, it is the best practice to cooperate with experiments based on the developed process to have more accurate validation data. Furthermore, the physical behavior of condensing process of bio-oil is recommended to be simulated at higher degree of complexity to increase the accuracy of the model.

REFERENCES

Abbas, A. and Ansumali, S. (2010). *Global Potential of Rice Husk as a Renewable Feedstock for Ethanol Biofuel Production*. Springer.

Adjaye, J.D. (1993). *Catalytic conversion of biomass-derived oil to fuels and chemicals.* University of Saskatchewan. Saskatoon, Saskatchewan. S7N 0W0.

Ancheyta, J. and Sotelo, R (2002). Kinetic Modeling of Vacuum Gas Oil Catalytic Cracking. Journal of the Mexican Chemical Society, pp. 38-42.

Akinbile, C.O. (2011). *Rice Production and Water use Efficiency for Self-Sufficiency in Malaysia: A Review*. Trends in Applied Sciences Research, 6: 1127-1140.

Bridgwater, A.V, Meier, D. and Radlein, D. (1999). An Overview of Fast Pyrolysis of Biomass. PERGAMON. Organic Geochemistry 30 (1999) 1479-1493.

Centi, G. and Santen, R.A.V (2007). Catalysis for Renewables, From Feedstock to Energy Production. WILEY-VCH.

Estimated 2012 Gasoline Price Breakdown & Margins Details (2012). The California Energy Commission. Retrieved in August, 2012 from http://energyalmanac.ca.gov/gasoline/margins/index.php.

Fuel Consumption Conversions. Retrived in December, 2012 from http://www.calculatenow.biz/conversions/consumption.php

Guo, X. et.al. (2011). *Properties of Bio-oil from Fast Pyrolysis of Rice Husk*. Chinese Journal of Chemical Engineering, 19(1) 116 – 121.

Hew, K.L et.al (2010). Catalytic Cracking of Bio-oil to Organic Liquid Product (OLP). Bioresource Technology 101 (2010) 8855-8858.

Inayat A. et.al. (2011).*Process Modeling for Parametric Study on Oil Palm Empty Fruit Bunch Steam Gasification for Hydrogen Production.* Fuel Processing Technology 93 (2012) 26–34.

Koufopanos, C.A. (1991). *Modeling of the Pyrolysis of Biomass Particles. Studies on Kinetics, Thermal and Heat Transfer Effects*. The Canadian Journal of Chemical Engineering, 69: 907-915.

Marneni, N. (2012). MATLAB Laboratory Manual. Department of Electrical and Electronics. Universiti Teknologi PETRONAS, Malaysia.

Mortensen, P.M. et.al. (2011). *A Review of Catalytic Upgrading of Bio-Oil to Engine Fuels*. Applied Catalysis A: General 407 (2011) 1– 19.

Oil Production and Consumption Running Dry. The Economist online, June 9th 2011. Retrieved in June, 2012 from http://www.economist.com/node/21519035

Prakash N. and Karunanithi T. (2008). *Kinetic Modeling in Biomass Pyrolysis – A Review*. Journal of Applied Sciences Research, 4(12): 1627-1636, 2008. INSInet Publication.

Production Quantities by Country (tonnes) (2010). FAOSTAT. Retrieved in June, 2012 from http://faostat3.fao.org/home/index.html#VISUALIZE_BY_DOMAIN

Renewable Energy: What are My Options? GreenENERGYCHOICE, 2012. Retrieved in November, 2012 from http://www.greenenergychoice.com/green-guide/renewable-energy-types.html

Sadaka, S. and Boateng, A.A. (2012). *Pyrolysis and Bio-Oil*. University of Arkansas, Division of Agriculture.

Sharma, R.K and Bakhshi, N.N (1992). *Catalytic Upgrading of Pyrolysis Oil*. ACS Publications. *Energy & Fuels*, 7, 306-314.

Srivastava, V.K., Sushil and Jalan, R.K. (1996). *Prediction of Concentration in the Pyrolysis of Biomass Materials-II*. Energy Conversion and Management 37(4): 473-483.

Tsai, W.T. (2005). *Fast Pyrolysis of Rice Husk: Product Yields and Compositions*. Bioresource Technology 98 (2007) 22–28.

Twaiq, F., Mohamed, A.R. and Bhatia S. (2003). *Catalytic Cracking of Palm Oil into Liquid Fuels: Kinetic Study*. The Seventh Asia-Pacific International Symposium on Combustion and Energy Utilization. Hong Kong SAR.

What is BIOMASS?. BIOMASS Energy Centre, 2012. Retrieved in June, 2012 from http://www.biomassenergycentre.org.uk/portal/page?_pageid=76,15049&_dad=portal

Zheng, J. (2006). *Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system.* J. Anal. Appl. Pyrolysis 80 (2007) 30–35.

Zhu, X. (2008). *Biomass Fast Pyrolysis for Bio-oil*. 5th Biomass-Asia Workshop.

APPENDIX

A1 - Pyrolysis kinetic coding: function file

```matlab
% Pyrolysis kinetic
% Apply Koufopanos et.al. (1989) mechanism

function dC = kinetic_pyrolysis (t,C)

global k1 k2 k3;
dC = zeros(size(C));

% dC(1), C(1) = Biomass
dC(1) = -(k1+k2)*C(1).^0;

% dC(2), C(2) = Gas 1
dC(2) = k1*C(1).^0-k3*C(2).^1.5*C(3).^1.5;

% dC(3), C(3) = Char 1
dC(3) = k2*C(1).^0-k3*C(2).^1.5*C(3).^1.5;

% dC(4), C(4) = Gas 2
dC(4) = k3*C(2).^1.5*C(3).^1.5;

% dC(5), C(5) = Char 2
dC(5) = k3*C(2).^1.5*C(3).^1.5;
```

A2 – Catalytic cracking coding: function file

```matlab
% Fluid Catalytic Cracking kinetic
% Adopt Twaiq et.al. (2004) mechanism

function dC = kinetic_cracking(t,C)
 global k
dC = zeros(size(C));
k1 = k(1); k2=k(2); k3=k(3); k4=k(4); k5=k(5); k6=k(6); k7=k(7);
k8=k(8); k9=k(9); k10=k(10); k11=k(11);

% dC(1), C(1) = Bio-oil
dC(1) = -(k1+k2+k3+k4+k5)*C(1);

% dC(2), C(2) = Diesel
dC(2) = k1*C(1)-(k6+k7+k8+k9)*C(2);

% dC(3), C(3) = Kerosene
dC(3) = k2*C(1)+k6*C(2);

% dC(4), C(4) = Gasoline
dC(4) = k3*C(1)+k7*C(2)-k10*C(4);

% dC(5), C(5) = Gas
dC(5) = k4*C(1)+k8*C(2)-k11*C(5);
```

```
% dC(6), C(6) = Coke
dC(6) = k5*C(1)+k9*C(2)+k10*C(4)+k11*C(5);
```

A3 - Flowsheet mass balance calculation coding: script file

```
% Script file to study the mass balance at diffirent operating
conditions


  %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% clearing memory and closing all figures
clear all;
close all;


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% PYROLYSIS MASS BALANCE
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


global Rc k1 k2 k3;

mass_RH_input = 1000;
% Operating temperature, K
T = 783;
% define constants
Rc = 8.314;
D1 = 17254;           % from Prakash & Karunanithi (2008)
D2 = 10224;
L1 = -9061227;
L2 = -6123081;
A1 = 9.973*10^(-5);
A2 = 1.068*10^(-3);
A3 = 5.7*10^5;
E3 = 81;
k1 = A1*exp((D1/T)+(L1/T^2));
k2 = A2*exp((D2/T)+(L2/T^2));
k3 = A3*exp(-E3/(Rc*T));
% Initial concentration and residence time
C0 = [1,0,0,0,0];
tspan = 0:1:5;
% ODE solver for concentration
[t,C]=ode45('kinetic_pyrolysis',tspan,C0);

mass_pyro_prod.gas = mass_RH_input*(C(6,2)+C(6,4));
mass_pyro_prod.solid = mass_RH_input - mass_pyro_prod.gas;


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% CYCLONE
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


eff = 0.98;
mass_cyclone.solid = mass_pyro_prod.solid * eff;
mass_cyclone.gas = mass_pyro_prod.gas + mass_pyro_prod.solid * (1-eff);


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% CONDENSER
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


% T = 783K;
gas_liquid_ratio = 0.49;
mass_condense_oil = mass_pyro_prod.gas/(1+gas_liquid_ratio);
disp(mass_condense_oil)
```

```matlab
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% CATALYTIC CRACKING MASS BALANCE
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% operating temperature, K
T = 723;
global k
k = [1.522 0.625 0.9388 0.25 0.115 0.1328 1.522 0.9105 0.36 0.2 0.0606];

% % operating temperature, K
% T = 698;
% global k
% k = [0.3 0.1 0.1 0.05 0.069 0.079 0.6 0.546 0.08 0.01 0.084];

% % operating temperature, K
% T = 673;
% global k
% k = [0.2 0.07 0.1 0.0072 0.0229 0.026 0.32 0.1 0.04 0.0045 0.025];

% Initial concentration and residence time
C0 = [1,0,0,0,0,0];
tspan= 0:0.25:1.25;

% ODE solver for concentration
[t,C]=ode45('kinetic_cracking',tspan,C0);

mass_gasoline = mass_condense_oil * C(6,4);
yield_gasoline = mass_gasoline/mass_RH_input*100;

disp('Amount of gasoline produced: ')
disp(mass_gasoline)
disp('Yield of gasoline produced: ')
disp(yield_gasoline)
```