Process Modeling of Bio-gasoline Production from Rice Husks

by

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

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
UniversitiTeknologi PETRONAS
in partial fulfilment of requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____

(Dr Murni Melati binti 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.

NOR HAZWANI BINTI AMIR HAMZAH

ABSTRACT

Rice husks are an abundant waste from agricultural activities which have great potential as an alternative for fossil fuel. Rice husks converted to bio-gasoline by two main thermo-chemical processes: pyrolysis and upgrading process. In this project, fast pyrolysis and catalytic cracking process are chosenandrepresents through modeling. The results obtained from the modeling agrees with the theoretical value proven that the computational approach is an option instead of experimental works. From process modeling of bio-gasoline production, the effect of the temperature towards product yields is investigated. The highest yield of bio-oil and bio-gasoline achieved at temperature 773K and 823K respectively. Lowest cost of bio-gasoline production is obtained at range of temperature for fast pyrolysis and catalytic cracking process. In conclusion, products yield and total production cost of bio-gasoline depends on temperature of the process.

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NOMENCLATURE

A_i	frequency factor of reaction i, s^{-1}
C_B	concentration of biomass, kg/m^3
C_{BO}	concentration of bio-oil, kg/m^3
C_D	concentration of diesel, kg/m^3
C_{CH}	concentration of char, kg/m^3
C_{CK}	concentration of coke, kg/m^3
C_G	concentration of gas from catalytic cracking, kg/m^3
C_{GL}	concentration of gasoline, kg/m^3
C_K	concentration of kerosene, kg/m^3
C_{PG}	concentration of pyrolysis gas, kg/m^3
D_i	constants defined by expression of $k_{i,}$ K
E_i	activation energy defined by expression of $k_{i,}$ J/mol
F	biomass feed rate, tonne/year
H	capital and capital related charge
k_i	rate constant of reaction i, s^{-1}
L_i	constants defined by expression of k_i, K^2
R_c	universal gas constant, J/mol
T	temperature, K
t	time, s
Y	fractional bio-oil yield
$\emptyset$	catalyst activity

Subscripts

P	pyrolysis process
C	catalytic cracking process
B	biomass

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDIES

1.1.1 Global Energy Demand

Energy is an essential element to the world. There are many types of energy such as kinetic energy, mechanical energy, solar energy or even the energy produced by our body to do our routine life.

In 21st century, the global demand of energy is very high due to industrial revolution, advent and development of transportation industries. International Energy Analysis (IEA) predicts that the global demand of the energy will increase by 1.8% per year and will rise up to 55% by 2030.

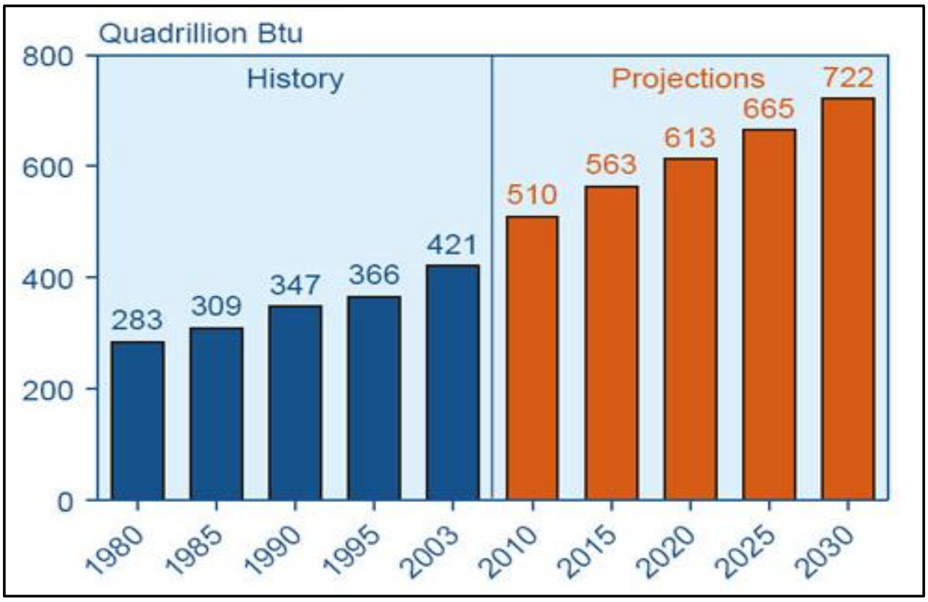


Figure 1: World Marketed Energy Consumption 1980-2030 (EIA, 2003)

There are three main sources of energy which are non-renewable energy, renewable energy and nuclear energy.

i. Non-renewable energy - fossil fuel, coal, crude oil, natural gas
ii. Renewable energy – solar, wind, hydro, biomass, geothermal
iii. Nuclear energy – fusion and fission

1.1.2 Fossil Fuel Energy Crisis

Fossil fuel had been widely used as a main and reliable source of energy since Industrial Revolution in 20th century until now since it can produce more energy than other sources of energy. Currently, 85% of the global sources of energy are fossil fuel, coal, crude oil and natural gas.

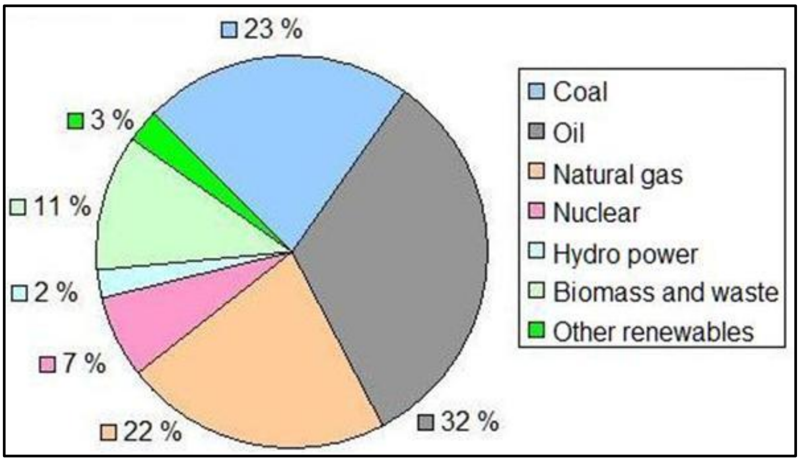


Figure 2: Global Energy Demand (Stangeland, 2007)

Although, fossil fuel had a good market and economically stable, but fossil fuel is non-renewable energy which will not last forever. The burning of fossil fuel will give a bad impact toward environment. Sulphur, carbon and nitrogen will be release from fossil fuel burning and will harm people and environment and caused air pollution.

Acid rain will happen when sulphur contacted with water vapour and high carbon dioxide released will caused global warming. Therefore, biomass is found to be the potential alternatives for fossil fuels.

1.1.3 Biomass as Alternatives Source

Biomass is energy produced from organic substances such as plants and animal wastes. For plant, the basic need of biomass is sunlight itself. Chlorophyll in plant will convert the energy from the sun ray into stored energy in the plant during photosynthesis process.

$$CO_2 + H_2O \xrightarrow[\text{chlorophyll}]{\text{light}} (CH_2O)_n + O_2$$

In Malaysia, one of the agricultures activities is paddy plantation. Malaysia produces about 2.4 million tonnes of paddy per year. The production is increase by 28,000 tonnes annually. (Teh, C., 2010).

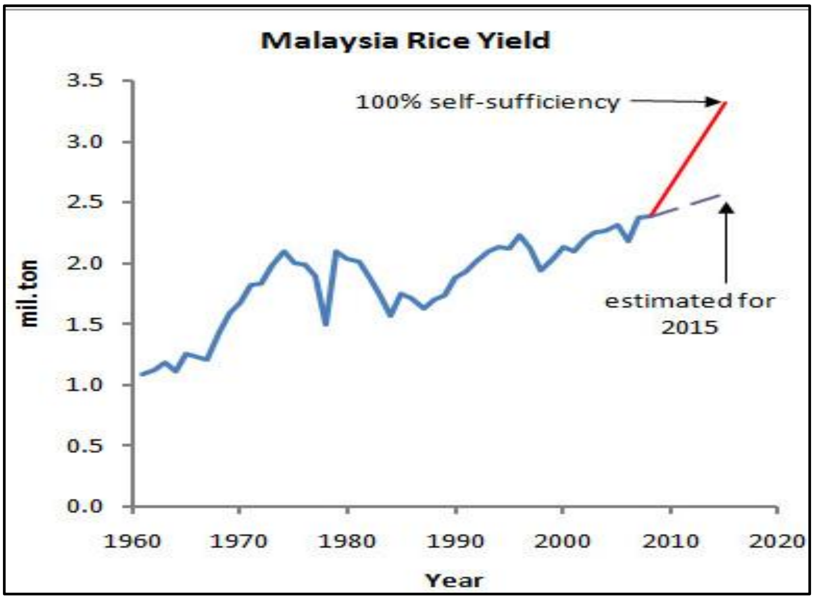


Figure 3: Malaysia Rice Yield (Teh, 2010)

Rice husk is the outer layer of the paddy grains which act as a coating of the seed and protect it during growing season. According to Malaysia Ministry of Agriculture, there are more than 408, 000 tonne of rice husk produced annually. (Daffalla, S.B., 2010).

Rice husks are wastes from rice milling process. Usually, it used as component of animal beddings or just left to rot slowly or burnt. (Taib,M.R, 2007). Therefore, rice husks can be used as raw materials to generate energy.

Table 1: Main Characteristic of Rice Husk (Tsai, 2007)

Proximate Analysis	
Combustible Matter	6.37%
Ash	11.70%
Moisture	6.37%
Elemental Analysis	
Carbon	45.28%
Hydrogen	5.51%
Nitrogen	0.67%
Sulphur	0.29%
Chlorine	0.19%
Heating Value Analysis	
Calorific Value	4012 kcal/kg

1.1.4 Conversion of Rice Husks into Bio-oil

Rice husks are converted to bio-oil through pyrolysis process. There are several type of pyrolysis process such as fast pyrolysis, intermediate pyrolysis, slow pyrolysis and gasification. Each process gave difference percentage of product. Fast pyrolysis produced more bio-oil compared to other process. Figure 4 shows the product distribution of each type of pyrolysis. Fast pyrolysis can produce highest bio-oil yield compared to other type of pyrolysis.

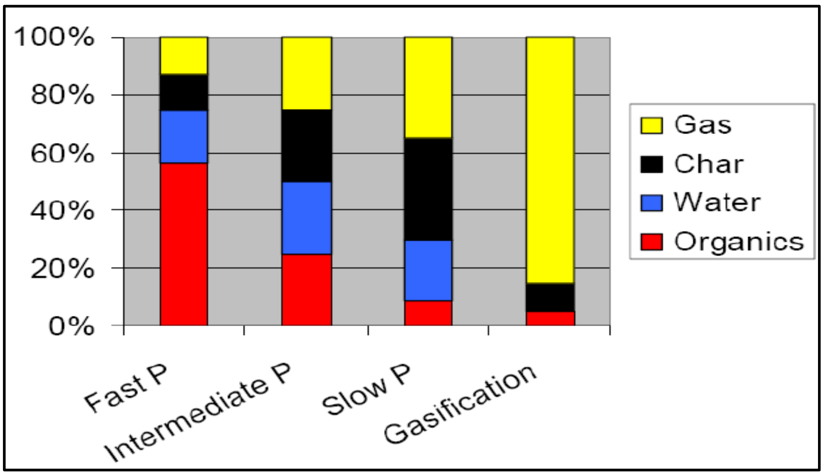


Figure 4: Product Distribution of Pyrolysis Process (Broust, 2009)

The composition of bio-oil from rice husks are shown in Table 2.

Table 2 : Composition of Bio-oil (Isa, 2010)

Component	**Percentage, wt. %**
C	50.6
H	40.8
O	7.6
N	0.4
S	0.3
Acetic acid	14.5
Phenol	3.3
Toluene	5.3
Benzofuran,2,3-dyhydro-	6.6
Phenol,2-methoxy	2.2
1,2-Benzencarboxylic acid	0.8

1.1.5 Upgrading of Bio-oil into Bio-gasoline

Bio-oils from biomass still have drawbacks compared to diesel and does not suitable to be used as transportation fuel. Upgrading of bio-oil is important to improve quality and usage of bio-oil from rice husks. Table 3 shows the comparison between bio-oil and fuel oil.

Table 3: Comparison between Bio-Oil and Fuel Oil (Edward, 2008)

	Bio-Oil	**Fuel Oil**
Water (wt %)	15-30	0.1
Solid (wt%)	0.1-0.2	0.2-1.0
Oxygen (wt%)	35-60	0.6-1.0
Specific Gravity	1.2	0.94
Heating Value (MJ/kg)	13-19	40
pH	2.5 (acidic)	Neutral
Density (kg/l)	1.2	0.86
Viscosity (cP)	40-100	180

In upgrading process, there are several methods can be used to produce bio-gasoline such as catalytic cracking, steam reforming and hydrogenation. Catalytic cracking is a process to break the large hydrocarbon into smaller hydrocarbon to produce lighter and useful hydrocarbon. There are several type of catalyst can be used but zeolite produce more product rather than other catalyst. The product of catalytic cracking is organic liquid product (OLP), gas, coke and water with main product in OLP is bio-gasoline.

The summary of bio-gasoline production from rice husks is shown in Figure 5.

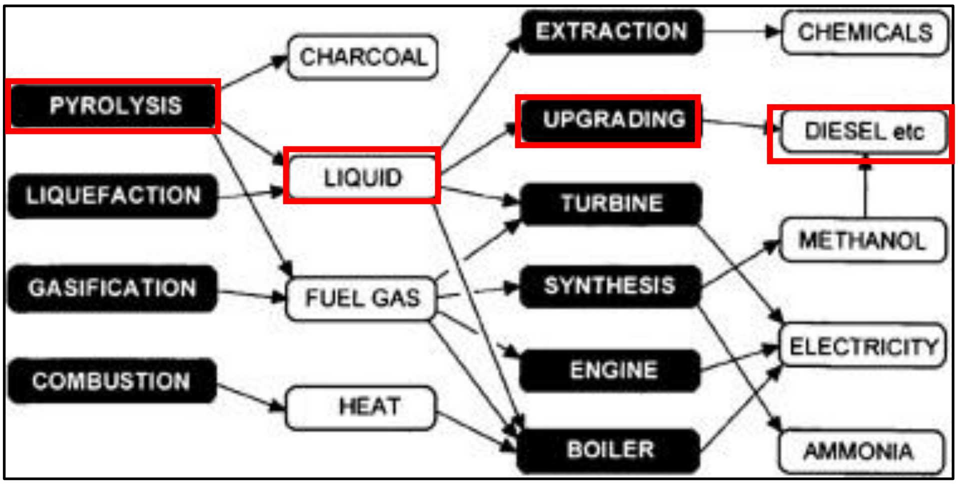


Figure 5: Thermo-chemical Process (Zhang, 2010)

1.2 PROBLEM STATEMENT

Although bio-oil is the environmental friendly alternatives, but bio-oil have some disadvantages as a direct fuel compared to oil from fossil fuel. Bio-oil has low stability, low heating value, low energy contents, high oxygenates content, high viscosity and high acidity compared to fossil fuel. Upgrading process via catalytic cracking is a method to improve the quality of bio-oil. To catalytically crack the bio-oil,large range of parameter should be considered in term of pressure, temperature and other properties. The experimental method may consume time, energy and cost. Therefore, computational method is one of the options we have to investigate the effect of the parameter to production yields.

1.3 OBJECTIVES

The objectives of the project are as follows:

- To develop a processmodelfor the pyrolysis of rice husks into bio-oil and cracking of bio-oil into bio-gasoline.
- To investigate effect of temperature on fast pyrolysis and catalytic cracking process via computational approach.
- To estimate total production cost for continuous bio-gasoline production from rice husks.

1.4 SCOPE OF STUDY

Scopes of study in the project are as follows:

- Development of process models for bio-oil and bio-gasoline production.
- Perform effect of operating parameter to bio-gasoline production using computational approach.
- Estimation of total production cost to ensure the feasibility of the production.

The main software use in this project is MATLAB.

CHAPTER 2
LITERATURE REVIEW

2.1 FAST PYROLYSIS PROCESS

2.1.1 Introduction

Fast pyrolysis is a thermo-chemical decomposition process which occurs in absence of oxygen. Fast pyrolysis differs from the other process because it dealing with high heating rate and short vapour residence times. (Brownsort, 2009)

In pyrolysis process, rice husks will undergo pretreatment process. In pretreatment process, the rice husks will be dried to eliminate water content which will effect the process. The allowable moisture of feedstock is 10%. (Bridgwater, 2000)

The product of the reaction is vapor, gas and char. Char will then separated from vapor and gas using cyclone. The condenser will condensed the vapor and gas and form bio-oil.

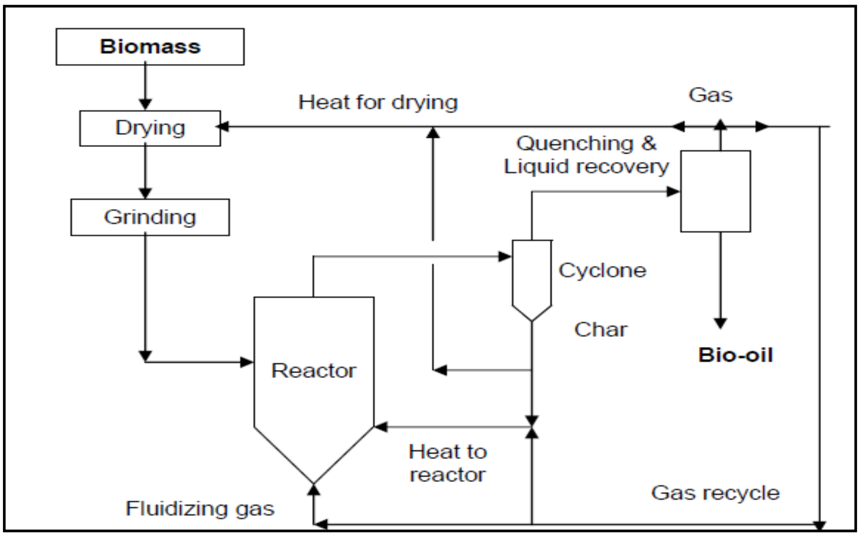


Figure 6: Schematic Diagram of Fast Pyrolysis Process (Bridgwater, 2000)

According to Faisal,A. *et al*(2011) the operating condition of pyrolysis process are at temperature of 500°C and particle size of 2mm While, according to Natarajan, E., (2009) found that the highest yield achieve with temperature of 500°C, particle size of 1.18mm-1.80mm, heating rate of 60°C/min. The reaction time of fast pyrolysis is less than 2 seconds.

2.1.2 Pyrolysis Kinetic Models

There are several model have been developed on pyrolysis process such as one step global models, competing models, parallel reaction models and models with secondary tar cracking. Each of the model come out with own assumptions.

One Step Global Models

One Step Global Model considered pyrolysis as a single step first order reaction. In this model, organic fuels decomposed into volatiles and coke with a fixed char yield. Kung (1972), Kansa *et al* (1977), Kanury (1972) and Lee *et al* (1976) had used this model. However, this model does not represent the real situation.

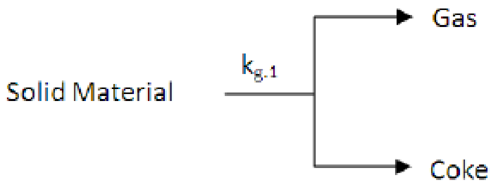


Figure 7: One Step Global Model Kinetic Scheme

Competing Reaction Models

Thurner, *et al* (1981) had proposed the competing reaction models, the most classical model which comprise of secondary reactions lumped with primary reaction. Since the model is empirical, it kept as simple as possible. The model restricted to determine the kinetic data of the primary reactions. Shen *et al* (2007) used this model in modeling of pyrolysis of wet wood under external heat flux.

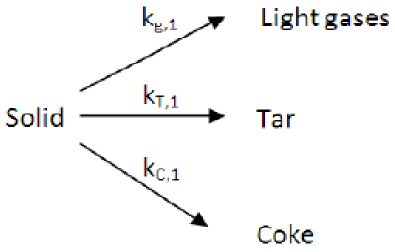


Figure 8: Competing Reaction Model Kinetic Scheme

Parallel Reaction Models

Alved *et al* (1989) came out with parallel reaction model which had identified six independent reactions as follows where S_{vi} is the volatile part of component i.

$$S_{v1} \xrightarrow{1} G \uparrow$$

$$S_{v2} \xrightarrow{2} G \uparrow$$

$$S_{v3} \xrightarrow{3} G \uparrow$$

$$S_{v4} \xrightarrow{4} G \uparrow$$

$$S_{v5} \xrightarrow{5t} G \uparrow$$

$$S_{v6} \xrightarrow{6} G \uparrow$$

The model had been applied by Gronli (1996), Larfeldt *et al* (2000) and Svenson *et al* (2004). The model comprises of four constituents which the decomposition of each constituent expressed in first order kinetic or by two exponential functions. This scheme has a fixed char yield but does not feature secondary reactions.

$$\left.\begin{array}{l} Hemicellulose(1)\\ Hemicellulose(2)\\ Cellulose\\ Lignin \end{array}\right\} \rightarrow \beta(1-\lambda)gases+(1-\beta)(1-\lambda)tar+\lambda Char$$

Figure 9: Parallel Reaction Model Kinetic Scheme

Models with Secondary Tar Cracking

If tar cracking and repolymerization was added into the competing reaction model which proposed by Thurner *et al* (1981), then tar will decomposed into lighter gas or polymerized into coke. These call as secondary stages of biomass pyrolysis process. Janse *et al* (2000) and Mousque's *et al* (2001) used this reaction scheme for wood pyrolysis.

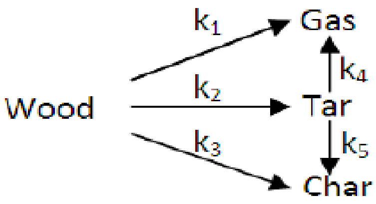


Figure 10: Primary and Secondary Stage of Pyrolysis Process

Broido *et al* (1975) used multistep mechanism at low temperature for cellulose decomposition. This reaction later simplify by Bradbury *et al* (1979) known as 'Broido-Shafizadeh Model'. This model used two competing reaction model pathways as follows:

(a) intermolecular dehydration which predominating at low temperatures, leading to char and gas

(b) depolymerization reaction which predominating at high temperature leading to tar and flaming combustion

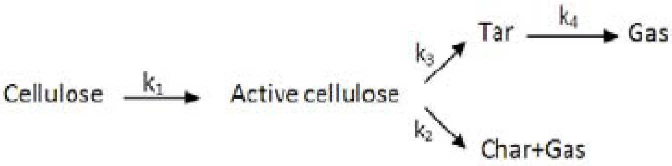


Figure 11: Broido-Shafizadeh Kinetic Scheme

Koufopanos *et al* (1991) proposed the pyrolysis model which biomass will decomposed to volatiles, gas and char. The volatiles and gas will further react with char and produces different type of volatiles, gas and char. This model can predict the final char yield in different temperatures.

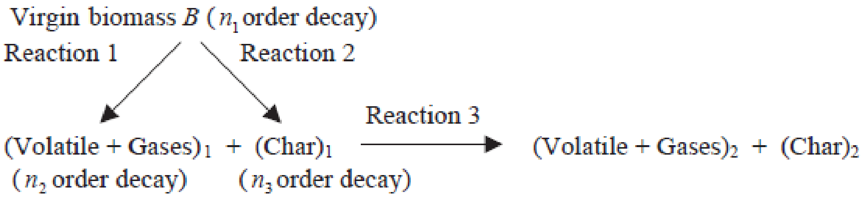


Figure 12: Koufopanos et al Kinetic Scheme

Partial reaction may happen in reality and these eliminate the simplicity of Broido-Shafizadeh model. Using experimental condition, Varhegyi*et al* (1994) proved the validity of following kinetic scheme.

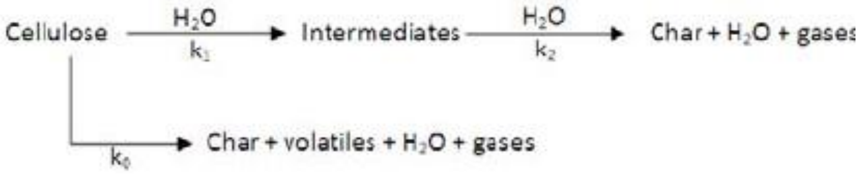


Figure 13: Varhegyi et al Kinetic Scheme

Table 4: Kinetic models and parameter collected from literature (Prakash, 2008)

Author & Scheme of Reaction	Kinetic Model	Kinetic Parameters	
		Activation energy E or Ei(kJ/mol)	Pre-exponential factor A or Ai (s-1)
Kung[10] - One step global mechanism	$\frac{\partial\rho}{\partial t} = -a_p \frac{(\rho-\rho_f)e^{-E_p/RT(t)}}{(1-\frac{\rho_f}{\rho_w})}$	30 kcal/mole[45]	5.25 × 107[45]
Thurner *et al*[14] – Three Competing reactions model with primary reactions only	$\frac{dY_i}{dt} = -k_iY_i; \quad k_i = A_i \exp^{(-E_i/RT)}$	84 112.7 106.5	5.16 ×10^6 1.48 × 10^{10} 2.66 × 10^{10}
Alves *et al*[16] - Six independent first order reactions	$-\frac{\partial\rho_i}{\partial t} = \rho_i k_i \exp(-E_i / RT)$	83, 146, 77, 60, 139, 130	0.70 × 10^5, 0.20 × 10^{10}, 0.43 × 10^4, 0.29 × 10^2, 0.51 × 10^7, 0.32 × 10^6
Koufopanos *et al*[18] - Mechanism with secondary interactions between charcoal and volatiles, described by first order kinetics	$\frac{dC_B}{dt} = -k_1C_B^{n_1} - k_2C_B^{n_1}$ $\frac{dC_{G_1}}{dt} = k_1C_B^{n_1} - k_3C_{G_1}^{n_2}C_{C_1}^{n_3}$ $\frac{dC_{C_1}}{dt} = k_2C_B^{n_1} - k_3C_{G_1}^{n_2}C_{C_1}^{n_3}$ $\frac{dC_{G_2}}{dt} = k_3C_{G_1}^{n_2}C_{C_1}^{n_3}$ $\frac{dC_{C_2}}{dt} = k_3C_{G_1}^{n_2}C_{C_1}^{n_3}$ $k_1 = A_1 \exp[(D_1 / T)+(L_1 / T^2)]$ $k_2 = A_2 \exp[(D_2 / T)+(L_2 / T^2)]$ $k_3 = A_3 \exp[(-E_3 / R_cT)]$	Constants for E_1 and E_2 D_1=17254 K D_2=10224K L_1=-9061227K^2 L_2=-6123081K^2 and E_3=81	 A1=9.973× 10^{-5} A2=1.068 × 10^{-3} A3=5.7 × 10^5
Bonnefoy *et al*[46] - One step endothermic devolatilization kinetic model	$\frac{\partial\rho}{\partial t} = -A\rho \exp(-E / RT)$	120	5 × 10^6
Janse *et al*[36] - Lumped consecutive reaction scheme similar to Di Blasi[47]	For reactions (1)-(3) $r_i = A_i e^{(-E_i/R_gT)}(1-\varepsilon_m-\varepsilon_M)\rho_W$ For reactions (4),(5) $r_i = A_i e^{(-E_i/R_gT)} \frac{y_i P M_i}{RT}$	177.0[48] 149.0[48] 9.28 × 10^4[48] 125.0[48] 87.8[34] 87.8[34]	 1.11 × 10^{11}[48] 3.05 × 10^7[48] 8.60 × 10^4[34] 7.70 × 10^4[34]
Hagge *et al*[49], Bryden *et al*[50] - one step multi reactions kinetic model	Rate of production of wood: $\dot{\omega}_W = -(k_1+k_2+k_3)\rho_W f$ Rate of production of char: $\dot{\omega}_C = k_3\rho_W f + \varepsilon k_5\rho_T f$	88.6[14] 112.7[14]	1.44 ×10^4 [14] 4.13 ×10^6 [14]
	Rate of production of moisture: $\dot{\omega}_T = k_1\rho_W f - \varepsilon f(k_4+k_5)y_T\rho_g$ Rate of production of tar: $\dot{\omega}_V = k_6\rho_M f - k_7G_V$ Rate of production of vapor: $\dot{\omega}_g = (k_1+k_2)\rho_W f - \varepsilon f k_5\rho_T + k_6\rho_M - k_7G_V$ Rate of production of gas:	106.5[14] 107.5[26] 107.5[31] 88 [32] (k_7=125cm^{-1})[32]	7.38 ×10^5 [14] 4.28 ×10^6 [24] 1 ×10^5 [31] 5.13 ×10^{10} [32]
Peters *et al*[33] - Single step pyrolysis model	For beech wood: 123.1 $r_i = k_0 \exp\left(\frac{-E_a}{RT}\right)\prod_{k=1}^{3} c_{i,k}$	For beech wood: 1.35 × 10^9 For wood char: 149.38	For wood char: 3.01 × 10^2
Bellais *et al*[34]-Two parallel reactions of wood decomposition into volatiles and char	$w_i = k_i\, m_{wood}$ i = char or volatiles	E_1=74.13; E_2=54.919	A_1=10.356; A_2=114
Branca *et al*[41] - Proposed a three step mechanism involving m independant parallel reactions	$\frac{\partial Y_i}{\partial t} = -k_ic_i$	E_1=147 ; E_2=193; E_3=181;	A_1=2.527×1011; A_2=1.379×1014; A_3=2.202×1012
Grioui *et al*[44] - Developed a two-stage, semi-global multi-reaction kinetic model, involving three primary pseudo components and an intermediate solid	$\frac{dm_{A_1}}{dt} = -k_1m_{A_1}$ $\frac{dm_{A_2}}{dt} = -k_2m_{A_2}$ $\frac{dm_{A_3}}{dt} = -k_3m_{A_3}$ $\frac{dm_{C_2}}{dt} = \gamma_2k_2m_{A_2}$ $\frac{dm_B}{dt} = \beta k_3m_{A_3} - k_4m_B$ $\frac{dm_{C_3}}{dt} = \gamma_3k_4m_B$	105.89, 106.78, 169.56, 51.04	3.5 ×10^7, 3.72 ×10^6, 7.23 ×10^{11}, 3.4 ×10^{11}
Shen *et al*[15] - Used Thurner *et al*[14] one-step, multi reactions kinetic model	$\frac{\partial\rho_w}{\partial t} = -(k_1+k_2)\rho_w$ $\frac{\partial\rho_c}{\partial t} = k_1\rho_w$ $\frac{\partial\rho_g}{\partial t} = k_2\rho_w$ $\frac{\partial\rho_l}{\partial t} = -k_3\rho_l$ $\frac{\partial\rho_v}{\partial t} = k_3\rho_l$	106.5[14] 88.6[14] 88[21]	7.38 × 10^5 [14] 1.44 × 10^4 [14] 5.13 × 10^{10} [21]

2.2 CATALYTIC CRACKINGPROCESS

2.2.1 Introduction

In catalytic cracking process, the bio-oil from pyrolysis process will be injected into the reactor. The product from the reactor sent to fractionator column to separate the product using differences of boiling point.

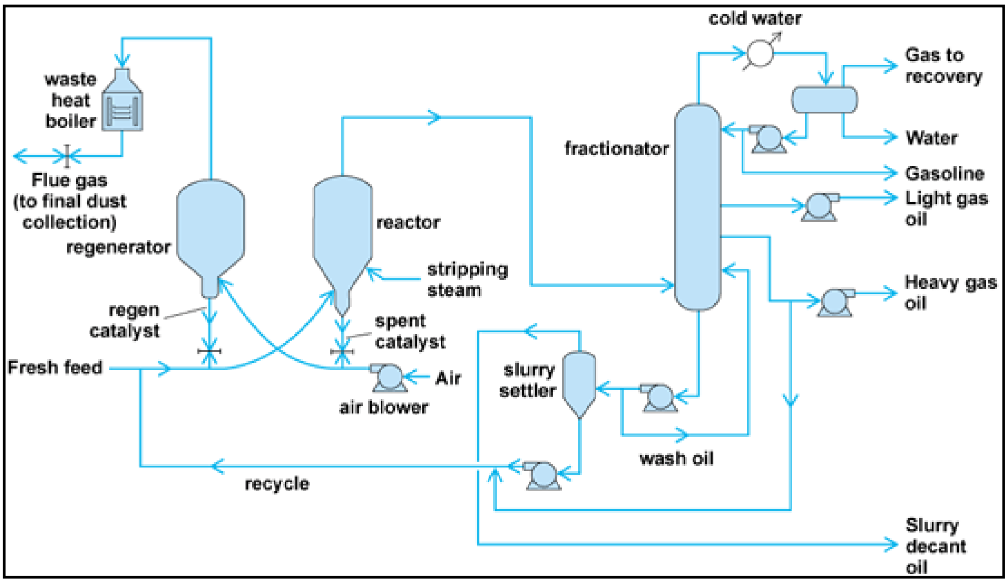


Figure 14: Schematic Diagram of Catalytic Cracking (Speight, 1999)

According to research done by Hew (2010), the operating condition of the catalytic cracking is 400°C, reaction time of 15 min and 30g of catalyst. With The yield of gasoline obtained from the condition are about 91.67%.

2.2.2 Catalytic Cracking Kinetic Models

Catalytic cracking kinetic model developed using lumping techniques since the feedstock contains large number of individual species. The lumping techniques used is 3-lumps, 4-lumps, 6-lumps and 7-lumps kinetic models.

3-lumps Model

In 3-lumps model proposed by Weekman (1968) where reactant and product lumped into three groups. The reactant, bio-oil, will cracked either to form gas and coke or to form organic liquid product (OLP). The OLP may undergo further cracking and forming gas and coke.

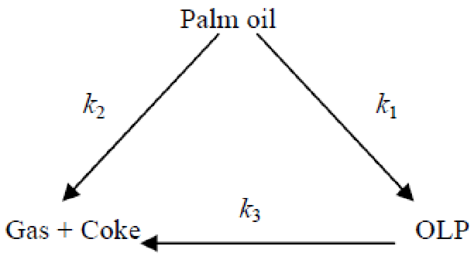


Figure 15: 3-lumps Model

4-lumps Model

In 4-lumps model, Yen *et al* (1987) and Lee *et al* (1989) had expanded the 3-lumps model by separating gas and coke into two different lumps.

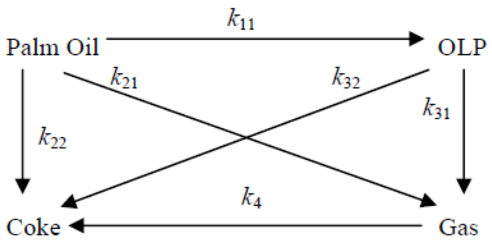


Figure 16: 4-lumps Model

6-lumps Model

6-lumps model introduce by Takatsuka (1987) by dividing the organic liquid product (OLP) into another three lumps which are diesel, kerosene and gasoline.

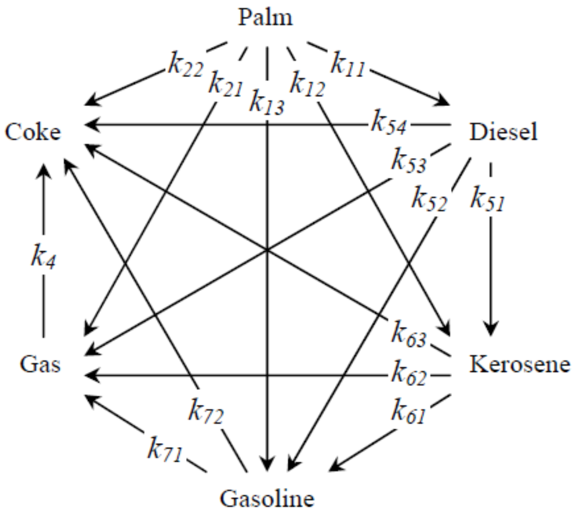


Figure 17: 6-lumps Model

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY

3.1.1 Summary of Work

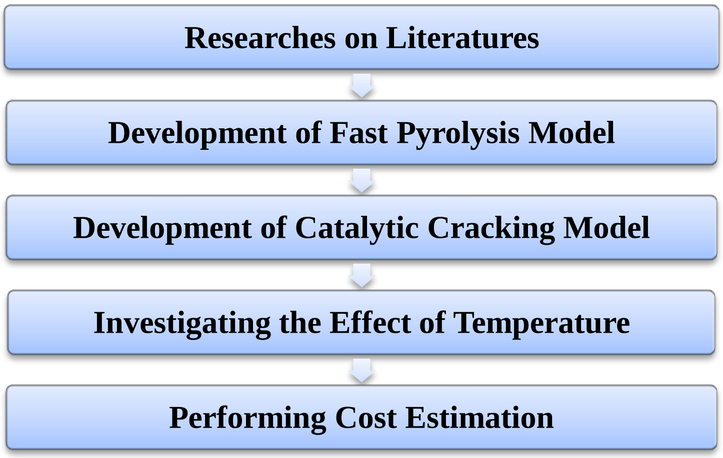
Several literatures on pyrolysis process and catalytic cracking were reviewed to get overview of the project and to understand the overall process on bio-gasoline production.

Second stage of the project is to develop the process model of pyrolysis process and catalytic cracking process. The suitable model from literatures is chosen and be implemented in the project.

The effect of temperature is investigated using the model developed before.

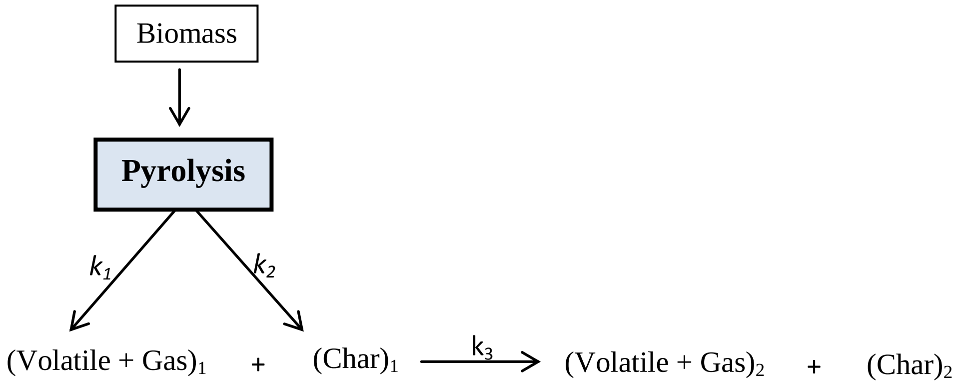
Lastly, the cost estimation for overall production is conducted to investigate the feasibility of the project.

3.1.2 Flowchart



3.2 MODEL DEVELOPMENT

3.2.1 Pyrolysis



Koufopanos et al (1991) proposed the kinetic model on pyrolysis process. The biomass (C_B) will decomposed into char (C_{CH1}) and volatile or gaseous (C_{PG1}). The reaction follows the Arrhenius law. Then, the products will react with each other and formed another char (C_{CH2}) and volatile or gas (C_{PG2}).

Model proposed by Koufaponos et al (1991) had been used Jalan (1999), Babu et al (2002) and Chaurasia et al (2007). They used the model in modeling and simulation of wood pyrolysis.

The kinetic model equations proposed by Koufopanos *et al* (1991) are presented in Equation 1 to 8.

$$\frac{dC_B}{dt} = -k_1 C_B - k_2 C_B \tag{1}$$

$$\frac{dC_{PG}}{dt} = k_1 C_B - k_3 {C_{PG}}^{1.5} {C_{CH}}^{1.5} \tag{2}$$

$$\frac{dC_{CH1}}{dt} = k_2 C_B - k_3 {C_{PG}}^{1.5} {C_{CH}}^{1.5} \tag{3}$$

$$\frac{dC_{BO}}{dt} = k_3 {C_{PG}}^{1.5} {C_{C1}}^{1.5} \tag{4}$$

$$\frac{dC_{CH2}}{dt} = k_3 {C_{PG}}^{1.5} {C_{C1}}^{1.5} \tag{5}$$

Where,

$$k_1 = A_1 \exp\left[\frac{D_1}{T} + \frac{L_1}{T^2}\right] \quad (6)$$

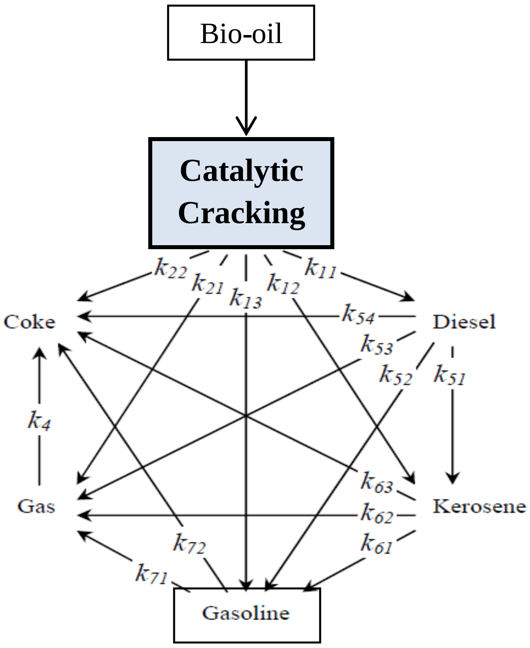
$$k_2 = A_2 \exp\left[\frac{D_2}{T} + \frac{L_2}{T^2}\right] \quad (7)$$

$$k_3 = A_3 \exp\left[\frac{-E_3}{R_c T}\right] \quad (8)$$

Table 5: Value of Parameter (Koufopanos, 1991)

Frequency factor of reaction 1 (s^{-1})	A_1	9.973×10^{-5}
Frequency factor of reaction 2 (s^{-1})	A_2	1.068×10^{-3}
Frequency factor of reaction 3 (s^{-1})	A_3	5.700×10^{5}
Constants defined by expression of k_1 (K)	D_1	17, 254.4
Constants defined by expression of k_2 (K)	D_2	10, 224.4
Constants defined by expression of k_1(K^2)	L_1	-9, 061, 227
Constants defined by expression of k_2(K^2)	L_2	-6, 123, 081
Activation energy defined by expression of k_3 (J/mol)	E_3	81, 000
Universal gas constant (J/mol)	R_c	8.314

3.2.2 Catalytic Cracking



6-lumps parameter model was chosen to be used in catalytic cracking process. This model proposed by Takatsuka (1987) by extending 3-lumps and 4-lumps model. Catalytic cracking will decompose mainly into two which are organic liquid product (OLP) and gas and coke. In 6-lumps model, gas and coke are separated into two lumps while OLP is divided into three lumps; diesel, kerosene and gasoline.

Twaiq (2004) used 6-lumps model for catalytic cracking of palm oil. The equation and reaction rates of 6-lumps model are presented in Equation 9 to 13.

$$\frac{dC_D}{dt} = \emptyset \left(k_4 C_{BO} - k_5 C_D\right) \tag{9}$$

$$\frac{dC_K}{dt} = \emptyset \left(k_6 C_{BO} + k_7 C_D - k_8 C_K\right) \tag{10}$$

$$\frac{dC_{GL}}{dt} = \emptyset \left(k_9 C_{BO} + k_{10} C_D + k_{11} C_K - k_{12} C_{GL}\right) \tag{11}$$

$$\frac{dC_G}{dt} = \emptyset \left(k_{13} C_{BO} + k_{14} C_D + k_{15} C_K + k_{16} C_{GL} - k_{17} C_{G2}\right) \tag{12}$$

$$\frac{dC_{CK}}{dt} = \emptyset \left(k_{18} C_P + k_{19} C_D + k_{20} C_K + k_{21} C_{GL} + k_{17} C_{G2}\right) \tag{13}$$

Where,

$$k_i = A_i \exp\left[\frac{-E_i}{R_c T}\right] \tag{14}$$

3.3 ASSUMPTIONS AND DEFINITIONS

In process modeling of bio-gasoline production, several assumptions are made:

1) Rice husk feed is 12 kg/s based on current rice husks production

2) The temperature range from 473 K to 923 K

3) The catalyst activity, $\emptyset$ is 1

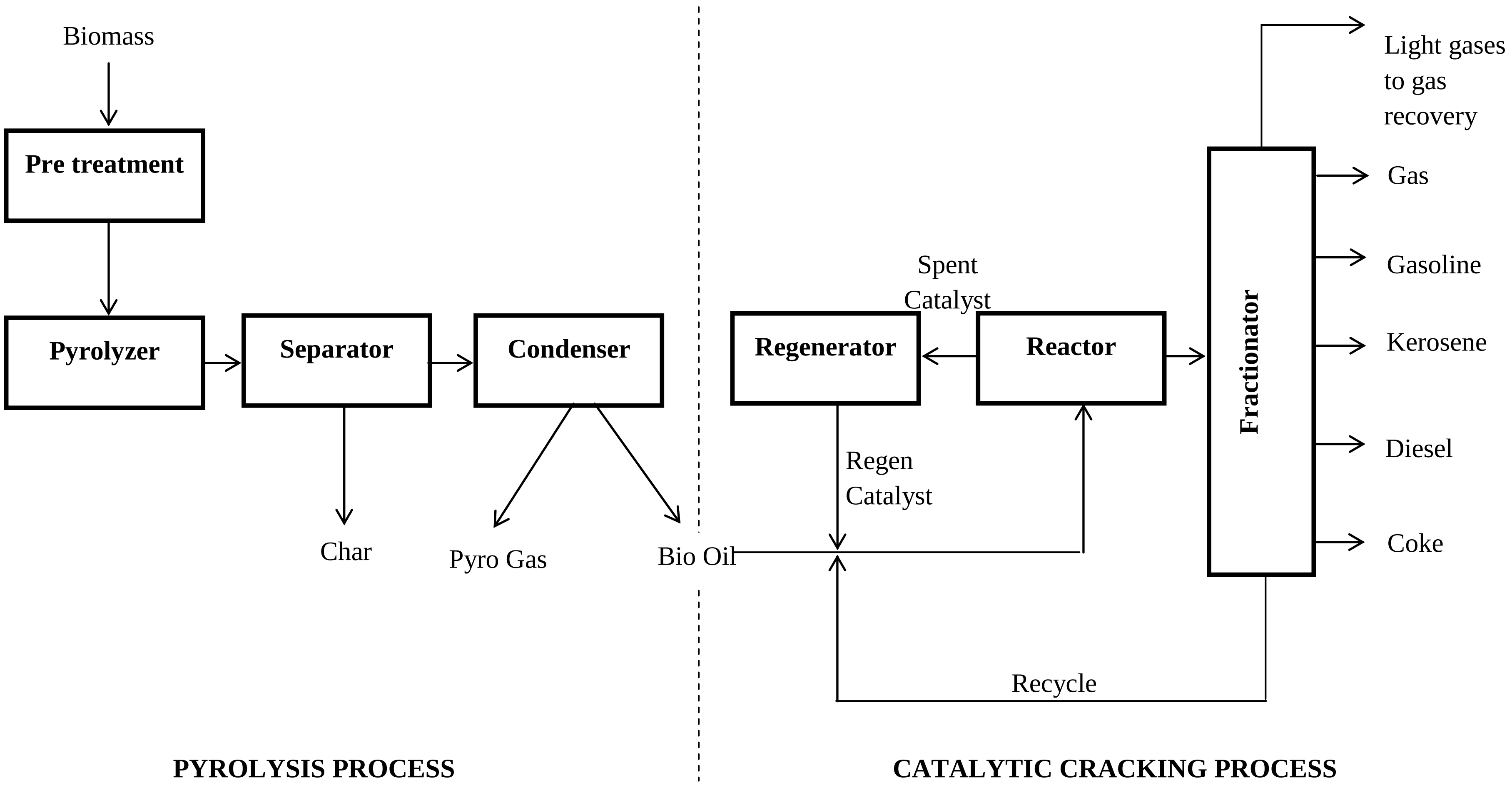
4) Model Validation based on percentage error (% error):

$$\% \text{ error} = \frac{Theoretical\ \ Value - Modeling\ \ Value}{Theoretical\ \ Value}$$

5) Production cost of pyrolysis process based on fractional yield of bio-oil, Y:

$$\text{Fractional Yield, Y} = \frac{Bio - oil\ Yield}{Biomass\ \ Feed}$$

3.4 PROCESS DEVELOPMENT



3.5 GANTT CHART

PROJECT ACTIVITIES	SEMESTER ONE														SEMESTER TWO														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Preliminary Research Work		■	■	■	■																								
Submission of Extended Proposal						■																							
Proposal Defense								■																					
Learn and Familiarize with MATLAB									■	■	■	■																	
Submission of Interim Draft Report													■																
Submission of Interim Report														■															
Develop Process Model of Bio-gasoline Production															■	■	■	■	■	■									
Effect of Operating Parameter Studies																					■	■							
Perform Cost Estimation																							■	■					
Submission of Progress Report																						■							
Pre-SEDEX																									■				
Submission of Draft Report																										■			
Submission of Dissertation (Soft Bound)																											■		
Submission of Technical Paper																											■		
Oral Presentation																												■	
Submission of Dissertation (Hard Bound)																													■

CHAPTER 4
RESULT AND DISCUSSION

4.1 MODEL VALIDATION

4.1.1 Fast Pyrolysis Model Validation

Fast pyrolysis model involves five differential equations to be solved simultaneously to find the concentration of pyrolysis product. The operating condition of pyrolysis process is 773 K. The results from the modeling are shown in Table 6.

Table 6: Product Yield of Pyrolysis Process at T = 773K

Time, t (s)	C_G (%)	C_{CH1} (%)	C_{BO} (kg/m^3)	C_{CH2} (%)
0.00	0.0000	0.0000	0.0000	0.0000
0.25	0.0628	0.0628	0.6025	0.0465
0.50	0.1161	0.1161	0.6911	0.0178
1.00	0.1315	0.1315	0.7175	0.0079
1.25	0.1367	0.1367	0.7200	0.0041
1.50	0.1387	0.1387	0.7197	0.0023
2.00	0.1396	0.1396	0.7192	0.0015

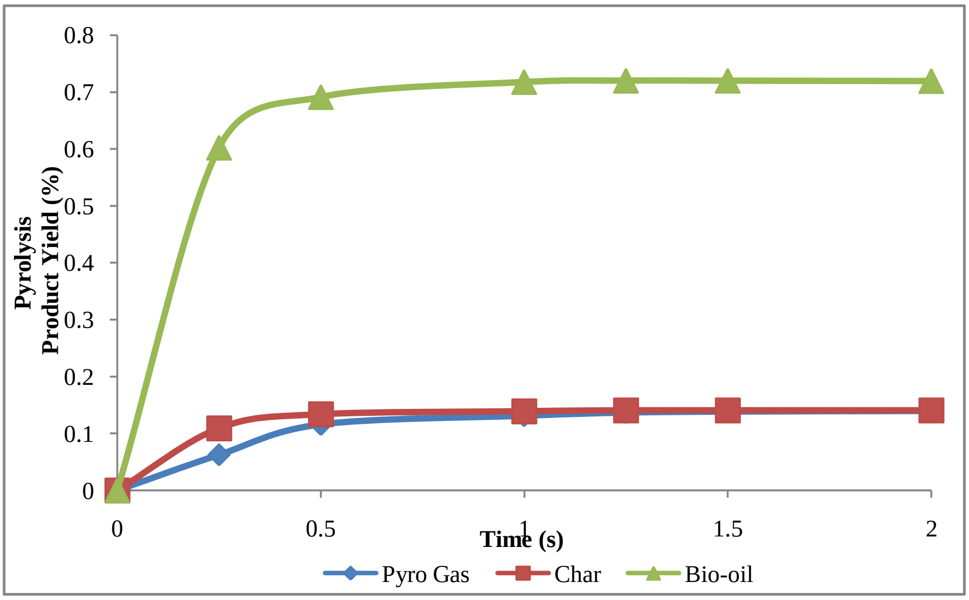


Figure 18: Effect of Reaction Time to Production Yield for Fast Pyrolysis

From Table 6 and Figure 18, the percentage yield of bio-oil, gas and char are about 72%, 14% and 14% respectively. The model is validated by comparing the product distribution from modeling with literature by calculating the percentage of error.

Table 7: Theoretical and Modeling Product Distribution of Fast Pyrolysis

Product Distribution	**Theoretical (%)** [Broust, F., 2009]	**Modeling(%)**	**% Error**
Bio-oil	75	72	4.00
Gas	13	14	7.14
Char	12	14	14.29

From Table 7, the value of product distribution for modeling and literature does not differ much with the percentage error less than 20%. Therefore, this model is valid and represents fast pyrolysis process.

4.1.2 Catalytic Cracking Process Model Validation

In model validation, the temperature and catalyst activity is set at 723 K and 1.00 respectively.

Table 8: Product Yield of Catalytic Cracking

T (s)	**C_D (kg/m^3)**	**C_K (kg/m^3)**	**C_{GL} (kg/m^3)**	**C_{G2} (kg/m^3)**	**C_{CK} (kg/m^3)**
0	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.1502	0.1914	0.3250	0.0568	0.1145
1.0	0.1688	0.2622	0.4020	0.0941	0.0436
1.5	0.1634	0.2865	0.4125	0.1209	0.0126
2.0	0.1538	0.2920	0.4066	0.1436	0.0032
2.5	0.1440	0.2933	0.3971	0.1646	0.0008
3.0	0.1347	0.2937	0.3869	0.1845	0.0002

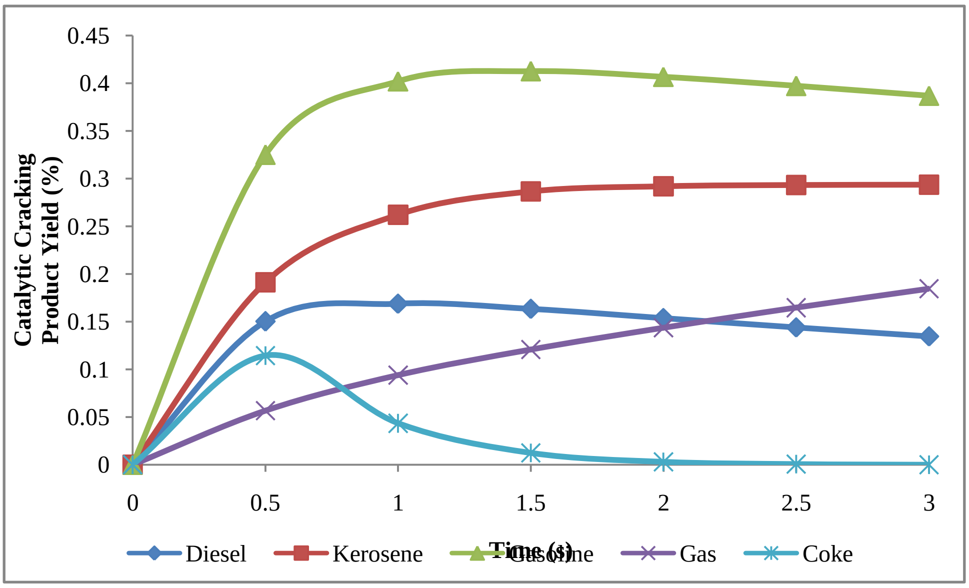


Figure 19: Effect of Reaction Time to Production Yield for Catalytic Cracking

From Table8 and Figure 19, the product distribution of gasoline, kerosene, diesel, gas and coke are 41.25%, 28.65%, 16.34%, 12.09% and 1.26% respectively.

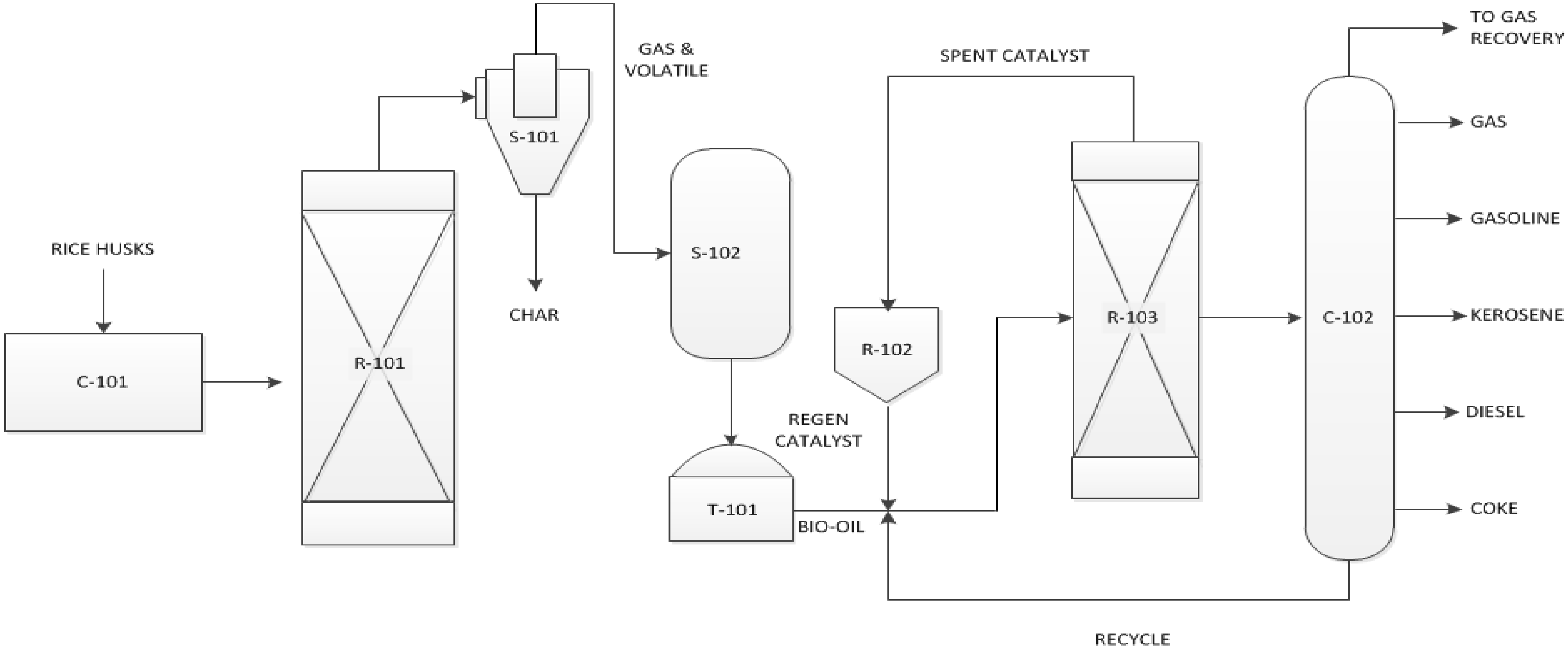
Table 9: Theoretical and Modeling Product Distribution of Catalytic Cracking

Product Distribution	**Theoretical(%)** [Twaiq, F., 2004]	**Modeling(%)**	**% Error**
Gasoline	42	41.25	1.79
Kerosene	28	28.65	2.32
Diesel	16	16.34	2.13
Gas	12.5	12.09	3.28
Coke	1.5	1.26	16.00

From Table 9, the error of gasoline production is 1.79% only and the highest error is coke production which is 16%. The model is valid since the percentage error is less than 20%. Therefore, this model can be used to represent catalytic cracking of bio-oil to produce bio-gasoline.

4.2 FLOW DIAGRAM OF BIO-GASOLINE PRODUCTION

C-101	R-101	S-101	S-102	T-101	R-102	R-103	C-102
PRE-TREATMENT	PYROLYZER	CYCLONE	CONDENSER	STORAGE TANK	CATALYST REGENERATOR	CATALYTIC CRACKING REACTOR	FRACTIONATOR



Major equipment in the bio-gasoline production are pyrolyzer, cyclone, condenser, reactor and fractionator.The equations are developed based on mass balance for equipment. The equations are shown in Equation 15-23.

Pyrolyzer:

$$2k_3C_{G1}C_{C1} = (2k_1 + 2k_2)C_B \quad (15)$$

Cyclone:

$$4k_3C_{G1}C_{C1} = (k_2 + k_1)C_B \quad (16)$$

Condenser:

$$k_3C_{G1}C_{C1} = ½\, k_3C_{G1}C_{C1} + ½\, k_3C_{G1}C_{C1} \quad (17)$$

Reactor:

$$C_{CK} + C_G + C_{GL} + C_K + C_D = C_{BO} \quad (18)$$

Fractionator:

$$dC_G/dt=k_4C_{BO} + k_5C_D – k_6C_G \quad (19)$$

$$dC_{CK}/dt= k_7C_{BO} + k_8C_D + k_9C_{GL} + k_6C_G \quad (20)$$

$$dC_D/dt = k_{10}C_{BO} - k_{11}C_D \quad (21)$$

$$dC_K/dt = k_{12}C_{BO} + k_{13}C_D \quad (22)$$

$$dC_{GL}/dt= k_{14}C_{BO} + k_{15}C_D - k_9C_{GL} \quad (23)$$

4.3 EFFECT OF TEMPERATURE TO BIO-GASOLINE PRODUCTION

Temperature is one of the factors which affect the overall bio-gasoline production. Different temperature will produce different product distribution and yields. Temperature is varies from 473K to 923K to study the effect of temperature towards bio-gasoline production.

4.3.1 Effect of Temperature to Pyrolysis Product Distribution

Table 10: Product Distribution of Pyrolysis at different T

T	Product Yield (kg/s)		
	Char	Pyro Gas	Bio-oil
473	0.000	0.000	0.000
523	0.001	0.000	0.001
573	0.006	0.005	0.010
623	0.024	0.034	0.059
673	0.068	0.133	0.201
723	0.145	0.338	0.483
773	0.252	0.642	1.370
823	0.378	0.992	1.300
873	0.500	1.300	0.894
923	0.000	1.000	0.200

From Table 10, the highest yield of bio-oil achieved at temperature 773K. At temperature lower than 673K, the yield of bio-oil is almost zero since the pyrolysis process required temperature at 673K to 873K. At temperature higher than 823K, the yield of pyro gas is more than char and bio-oil since gasification process occurred in this range of temperature.

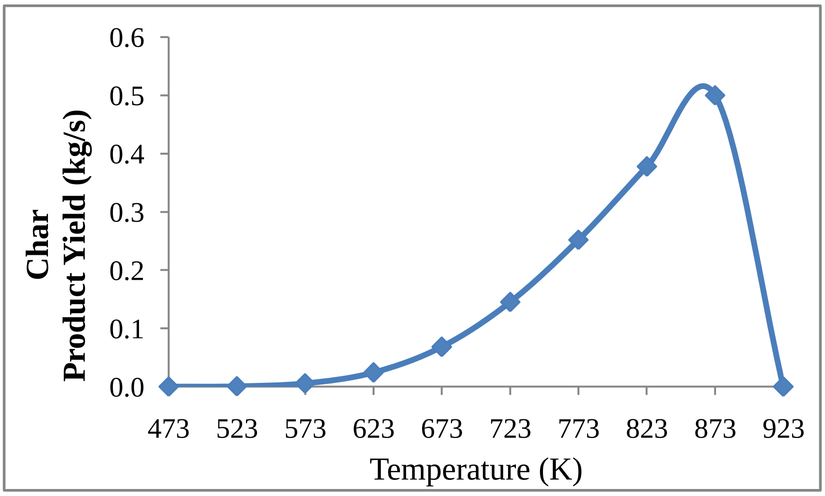


Figure 20: Effect of temperature to char product yield

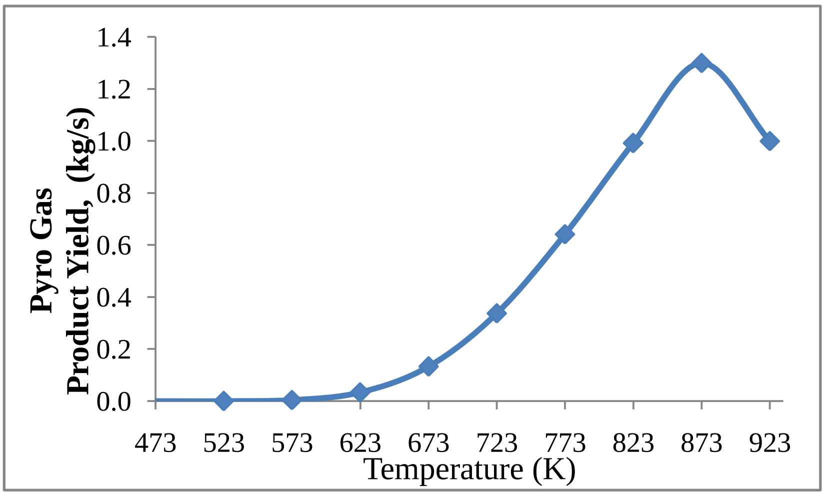


Figure 21: Effect of temperature to pyro gas product yield

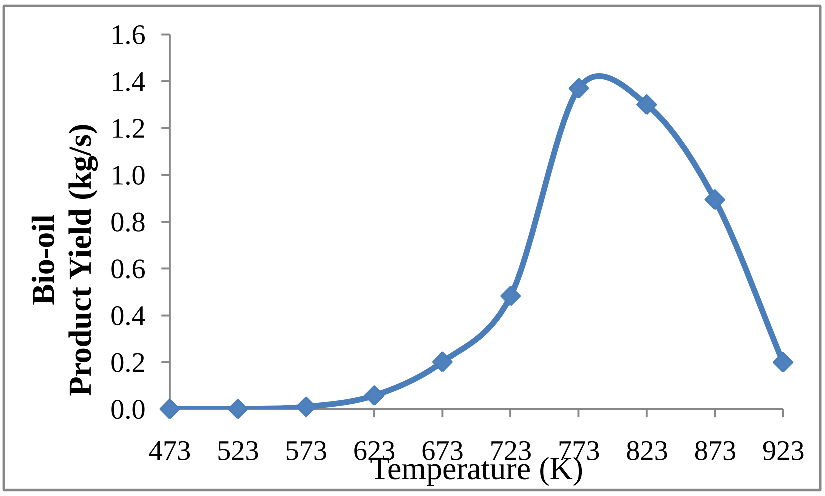


Figure 22: Effect of temperature to bio-oil product yield

4.3.2 Effect of Temperature to Catalytic Cracking Product Distribution

Table 11: Product Distribution of Catalytic Cracking at different T

T	Product Yield (kg/s)				
	Gas	Coke	Diesel	Kerosene	Gasoline
473	0.000	0.018	0.000	0.000	0.000
523	0.000	0.031	0.000	0.000	0.000
573	0.000	0.036	0.000	0.000	0.000
623	0.000	0.029	0.000	0.001	0.000
673	0.000	0.025	0.016	0.022	0.015
723	0.207	0.110	0.338	0.355	0.309
773	6.303	1.488	3.828	3.742	3.330
823	128.591	24.485	27.577	27.599	13.801
873	1812.500	358.300	141.200	151.800	-136.100
923	18293.000	4008.00	553.000	656.000	-3007.000

The bio-oil produced from pyrolysis process then became the feedstock forcatalytic cracking process. There are five main products of catalytic cracking which are diesel, kerosene, gasoline, gas and coke. The highest bio-gasoline yield achieved at temperature 823 K. At temperature lower than 673K, the yield of bio-gasoline is zero since the process only occurred at range temperature of 673K to 823 K. In Table 11, the negative value at temperature higher than 823K shows the process is no longer feasible. The process modeling of catalytic cracking is no more applicable at temperature more than 823K.

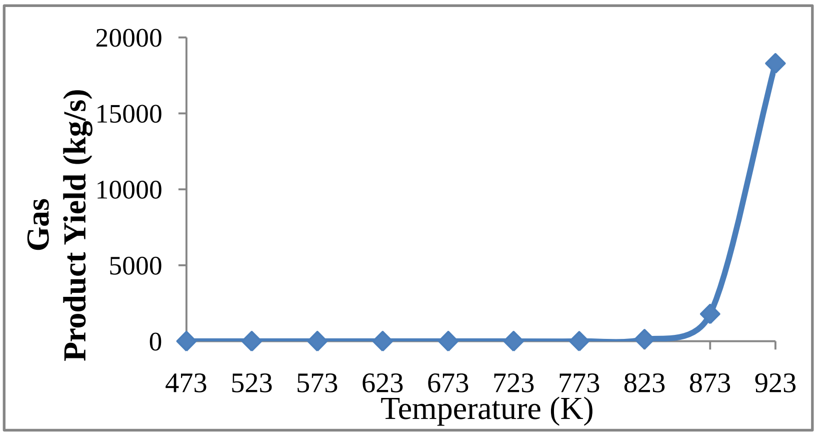


Figure 23: Effect of temperature to gas product yield

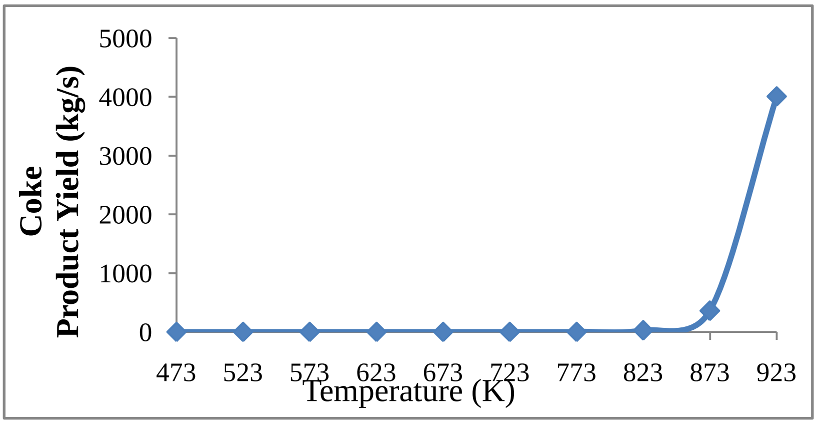


Figure 24: Effect of temperature to coke product yield

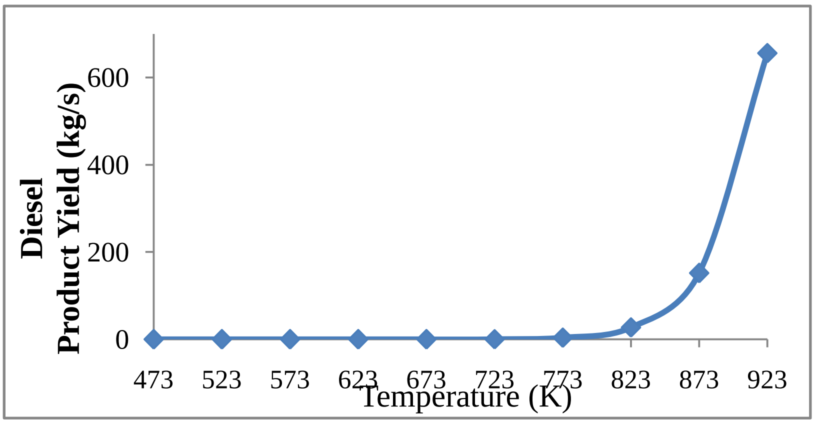


Figure 26: Effect of temperature to diesel product yield

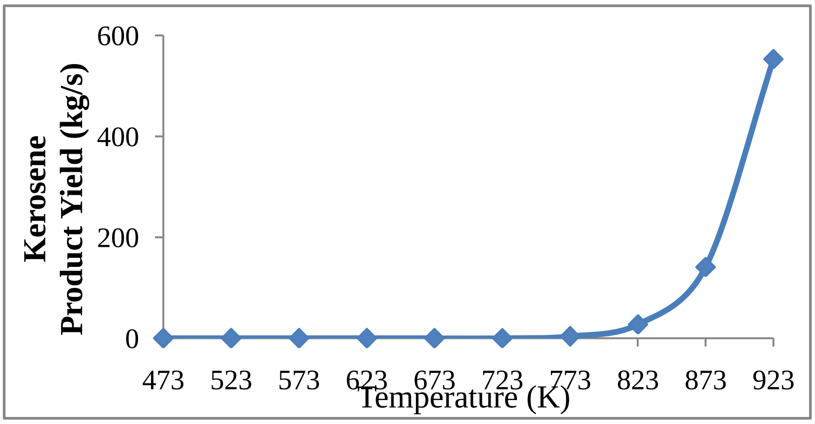


Figure 25: Effect of temperature to kerosene product yield

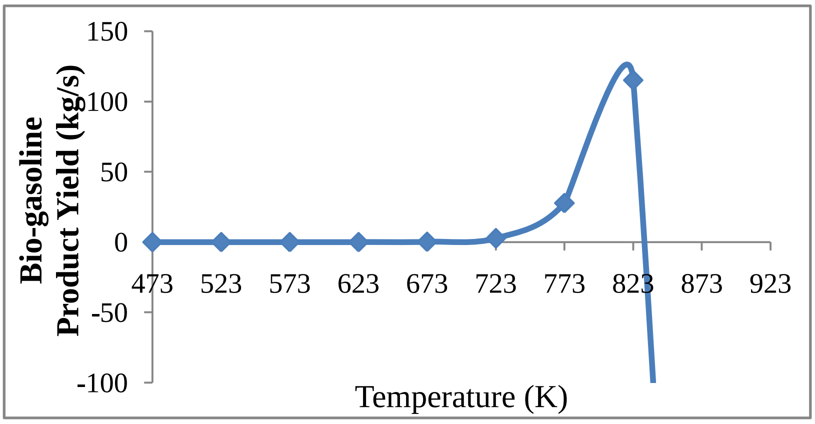


Figure 27: Effect of temperature to bio-gasoline product yield

4.4 ECONOMIC CONSIDERATION

The total bio-gasoline production cost is the total of capital cost and production cost. Total capital cost divided into two which are plant area costs and equipment costs.

According to Bridgwater (2011), the capital plant area costs given in Equation 24.

$$\text{Plant Area Cost} = 6.98 \text{ x } (\text{biomass feed rate (tonne/hr)})^{0.67} \tag{24}$$

From RTI International (2012), the equipment cost depends on the plant area cost.

$$(\text{Equipment Cost})_P = 0.176\ (\text{Plant Area Cost}) \tag{25}$$

$$(\text{Equipment Cost})_C = 0.091\ (\text{Plant Area Cost}) \tag{26}$$

The production cost of pyrolysis process suggested by Bridgwater (2012) is given in Equation 27.

$$(\text{Production Cost})_P = 1.1 \times [Cost_B + (H \times 16935 \times F^{-0.33})Y^{-1}] \tag{27}$$

Where,

$Cost_B$ =Biomass cost, euro per tonne

H =Capital and capital related charge = 0.18

F = Biomass feed rate, tonne/year

Y = Fractional bio-oil yield

Production costsfor catalytic cracking proposed by Gary J.H. (2007) in his journal are as follows:

$$(\text{Production Cost})_C = (24.67 \times C_{GL}{}^{0.461}) + (32.98 \times C_{GL}{}^{0.510}) \tag{28}$$

From Equation 27 and 28, the production cost of pyrolysis process depends on fractional bio-oil yield while catalytic cracking process depends on the capacity of bio-gasoline which depends on temperature of the process.

Biomass Feed Rate, F = 12kg/s = 43.2 tonne/hour = 378, 432 tonne/year

Rice Husks Cost, $Cost_B$ = $ 65/ tonne = 50.29 euro/tonne = RM 198.60

Simplified equation for pyrolysis process production cost is:

$(\text{Production Cost})_P = 1.1 \times (50.29 + 213.53Y^{-1})$ (29)

Table 12: Production Cost of Pyrolysis Process at Different Temperature

Temperature, K	Bio-oil Yield (kg/s)	Fractional Yield, Y	Production Cost (mil euro)	Production Cost (mil RM)
473	0.000	0.0000	-	-
523	0.001	0.0001	2.8189	11.2674
573	0.010	0.0008	0.2819	1.1268
623	0.059	0.0049	0.0478	0.1911
673	0.201	0.0168	0.0141	0.0564
723	0.483	0.0403	0.0059	0.0236
773	1.370	0.1142	0.0021	0.0084
823	1.300	0.1083	0.0022	0.0088
873	0.894	0.0745	0.0032	0.0128
923	0.200	0.0167	0.0141	0.0564

From Table 12, the lowest cost for pyrolysis process achieved at temperature 773K.

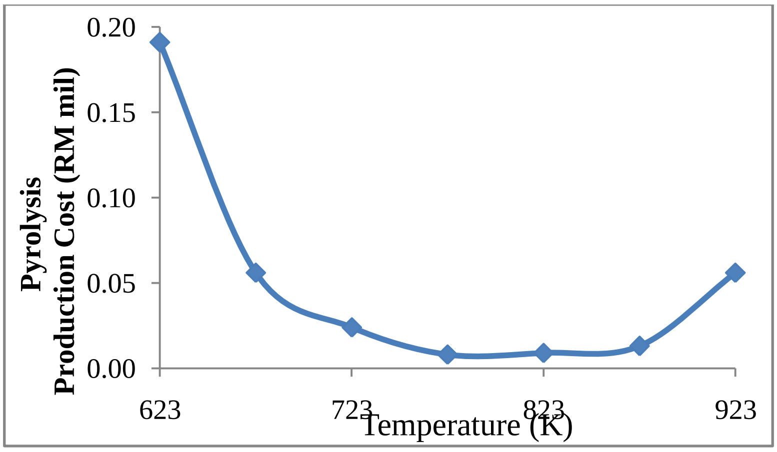


Figure 28: Effect of temperature to pyrolysis production cost

For catalytic cracking, the production cost calculated based on range temperature 673K to 823K since the process is not feasible at other temperature.

Table 13: Production Cost of Catalytic Cracking Process at Different Temperature

Temperature, K	**C_{GL} (kg/s)**	**C_{GL} (tonne/year)**	**Production Cost (mil euro)**	**Production Cost (RM mil)**
673	0.015	473	0.0012	0.0048
723	0.309	9740	0.0053	0.0212
773	3.330	105000	0.0171	0.0684
823	13.801	435000	0.0346	0.1383

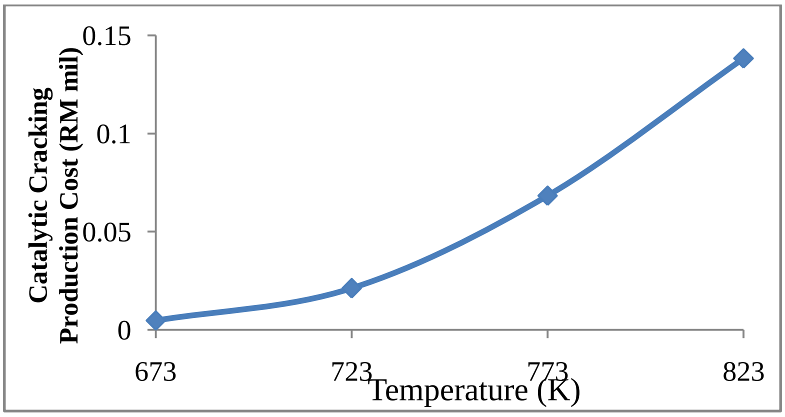


Figure 29: Effect of temperature to catalytic cracking production cost

Total costs of bio-gasoline production given by Equation 30.

Total Cost = Plant Area Cost + (Equipment Cost)$_P$ + (Equipment Cost)$_C$+ (Production Cost)$_P$ + (Production Cost)$_C$ (30)

Plant Area Cost = 6.98 x (43.2 tonne/hour)$^{0.67}$ = 87.02million euro

= **RM 347.83 millions**

(Equipment Cost)$_P$ = 0.176 (347.83 millions) = **RM 61.22 millions**

(Equipment Cost)$_C$ = 0.092 (347.83 millions) = **RM 32.00 millions**

Total Cost (RM)

= RM 347.83 million + RM 61.22 million + RM 32 million + (Production Cost)$_P$ + (Production Cost)$_C$

= RM 441.05 million +(Production Cost)$_P$ + (Production Cost)$_C$

Table 14: Total Bio-gasoline Production Cost at Different Temperature

T, K	(Production Cost)$_{P,}$ RM mil	(Production Cost)$_{C,}$ RM mil	Total Cost, RM mil
673	0.0564	0.0048	441.0612
723	0.0236	0.0212	441.0448
773	0.0084	0.0684	441.0768
823	0.0088	0.1383	441.1471

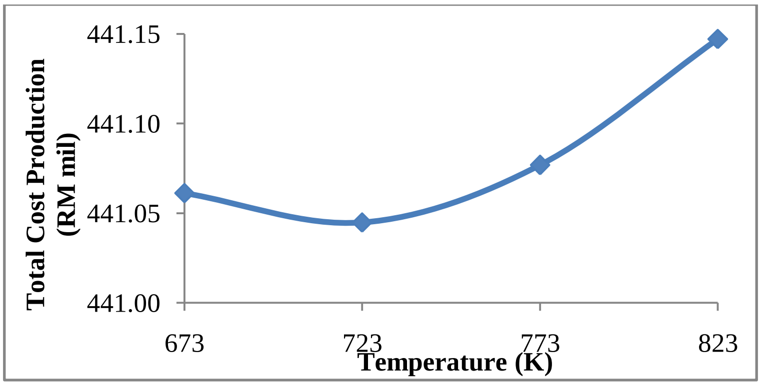


Figure 30: Effect of Temperature to Total Production Cost

Figure 30 shows, the temperature effects the production cost as well. Lowest cost of bio-gasoline achieved at range of temperature of pyrolysis process and catalytic cracking process.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

Rice husk are agriculture wastes which have possible future as alternative to replace fossil fuel. Two main thermo-chemical processes involve in converting rice husk into bio-gasoline which are pyrolysis and catalytic cracking. Fast pyrolysis process used to convert the rice husk into bio-oil while catalytic cracking process used to upgrade bio-oil into bio gasoline. Different temperature effects product yields and production cost. Since experiment method may consume time, energy and cost, therefore computational method will be the alternatives. From the studies, it shows highest yields of bio-oil and bio-gasoline achieved at temperature 773K and 823K respectively. The lowest cost of bio-gasoline production also obtained at temperature range of 723K to 823K.

In this project, only effect of temperature is investigated since the model proposed only involves this parameter. It is recommended to find other model which involves other parameter, such as pressure, size or quantity of feedstock and catalyst which effect yield of products as well. It also recommended to improve the results by doing optimization studies to get optimum condition of the process.

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APPENDICES

Appendix 1: Coding for Pyrolysis Process

Function File save as calc_conc.m

```
FunctiondCdt = calc_conc(t,C)
% C  = concentration in kg/m3
% C1 = concentration of biomass
% C2 = concentration of gas n volatile 1
% C3 = concentration of char 1
% C4 = concentration of gas n volatile 2
% C5 = concentration of char 2

dCdt = zeros(size(C));

global k1 k2 k3;
% ki = rate of reaction i

C1 = C(1);
C2 = C(2);
C3 = C(3);

dCdt(1) = -k1*C1 - k2*C1                   ;
dCdt(2) =  k1*C1- k3*(C2.^1.5)*(C3.^1.5)   ;
dCdt(3) =  k2*C1- k3*(C2.^1.5)*(C3.^1.5)   ;
dCdt(4) =  k3*(C2.^1.5)*(C3.^1.5)          ;
dCdt(5) =  k3*(C2.^1.5)*(C3.^1.5)          ;
```

Script File save as product_pyro.m

```
closeall;
clearall;

global R;
R = 8.314;

% A(i)    = frequency factor for reaction i (1/s)
% D(i)    = constant define(K)
% E(i)    = activation energy (W/mK)
% L(i)    = constant define (K2)

% parameter for pyrolysis
A1 = 9.973*(10^-5);
A2 = 1.068*(10^-3);
A3 = 5.700*(10^ 5);
D1 = 17254.4      ;
D2 = 10224.4      ;
E3 = 81000        ;
L1 = -9061227     ;
L2 = -6123081     ;

T  = 773;% temperature range from 473K to 923K
```

```
global k1;
k1 = A1 * exp((D1/T) + (L1/(T.^2)));

global k2;
k2 = A2 * exp((D2/T) + (L2/(T.^2)));

global k3;
k3 = A3 * exp(-E3/(R*T));

% C0 is initial concentration
C0(1)=1; C0(2)=0; C0(3)=0; C0(4)=0; C0(5)=0;

tspan = [0:0.25:2]; % reaction time is 2 seconds

% calculate concentration of pyrolysis product
[t,C] = ode45('calc_conc',tspan,C0);
```

Appendix 2: Coding for Catalytic Cracking Process

Function Filesave as calc_cracking.m

```
functiondCdt = calc_cracking(t,C)

global k

dCdt = 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);

% C(1)= concentration of bio-oil
% C(2)= concentration of diesel
% C(3)= concentration of kerosene
% C(4)= concentration of gasoline
% C(5)= concentration of gas
% C(6)= concentration of coke

dCdt(1)  = -(k1+k2+k3+k4+k5)*C(1);
dCdt(2)  = k1*C(1)-(k6+k7+k8+k9)*C(2);
dCdt(3)  = k2*C(1)+k6*C(2);
dCdt(4)  = k3*C(1)+k7*C(2)-k10*C(4);
dCdt(5)  = k4*C(1)+k8*C(2)-k11*C(5);
dCdt(6)  = k5*C(1)+k9*C(2)+k10*C(4)+k11*C(5);
```

Script file save as product_cracking.m

```
clearall;
closeall;

global k A E
% define frequency factor, A
A(1)= 7.18*10^(11);
A(2)= 2.38*10^(12);
A(3)= 5.31*10^(12);
A(4)= 1.46*10^(20);
```

```
A(5)= 4.39*10^(8);
A(6)= 1.78*10^(9);
A(7)= 5.36*10^(8);
A(8)= 1.07*10^(13);
A(9)= 1.86*10^(12);
A(10)= 1.39*10^(21);
A(11)= 2.52*10^(-10);

% define activation energy, E(kJ/mol)
E(1)= 162.95;
E(2)= 175.59;
E(3)= 178.75;
E(4)= 278.16;
E(5)= 132.19;
E(6)= 125.79;
E(7)= 132.44;
E(8)= 179.58;
E(9)= 176.92;
E(10)= 304.7;
E(11)= -115.23;

% operating temperature, K
T = 723;

% define rate constant, k
for n=1:11, k(n)= A(n)*exp(-E(n)*1000/(8.314*T));
end

% Initial concentration and residence time
C0 = [1,0,0,0,0,0];
tspan= 0:0.5:3;

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

Appendix 3: Coding for Bio-gasoline Production

```
function C = gasoline(C,k)

%%%%%%%%%%%%    PYROLYSIS   %%%%%%%%%%%%%%%

% Assumptions

CB    = 100; % biomass feed, kg/s
T     = 923; % temperature range, K (473-923)

% Rate of reaction, k(i)

k(1)  = (9.973*10.^-5)*exp((17254.4./T)+(-9061227./T.^2));
k(2)  = (1.068*10.^-3)*exp((10224.4./T)+(-6123081./T.^2));
k(3)  = (5.7*10.^5)*exp(-9742.6./T);
k(4)  = (1.46*10.^20)*exp(-34539.3./T);
k(5)  = (1.07*10.^13)*exp(-21599.7./T);
k(6)  = (2.52*10.^-10)*exp(13859.8./T);
k(7)  = (4.39*10.^8)*exp(-15899.7./T);
```

```
k(8)  = (1.86*10.^12)*exp(-21279.8./T);
k(9)  = (1.39*10.^21)*exp(-36649.0./T);
k(10)  = (7.18*10.^11)*exp(-19599.5./T);
k(12)  = (2.38*10.^12)*exp(-21119.8./T);
k(13)  = (1.78*10.^9)*exp(-15129.9./T);
k(14)  = (5.31*10.^12)*exp(-21499.9./T);
k(15)  = (5.36*10.^8)*exp(-15929.8./T);
k(11)  = k(5)+k(8)+k(13)+k(15);

% pyrolyzer

C(1)  = (((2*k(1) + 2*k(2))*CB)/(2*k(3)));

% char
C(2)  = (k(2))*(CB);

% gas
C(3)  = ((k(1))*(CB)) - ((1/2)*(k(3))*(C(1)));

% bio-oil
C(4)  = (1/2)*(k(3))*(C(1));

%%%%%%%%%%%%%% CATALYTIC CRACKING %%%%%%%%%%%%%%

G    = 0.43*(C(4));
D    = 0.168*(C(4));
GS   = 0.224*(C(4));

% Gas
C(5)  = (k(4)*C(4)) + (k(5)*D) - (k(6)*G);

% Coke
C(6)  = (k(7)*C(4)) + (k(8)*D) + (k(9)*GS) + (k(6)*G);

% Diesel
C(7)  = (k(10)*C(4)) - (k(11)*D);

% Kerosene
C(8)  = (k(12)*C(4)) + (k(13)*D);

% Gasoline
C(9)  = (k(14)*C(4)) + (k(15)*D) - (k(9)*GS);

end
```