

# **PYROLYSIS KINETICS OF BIOMASS**

**by**

**MUHAMMAD IMRAN AFIFI BIN MOHD MAHZAN**

**Thesis submitted in partial fulfilment of the requirement  
for the degree of Bachelor of Chemical Engineering**

**June 2018**

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## TABLE OF CONTENT

ACKNOWLEDGEMENT	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRAK	vii
ABSTRACT	viii
CHAPTER ONE : INTRODUCTION	1
1.1 Renewable Energy	1
1.2 Biomass	1
1.3 Advantages of Biomass	2
1.4 Application of Biomass	2
1.5 Problem Statement	4
1.6 Research objectives	5
1.7 Scope of study	5
CHAPTER TWO : LITERATURE REVIEW	6
2.1 Pyrolysis Kinetics	6
2.1.1 Single Particle Models	6
2.1.3 Biomass	12
2.2 Thermo-gravimetric Analysis (TGA)	14
2.3 Heating Rates	15
2.4 Chemical Additives	16

CHAPTER THREE : MATERIALS AND METHODS	18
3.1 Materials and Chemicals	18
3.2 Feedstock Preparation	20
3.3 Thermogravimetric Analysis (TA)	21
3.4 Chemical Additives	21
3.5 Safety and Precautions	22
CHAPTER FOUR : RESULTS AND DISCUSSION	23
4.1 Effects of Heating Rates	25
4.2 Chemical Additives	33
CHAPTER FIVE : CONCLUSION AND RECOMMENDATIONS	40
5.1 CONCLUSIONS	40
5.2 RECOMMENDATIONS	40
REFERENCES	41

## LIST OF TABLES

		Pages
Table 3.1	List of Chemicals	18
Table 4.1	Reaction model functions and its mechanism	23
Table 4.2	Kinetic Parameters By Kissinger Equation	24
Table 4.3	Kinetic Parameters By Jander Equation	24
Table 4.4	Kinetic Parameters For Reaction at Zone 1	28
Table 4.5	Kinetic Parameters For Reaction at Zone 2	29
Table 4.6	Kinetic Parameters For Reaction at Zone 3	29
Table 4.7	Kinetic Parameters For Reaction at Zone 1	36
Table 4.8	Kinetic Parameters For Reaction at Zone 2	36
Table 4.9	Kinetic Parameters For Reaction at Zone 3	37

## LIST OF FIGURES

		Pages
Figure 2.1	Sugarcane Bagasse	13
Figure 3.1	Flowchart of the process	19
Figure 3.2	Summary of Feedstock Preparation	20
Figure 4.1	The Graph of DTG against Temperature	27
Figure 4.2	The Graph of Weight Loss Versus Temperature	27
Figure 4.3	Graph of Ln K Versus 1/T	31
Figure 4.4	Graph of Ln K Versus 1/T	31
Figure 4.5	Graph of Ln K versus 1/T (Zone 3)	32
Figure 4.6	Graph of Ln K versus 1/T (Zone 3)	32
Figure 4.7	Graph of Ln K versus 1/T (Zone 3)	33
Figure 4.8	Graph of Weight Loss Versus Temperature	34
Figure 4.9	Graph of DTG Versus Temperature	34
Figure 4.10	Graph of Ln K versus 1/T	38
Figure 4.11	Graph of Ln K versus 1/T	38
Figure 4.12	Graph of Ln K versus 1/T	39

## **PENILAIAN KINETIK BIOJISIM SECARA PIROLISIS**

### **ABSTRAK**

Objektif kerja ini adalah untuk menilai kinetik kimia biojisim yang digunakan iaitu hampas tebu dengan parameter kadar pemanasan dan kepekatan bahan kimia yang berlainan. Bahan tambahan kimia yang digunakan untuk eksperimen ini adalah asid fosforik kerana ia merupakan salah satu ejen dehidrasi terbaik untuk membuang kandungan lembapan biojisim. Proses pirolisis dilakukan dengan menggunakan Penganalisa Gravimetritermal (TGA-7) sehingga suhu maksimum 750 ° C. Hampas tebu mengalami tiga langkah penurunan berat. Penguraian hemiselulosa, selulosa dan lignin adalah tiga langkah penurunan berat untuk biojisim yang digunakan. Perubahan dalam keadaan operasi (kadar pemanasan) memberikan sedikit kesan terhadap kinetik proses dan juga tiga langkah penurunan berat bahan. Untuk penambahan bahan kimia tambahan, dapat disimpulkan bahawa dengan enap jerap biojisim dengan bahan tambahan kimia tersebut memberikan kesan yang signifikan terhadap kinetik biojisim.



# **PYROLYSIS KINETICS OF BIOMASS**

## **ABSTRACT**

The objective of this work was to evaluate the chemical kinetics of the biomass used which was sugarcane bagasse with parameters namely heating rates and chemical additives concentration. The chemical additive used for this experiment was phosphoric acid as it one of the best dehydrating agent to remove moisture content of the biomass. The pyrolysis process was carried out using a Thermal Gravimetric Analyzer (TGA-7) until a maximum temperature of 750°C. Sugarcane bagasse experienced three steps of weight loss. The decomposition of hemicellulose, cellulose and lignin are the three steps of weight loss for the biomass used. A change in the operational condition (heating rate) gives very little impact of the kinetics of the process and also the three steps weight loss. For the addition of chemical additives, it can be concluded that by impregnating the biomass with the mentioned chemical additives gives significant impact on the kinetics of the biomass.

# **CHAPTER ONE**

## **INTRODUCTION**

### **1.1 Renewable Energy**

Global energy consumption has been a new major issue nowadays due to the rapid development of both household and industry. The highest contributor for this major problem is due to the high usage of fossil fuels. Fossil fuels are great in supplying high quality energies however it will cause pollution and contributes to the global warming. A lot of studies have been done in order to find other alternative sources to replace fossil fuels. One of the most famous studies that has been found is solar energy. Solar energy is so efficient that it can provide most of the total energy utilized in the world (Klass, 1998). Due to its huge energy source, it is very trivial to focus and utilize this energy source. Due to this field of study, solar collectors and many more devices have been created and incorporated into our daily life. Although it sounds very beneficial to us, however, there are some problems related to this source of energy. Some of the main disadvantages related to this matter are high capital costs, high maintenance, low performance, large land area needed and climatic restrictions (Holck et al., 2003). Due to all the reasons mentioned, solar energy is not fond of being the next energy source to replace fossil fuels.

### **1.2 Biomass**

One of the renewable energy that can be used is biomass. Biomass is now receiving a great deal of attention due to its advantages over the other renewable resources (Saidur et al., 2011). Solar energy can fix the structures of fresh biomass to produce hydrocarbons during photosynthesis. The main constituents of the hydrocarbons are in

the form of cellulose, hemicellulose and lignin. These hydrocarbons can be accepted as energy deposits. Next, biomass can be produced from anywhere in the world, and making it to be plentiful. It can capture even low intensity solar energy to produce high yields of hydrocarbons (Klass, 1998).

### 1.3 Advantages of Biomass

Furthermore, one of the main advantage of using biomass is that plant growth to generate biomass feedstock will lower down the carbon dioxide in the atmosphere (Mohan et al., 2006). Biomass derived fuels can be separated into first, second and third generation biofuels. First generation biofuels are made from food crops such as sugarcane, corn, potato and many more (Bach and Chen, 2017). The second generation biofuels are made from non-food such as husk, grass and wood chips (Bach and Chen, 2017). While the third generation biofuels are made from algal biomass (Bach and Chen, 2017). Biomass contains high moisture content with low density making the transportation, storage and usage of the biomass without any pretreatment to be likely difficult. This makes thermal conversion methods like pyrolysis, gasification and carbonization to treat the biomass to be more efficient as compared to the direct combustion of biomass.

### 1.4 Application of Biomass

A lot of technologies have been created in order to convert biomass into biofuels. The technologies can be categorized into 3 divisions which are thermo-chemical, bio-chemical and physico-chemical. Thermo-chemicals are then can be divided into three main processes namely pyrolysis, gasification and combustion. Pyrolysis is a

thermal process which requires no or controlled amount of oxidizing agents such as air and oxygen. In other words, pyrolysis is a process of heating under non-oxidizing conditions whereby solid, liquid and gaseous products can be obtained from the biomass (Yaman, 2004). The amounts of solid, liquid and gas products formed by pyrolysis depends highly on the feedstock characteristics and process variable (Holck et al., 2003). According to a literature, the main constituent that are produced from the volatile products by pyrolysis are cellulose and hemicellulose while the formation of solid char is due to the lignin content (Klass, 1998).

Based from the thermogravimetric analysis (TGA) of biomass, pyrolysis behaviour can be regarded as the superposition of three independent independent kinetics of primary components including hemicellulose, cellulose and lignin (Mészáros et al., 2004) leading to the contributions of individual kinetics can be weighed according to the relative amounts of biomass components. Reaction kinetics can be obtained from the thermal reaction. The kinetics parameter can be obtained by three kinds of conventional methods namely differential, integral and maximum-reaction-rate (Coats and Redfern, 1964). The differential method needs no approximation which is required in the integral method however it is very sensitive towards experimental noise. For the integral method, it is very hard to integrate an exponential function, therefore a lot of approximations is required in order to get the minimum errors of approximations (Huang et al., 2013). The last method uses the data from the experiment at the maximum reaction rate to provide exact determination of kinetic parameters.

## 1.5 Problem Statement

Biomass is now being a popular field of study in order to achieve a new type of renewable energy. The demands are growing rapidly due to the low cost of the feedstock and the availability of the feedstock. Currently, pyrolysis is one method to convert biomass into biofuels. Pyrolysis is a process of heating under non-oxidizing conditions whereby solid, liquid and gaseous products can be obtained from the biomass. Biomass contains high moisture content making it to be less efficient to be used before pre-treating it beforehand. Previous studies proposed that the heating rates during pyrolysis affect the main product of the biomass. However, heating rates which are too high will remain irrelevant to the whole process.

Pre-treating the biomass with chemical reagents which are known of its dehydrating capability will also affect the performance of the biomass. However, the best dehydrating agents to be used to the biomass still remains unknown. A chemical reagent with different compositions are used to study the effect of chemical additives to the biomass.

## 1.6 Research objectives

1. To find the reaction kinetics of sugarcane peel by using a Thermal Gravimetric Analyser (TGA-7).
2. To investigate the effect of heating rates on the biomass through the process of pyrolysis.
3. To study the effect of concentration of chemical additive on the biomass and the end product of the pyrolysis process.

## 1.7 Scope of study

The first step is to study the effect of various heating rates on the biomass. The heating rates is varied from lower heating rates to a much higher heating rates which is less than 100°C/min. The heating rates was found to play an important role in increasing the efficiency of the biomass which is relevant for this process.

The second step is to study the effect of chemical additives on the biomass or in other words is to pre-treat the biomass first before the pyrolysis process. The biomass is impregnated with the chemical additive. Different composition of the chemical reagent were used in order to find the best and most relevant to be used to treat the biomass.

# CHAPTER TWO

## LITERATURE REVIEW

### 2.1 Pyrolysis Kinetics

Chemical kinetics is the study of chemical reactions with respect to the reaction rates, effect of various variables, re-arrangement of atoms and formation of intermediates. Kinetics are referred as the movement of the particles. Chemical kinetics can give us various information which are the amounts of the reactant which has reacted, the amount of products formed and the rates of their production. Pyrolysis can be defined as the thermochemical degradation of organic materials or biomass without the presence of oxygen. The study of pyrolysis kinetics of biomass is important because it is involved in the first step for the process of combustion and gasification. Thermal decomposition of lignocellulosic materials is essential in order to design and optimize reactors can add up the importance of studying pyrolysis kinetics. Significant parameters include activation energy ( $E_a$ ), pre-exponential factor ( $k$ ) and the reaction order are needed in order to design reactors.

#### 2.1.1 Single Particle Models

For the past 60 years, a lot of models were published regarding the thermal degradation of a single biomass particle. The first model was formulated in 1946, where (Bamford et al.) develop the weight loss of wooden sheets being exposed to gas flames. The model was then modified by introducing the effect of internal convection by (Roberts and Clough). A more detailed kinetic modelling was introduced by Di Blasi and Bellan and co-workers (Miller and Bellan, 1997). Chemical kinetics, moisture evaporation, particle shrinkage, heat transfer (conduction, convection and radiation) and

convective mass transfer were included in the more detailed kinetic modelling. The diffusional flux can be neglected as compared to the convective flow (Kothari and Antal Jr, 1985) [77]. Arrhenius-type equation best describes moisture evaporation in a single particle model (Bryden and Hagge, 2003). A guidelines of identifying the controlling steps of wood pyrolysis was introduced by (Pyle and Zaror, 1984) for one dimensional pyrolysis model. The simplifications can be concluded to kinetically controlled, external heat transfer controlled and internal heat transfer controlled pyrolysis. This guidelines can be used to determine whether the heat transfer or reaction is a more faster mechanism. Arrhenius equation best describes the temperature dependant reaction rate of the pyrolysis. The equation describes the dependence of the reaction constant to the temperature.

$$k_r = Ae^{\frac{-E_a}{RT}} \quad (2.1)$$

where,

$K_r$  = rate constant

A = pre-exponential factor

$E_a$  = activation energy

R = universal gas constant

T = temperature

This equation was developed by Svante Arrhenius during the study of dissociation of electrolytes. The decomposition reaction can be described as below.



$$\left(-\frac{1}{w_0}\right)\left(\frac{dw}{dt}\right) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \bullet f\left(\frac{w}{w_0}\right) \quad (2.2)$$

where,

$W_0$  = original biomass weight

$W$  = weight of biomass

$t$  = time

$A$  = pre-exponential factor

$E_a$  = activation energy

$R$  = universal gas constant

$T$  = absolute temperature

The fractional conversion from reactants to products ranging from 0 to 1 can be described as:

The term  $f(w/w_0)$  is a function of biomass weight

$$f\left(\frac{w}{w_0}\right) = \left[\left(\frac{w - w_f}{w_0}\right)\right]^n \quad (2.3)$$

where,

$W_f$  = final weight of biomass

$N$  = kinetic order of reaction

The stoichiometric reaction orders are integers which is usually 1. At elevated temperatures, breaking of chemical bonds will occur and contributes to thermal degradation. The mass loss reaction is a combination of several chemical reactions. These reactions are lumped together allowing the usage of fractional reaction.

To simplify the calculations,  $n=1$  is considered. Eq (2.2) can be rearranged to:

$$-\frac{dw}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (w - w_f) \quad (2.4)$$

Equation 2.4 can be written as ( by taking A as gas product) :

$$-\frac{dw_a}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (w_{A,f} - w_a) \quad (2.5)$$

where,

$W_{A,f}$  = final weight of gas product A

A calibration curve is drawn in order to accomplish the quantitative analysis. The calibration curve shows the relationship between the response signal and the and

quantities of products which is best suited with a linear regression. A relationship between the response signal ( $S_A$ ) and the weight ( $w_A$ ) of gas product A can be expressed as :

$$S_A = m_A \cdot w_A + S_{A,0} \quad (2.6)$$

where,

$m_A$  and  $S_{A,0}$  are slope and intercept of the straight line obtained by linear regression, respectively. Upon substitution and rearrangement Equation 2.5 becomes:

$$\frac{1}{S_{A,f} - S_A} \frac{dS_A}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (2.7)$$

where,

$S_{A,f}$  = final signal of gas product A

With constant heating rates, Equation 2.7 can be written as:

$$\frac{1}{S_{A,f} - S_A} \frac{dS_A}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) \quad (2.8)$$

Taking natural logs for both sides yields:

$$\ln\left(\frac{1}{S_{A,f} - S_A} \frac{dS_A}{dT}\right) = -\frac{E_a}{R} \frac{1}{T} + \ln\left(\frac{A}{\beta}\right) \quad (2.9)$$

Equation 2.9 can be further integrated to:

$$\int_{S_{A,0}}^{S_A} \frac{dS_A}{S_{A,f} - S_A} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (2.10)$$

The integration is approximated to be :

$$\int_0^T \exp\left(-\frac{E_a}{RT}\right) dT = \frac{RT^2}{E_a} \cdot \left(1 - \frac{2RT}{E_a}\right) \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (2.11)$$

With further integration,

$$\ln\left(\frac{S_{A,f} - S_{A,0}}{S_{A,f} - S_A}\right) = \frac{ART^2}{\beta E_a} \cdot \left(1 - \frac{2RT}{E_a}\right) \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (2.12)$$

Taking natural logarithms for both sides Equation 2.12 leads to :

$$\ln\left[\frac{1}{T^2} \ln\left(\frac{S_{A,f} - S_{A,0}}{S_{A,f} - S_A}\right)\right] = -\frac{E_a}{R} \frac{1}{T} + \ln\left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)\right] \quad (2.13)$$

### 2.1.3 Biomass

The type of biomass used during the beginning of the experiment is one of the most important main ideas before planning to start the experiment. One of the best method to achieve the best biomass is to pre-treat it first before running the experiment. Torrefaction is a method of pre-treating the biomass in order to upgrade its fuel properties nearer to coal. It is defined as the thermal treatment of biomass in an inert environment at atmospheric pressure and the range of temperature is between 200-300°C (Chen et al., 2015).

Three kinds of product are produced during this treatment which are a solid product, gases including hydrogen, carbon dioxide, carbon monoxide and hydrocarbons such as methane and lastly a mixture containing water, organic compounds and lipids. The solid product accounts for 70% of the total mass and 90% of the raw energy (Bergman et al., 2005). The advantages of the of pre-treating the biomass is that torrefied biomass is more hydrophobic, has lower moisture content, better grinding capability and higher heating value. It is best when it comes to pyrolysis for further conversion process.

Although there are very beneficial for this process, there are also a few disadvantages of this torrefaction process which includes economical and technical-wise features. One of the main problem is the energy efficiency. A few strategies have been imposed in order to overcome this problem such as the produced volatiles are burnt in air and the produced heat should be recycled can maximize the torrefaction process which is proposed by (Bergman et al., 2005). Air is used as the oxidizer for the combustion. This requires very high fuel consumption due to the content of nitrogen which upholds four fifths of air. Large amount of flue gas will increase the investment cost and with little amount of carbon dioxide gas contained in the flue gas will make the

carbon capture and storage (CCS) more difficult. An oxy-fuel combustion uses oxygen as the main oxidizer and will produce flue gases with no nitrogen content (Toftegaard et al., 2010) By using oxy-fuel instead of air will give lower fuel consumption, reduced NO<sub>x</sub> emissions and more efficient CCS (Buhre et al., 2005).

Another type of biomass used in pyrolysis is microalgal biomass. A report showed that bio-fuels produced from microalgal biomass are more stable than the bio-fuels produced from lignocellulosic biomass (Suali and Sarbatly, 2012). Next, bio-fuels from microalgae contains less oxygen and greater heating value compared to lignocellulosic bio-fuels (Kim et al., 2014). The pyrolysis of microalgae undergoes three main stages. The first stage is known to remove the water content from the microalgae. In the following stage, carbohydrate, protein and lipids which are the main constituents of microalgae is thermally degraded. The last stage will only experience a slight change of mass which is due to decomposition of carbonaceous material. However, the implementation of using microalgae is usually being used due to the usage of simplified kinetics models. This causes the kinetic data to be insufficient in order to understand better understanding about the reaction mechanism (Bach and Chen, 2017) .



Figure 2.1 : Sugarcane Bagasse

## 2.2 Thermo-gravimetric Analysis (TGA)

Thermo-gravimetric analysis is one of the best technique to study the kinetics pyrolytic behaviour of biomass. Two main methods are conventionally used based on the TGA data, which are iso-conversional and model-fitting methods. These two methods are often used to find the kinetic parameters and mechanism model (Vyazovkin et al., 2011). Iso-conversional methods are best when it comes to estimating the apparent activation energy without even knowing the model of the mechanism. Unfortunately, pyrolysis process is a complex process due to the interaction of devolatilization, diffusion effect, catalyst and secondary reactions (Hu et al., 2007). The iso-conversional method is suitable for one-step reaction and thus conflicting the kinetics of complex reaction system (Anca-Couce et al., 2014).

For the model-fitting method, the model of the mechanism is assumed first. The kinetic parameters is estimated by using optimization to fit the experimental data. This method assumes infinity first-order reactions to the pyrolysis process. However, this two methods are weak in interpreting the reaction mechanism. The n-th order reaction mechanism, is semi-empirical without any physical meaning when it is introduced in solid state material thermal decomposition kinetics (Pérez-Maqueda et al., 2014). The distributed activation energy model (DAEM) is difficult to use the kinetic data to interpret the reaction mechanism due to the empirical nature (Jiang et al., 2010).

A new proposed model suggested by Sestak and Berggren (SB) can fit all the models which have straightforward physical meanings and also the n-th order models (Vyazovkin et al., 2011). One powerful way to avoid the lacking of n-th order and DAEM mechanisms is to use SB mechanism model to use the combined kinetics.

## 2.3 Heating Rates

Maximum temperature and heating rates influence the yield and composition of pyrolysis products (Topsak et al.). A high heating rate but with final temperature less than 650°C will favor the formation of liquids and minimize char production. A high heating rate with a final temperature higher than 650°C will favor the formation of gaseous product while heating at low rates and low final temperature will increase the char yield. A heating rate between 20-100°C /min reaching a final temperature of 600°C tends to increase the yield to liquid and gaseous product (Yan et al., 2014). (Hecker et al.)found that the H/C ratio of char increases with high heating rates but decreases with lower final temperature of pyrolysis. (Zanzi et al., 1996) studied about the slow and fast pyrolysis with high and low heating rates. Based from their observation, a high heating rate of pyrolysis process will result in decrease in char yield. At low heating rates, the chars obtained tend to have lower porosity and lower reactivity (Cetin et al., 2005).

Another study done to study the effect of heating rates on the biomass (rapeseed) showed that at lower heating rates, the maximum rates of mass losses was relatively low while at high heating rates, the maximum rates of mass losses has increased. Heating rates also affect the shape of the DTG peaks. Higher heating rates shifted the main peak on the DTG profile to the lower temperature. There are probably resistance from the heat or mass transfer inside the biomass particle at low heating rates. By increasing the heating rates, the resistance can be overcome and gives higher conversion rates (Haykiri-Acma et al., 2006).

A study of pyrolysis by using sugarcane bagasse as the biomass was done by (Wang et al., 2006). They studied the effect of heating rates on the pyrolysis process. They have found that the yield of fragmentation and dehydration products increased as



heating rates increased. However, the heating rates are only relevant as it is below 100C/s. At higher heating rates, no significant difference are recorded. At high heating rates and high temperature, they obtained bio-oils enriched in lignin and sugars oligomers which suggested good yields of fermentable sugar can be obtained at intermediary pyrolysis condition.

## 2.4 Chemical Additives

Chemical additives are added to the biomass before pyrolysis in order to study the dehydrating activity of the process. The biomass is impregnated with the additives just the amount to fill the pores in the solid. The biomass being studied in this literature is apple pulp. The chemical additives is added necessary just to produce swelling on the solid particles. The chemical reagents used in this literature are  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ .  $\text{H}_3\text{PO}_4$  shows the greatest impact on the apple-pulp pyrolysis. It caused significant amount of weight loss during the second-weight loss step with a sharp change in the slope of the TG curve (Suarez-Garcia et al., 2002).

A study of pyrolysis by using pine wood, cotton stalk and fir wood were added 6 kinds of chemical additives ( $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SiO}_3$ ,  $\text{TiO}_2$  and HZSM-5). It shows that by using  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{NaCl}$ , and  $\text{Na}_2\text{SiO}_3$  made the devolatilization occurred at lower temperature regions on the biomass. However, by using  $\text{TiO}_2$  and HZSM-5 had no change on the pyrolysis temperature for pine wood and fir wood but increased the devolatilization temperature regions for cotton stalk.  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SiO}_3$  made the the pyrolysis of all the biomass to be more exothermic probably due to the char formation. In terms of weight loss,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$  and  $\text{Na}_2\text{SiO}_3$  will decrease the maximum weight loss but  $\text{NaCl}$  and HZSM-5 tend to increase the maximum weight loss (Wang et al., 2006).

Another study by using pine wood sawdust as the biomass and used NaOH, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, NaCl, TiO<sub>2</sub>, HZSM-5, H<sub>3</sub>PO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as the chemical additives. It shows that all the additives have increased the yields of solid products and decreased the yields of gaseous product. Incondensable gases as products of pyrolysis are mainly consist of H<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>. It was reported that all the additives have made these gases evolve faster. The amount of CH<sub>4</sub> and CO<sub>2</sub> experienced a decrease in number for all the additives used. Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, HZSM-5 and H<sub>3</sub>PO<sub>4</sub> have made the H<sub>2</sub> decrease while the others did the otherwise. All of the additives except for Na<sub>2</sub>SiO<sub>3</sub> and HZSM-5 have made the CO decrease. Most of the H<sub>2</sub> formation are favored by the sodium compounds additives. Acetol formation reaction are favored by the sodium additives. HZSM-5 has no effect on the formation of acetol while TiO<sub>2</sub> shows a negative feedback on the formation of acetol (Chen et al., 2008).

## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1 Materials and Chemicals

This study focused on the pyrolytic behavior of sugarcane peel. The biomass feedstock was collected in Pekan Parit Buntar, Malaysia. Before being put into the thermogravimetric system, the biomass feedstock were air-dried, milled, and sieved (40 mesh) to yield powder samples. The sample size chosen for this experiment is 1.0-2.0mm. Phosphoric Acid ( $H_3PO_4$ ) was obtained from the analytical laboratory.

Table 3.1 : List of Chemicals

Chemical/Reagent	Purity	Supplier	Purpose
Sugarcane Peel	100 %	Pekan Parit Buntar	Biomass
Phosphoric Acid	99 %	Sigma-Aldrich	Biomass Impregnation
Nitrogen Gas	99%	ELGA Purelab Option Q	Pyrolysis

Figure 3.1 shows the flowchart of this study.

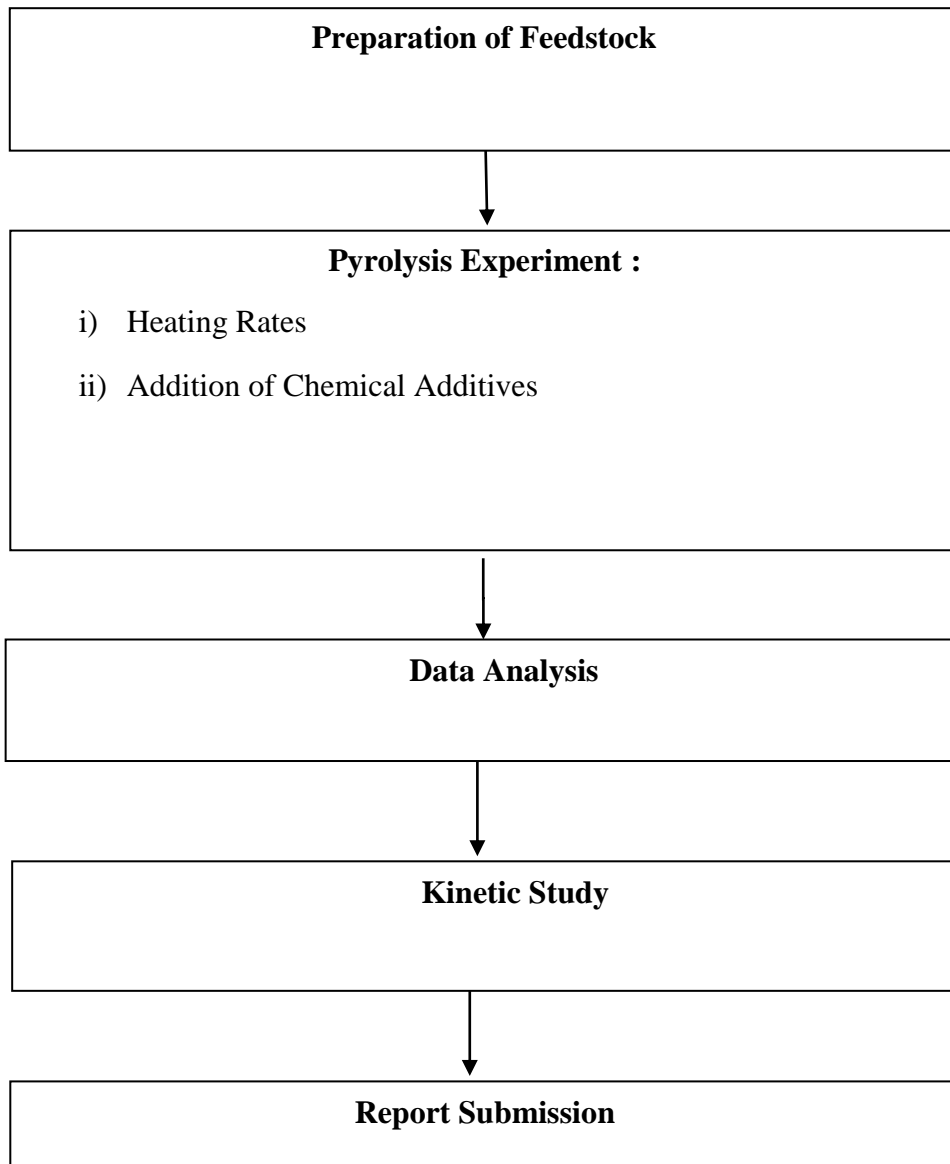


Figure 3.1 Flowchart of the process

### 3.2 Feedstock Preparation

Sugarcane bagasse was air-dried for three days, ground and sieved (40 mesh) to yield powder samples. The powder samples were weighted to see the humid weight of the sample. The powdered samples were then dried inside an oven at 105°C for 12 hours and weighted to find the mass after being dried. After the changes in mass were constant, the samples were put inside an air-tight container to prevent the samples to be in contact with the moisture.

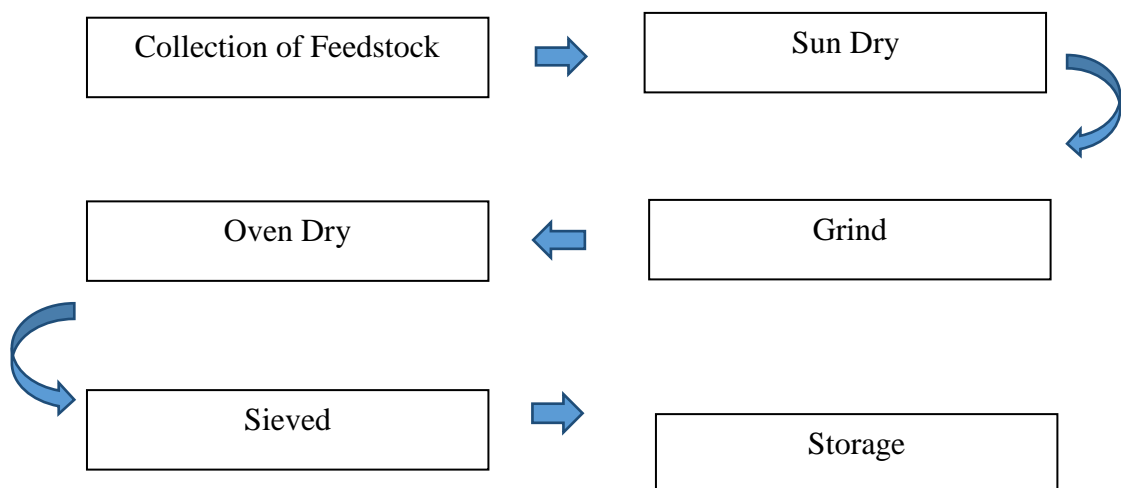


Figure 3.2 : Summary of Feedstock Preparation.

### 3.3 Thermogravimetric Analysis (TA)

Thermal Gravimetric Analyzer (TGA-7) was used in order to conduct the pyrolysis process. It was supplied by Perkin-Elmer, USA. The samples were weighted of 100mg by using a micro balance. Different operational variables during pyrolysis were modified. The effect of heating rate was studied by setting this parameter to 10,20 and 30°C/min under a constant nitrogen flow of 100ml/min and used for the purposes of maintaining the inert atmosphere and purging volatiles generated from biomass pyrolysis in all experiments. The final temperature of the process is 800°C. The experiments were carried out in which the samples were heated for 10°C/min to 200, 210, 300, or 500°C, keeping these temperatures constant for 100 minutes and then heating it back with the same heating rate to 800°C.

### 3.4 Chemical Additives

The introduction of chemical additive in the biomass is famous for its dehydrating activity. The biomass was impregnated with aqueous solution of phosphoric acid ( $H_3PO_4$ ). The amount used to impregnate the biomass was just enough until all the pores in the solid biomass was filled. The reagent is added drop by drop while stirred with the biomass. The stirring was just to ensure the reagent is fully absorbed by the sample. After impregnation, the samples were dried for 4 hours in air. Different concentration of the chemical was used to vary the content of the impregnating agent. The samples were impregnated at 10, 15 and 20 wt%.

### 3.5 Safety and Precautions

1. The experiment conducted must be in a responsible manner at all times while in the laboratory.
2. Be prepared before entering the lab, the procedures should be read thoroughly before entering the lab.
3. Work in a well ventilated area.
4. Dispose of chemical waste properly. Never mix chemicals in sink drains because sinks are only usable when disposing water.
5. Gloves and safety PPE should be worn at all times while conducting the experiment.
6. Keep hands away from face, eyes and mouth while using chemicals. Wash hands with soaps after performing all the experiments.
7. Lab coat should be worn at all times while conducting the experiment.
8. Never return unused chemicals to their original container.
9. Never remove chemicals from the laboratory area.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### Comparison Between Models Used

Two types of kinetic modelling were used during the findings of the kinetic value. This is to ensure the most accurate results of kinetics obtained and also to check on which models are more suitable for the study of kinetics by using biomass. The models were the iso-convensional method, Kissinger and also Jander Equation. Both were derived using the Arrhenius equation, however the main difference of this two model is the mechanism function,  $g(a)$ . Below are the mechanism functions for both Kissinger and Jander equation.

Table 4.1: Reaction model functions and its mechanism

Model	Model Name	Reaction mechanism	$g(a)$
1	Kissinger	Nucleation And growth	$-\ln(1-a)$
2	Jander	Three-dimensional Diffusion, 3D	$[1-(1-a)^{1/3}]^2$



From both the equation above, the kinetics of the biomass can be calculated and shown in the tables below.

Table 4.2: Kinetic Parameters By Kissinger Equation

Phosphoric Acid , (% wt)	Activation Energy, (kJ/mol)	Reaction order,n	Frequency factor, A (s <sup>-1</sup> )	R <sup>2</sup>
10	28.84	2.1	2026.73	0.99
15	19.41	1.9	137.34	0.99
20	16.26	2.0	52.22	0.99

Table 4.3: Kinetic Parameters By Jander Equation

Phosphoric Acid , (% wt)	Activation Energy, (kJ/mol)	Reaction order,n	Frequency factor, A (s <sup>-1</sup> )	R <sup>2</sup>
10	17.91	2.1	136718.51	0.98
15	18.96	1.9	164337.70	0.92
20	20.04	2.0	201157.82	0.86