DESIGN AND EVALUATION OF A CHEMICAL REACTOR

FOR THE PYROLYSIS WOOD PELLETS

by

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ABSTRACT

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Currently there is interest in converting waste biomass into valuable products, such as fuels and specialty chemicals. However, the product composition, yield, the energy required to run the reaction, and the required residence time are all factors influence the economics of the process. Estimate of these factors at the laboratory scale is important for evaluating whether a pilot or demonstration scale study is warranted.

In this work, a bench-scale chemical reactor was designed and constructed to conduct the batch pyrolysis of pelletized biomass. The reactor was tested using pine wood pellets as the feedstock. The feedstock weight to reactor volume ratio was varied to see the impact on required energy input, product yield, composition, and distribution, and conversion time. The products were collected and characterized. Mass and energy balance calculations were performed as well.

The products from pyrolysis experiment, bio-oil, bio-char, and gases were collected during the experiment. The liquids and gases were analyzed by gas chromatography (GC). Simulated distillation was performed on the oil by GC to determine boiling point distributions.

The char was characterized by TGA and element analysis. Thermal losses of the system were determined through energy balance to give an estimation of thermal efficiency. The energy value of the products was estimated using data obtained from the literature.

In additional the chemical kinetics of the reaction were also investigated. The Arrhenius equation was introduced into this experiment in order to understand and the rate of evolution of products from the pyrolysis reaction. The empirical data from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine reaction rate constant and the calorific requirements for the reaction. The TGA data also guided the choice of maximum reactor temperature.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

An energy crisis has developed over the last decade due to the limitation of natural resources. This problem could lead many countries into conflict including wars. Recently, there is great interest in renewable energies for example, wind, solar, hydro, and biomass to increase reliability in energy. Pyrolysis is one method which is a chemical reaction used to converts biomass into valuable products by using high temperature in an oxygen free atmosphere. Pyrolysis basically produces bio-oil, gases, and char. The pyrolysis process is attractive because there is little waste barely obtained from the process. Moreover, most products from the pyrolysis process can be used as a source of power generation with or without treating process. The liquids may contain valuable chemical products as well.

During the pyrolysis process a lot of power is consumed in order to convert the feedstock into products. Loss can occur in many part of the pyrolysis reactor. Small scale experimental data from laboratory can be used to obtain data to help understand a large scale pyrolysis process. Experimental results from a laboratory set up are a significant guide for the design and optimization of energy usage for the pyrolysis process. Hence, a lab scale pyrolysis prototype reactor was designed, built and investigated.

The energy consumption per mass of feedstock of the prototype reactor was investigated. The energy balance was applied to the system. Empirical data from experiment was collected and analyzed to estimate the energy consumption of the system. As a result of the investigation, the energy per unit mass can be used to determine the economics of the industrial pyrolysis system in the future.

1.2 Research Objectives

The following are the research objectives: Use Thermogravimetric analysis (TGA) determines proximate analysis of feedstock, products of the reaction, and also the calorific requirement of the pyrolysis reaction. Also, determine the experiment parameter by using the collected data. Analyze the solid products from the pyrolysis experiment by using TGA and gas chromatography (GC). Determine the energy and mass balance of the system by using the empirical data from the experiment analysis of gas and liquid products and determine yield of products.

1.3 Outline of the Thesis

The organization of the remaining dissertation is as follows:

Chapter 2 is literature review related to pyrolysis

Chapter 3 describes procedures, instruments, and experimental parameter applied in this study.

Chapter 4 provides results and discussion.

Chapter 5 provides a calculation of the energy balance of the system

Chapter 6 summarizes important results and conclusion.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The interested in the renewable energy have been increasing recently. People now pay more attention to the price of fossil fuel and the impact of the fossil fuel and nuclear energy on the environment (Lu et al., 2008). Climate change (global warming) is a result of the emitted of greenhouse gas (CO_2). In order to reduce the effect from the global warming is, a significant reduction in CO_2 emissions is required. Renewable energy is an alternative energy from wind, solar, geothermal, hydro, and biomass. However, biomass gives better reliability in the energy use than the other sources. The biomass is renewable unlike fossil fuel.

2.2 Conversion of Biomass/Waste to energy

Biomass and waste can be converted by 2 methods, biological or thermal conversion. The micro-organism and time plays an important role in the biological method. Thermal conversion method is gaining attention because it is a faster process. Moreover, thermal methods can convert other feedstock such as plastic and waste tires into energy while the biological methods cannot process them. Different thermal conversion method are used for power generation. For example direct combustion, gasification, liquefaction, and pyrolysis. Basically, the direct combustion method transforms raw material into energy by combusting the feedstock in air. Gasification and pyrolysis will provide combustible gases as a product. Not only gas but liquid products, bio-oil, are also obtained from the pyrolysis method. Demirbas (2001) showed that liquefaction also give liquid product like pyrolysis but use wet feedstocks instead of dry. He also showed that the difference between liquefaction and pyrolysis are the temperature and pressure in the system. Pyrolysis uses higher temperature conditions to

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convert raw material into products, but the pressure in liquefaction is much higher. Demirbas (2002) proposed that the production from pyrolysis is higher than other methods when comparing with the fuel-to-feed ratios. Moreover, the products from pyrolysis are easy to collect and transport compare to gasification and direct injection process. Moreover, the cost of pyrolysis reactor is cheaper than liquefaction reactor as the pyrolysis reaction can be run at low pressure, and direct injection system (McKendry, 2002). Mohan et al. (2006) proposed that during the pyrolysis no waste from the process is generated because bio-oil and bio-char can be used as the energy source. Moreover, a portion of the products can be circulate back and reused in the system. The biomass conversion methods can be illustrated as shown in figure 2.1.
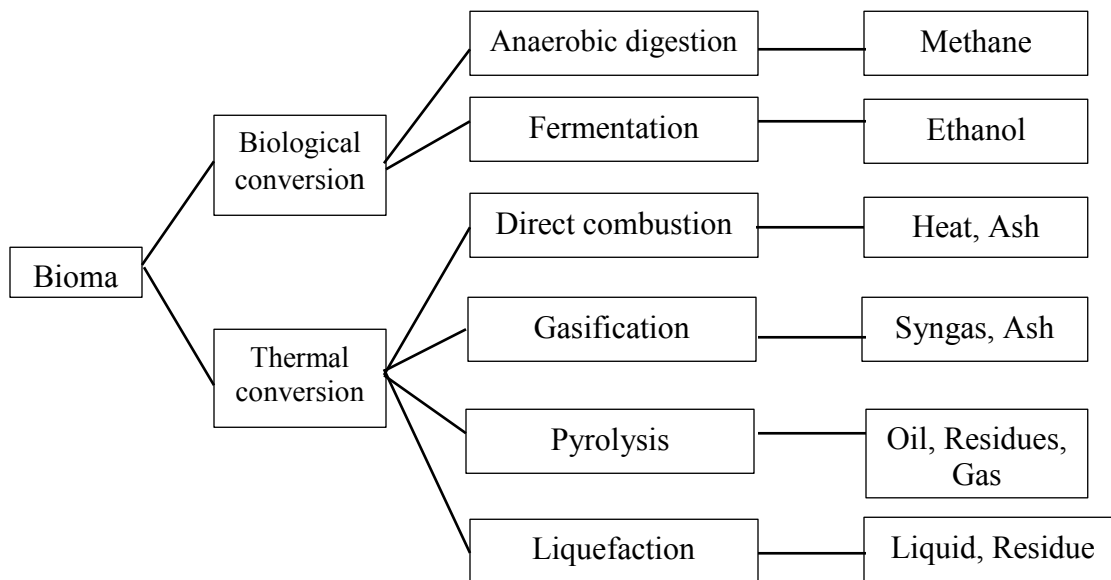
Figure 2.1 Conversion process for biomass

2.3 Pyrolysis

Pyrolysis is the thermal decomposition process operated under the absence of oxygen. Pyrolysis can categorized into 2 types, conventional (slow) and fast pyrolysis depending on the heating rate (Mohan et al.,2006). The slow pyrolysis, temperature of the system is kept constant or slowly heated, so vapors are slowly extracted from where they are formed (Mohan et al.,2006). The reaction usually occurs between 400-500°C (Bridgwater, 2003). Three major products are defined as bio-oil (30-75%), bio-char (10-35%), and non-condensable gas (10-35%) (Balat et al., 2009). The bio-oil, which is the condensable vapor phase of the pyrolysis reaction, is the most attractive product because it can reproduce as the engine fuel such as gasoline, diesel, gas oil, and may contain valuable chemicals. Nevertheless, properties of bio-oil are not stable and the heating value will decrease as the oxygen component increase (Barth et al.,2008). The refinery process is needed to improve the quality of the bio-oil by deoxygenation and hydrotreating (Bridgwater et al., 2002) as shown in table 2.1.

Table 2.1 The component of heavy fuel and bio-oil are compared (Bridgwater et al., 2002)

Properties	Bio-oil	Gasoline	Diesel
C (%)	55-58	85-88	84-87
H (%)	5.5-7.0	12-15	16-33
O (%)	35-40	0	0
HHV (MJ/Kg)	16-19	43-47	44-46

Bio-char and non-condensable gas from pyrolysis are also important. Thangalazhy-Gopakumar et al., (2010) said that the heating value of bio-char is higher than the feedstock, increased by the pyrolysis process. The high heating of bio-char make it an interesting fuel for energy production as the feedstock (Thangalazhy-Gopakumar et al., 2010). Moreno-Pirajan et al. (2010) created the absorption carbon from pyrolysis char in order to remove metal ions from

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the water. Gas products can be re-circulated to the process and used as the additional heat source (H_2 and CH_4).

According to National Renewable Energy Laboratory (NREL,2006), the pyrolysis reactor design was introduced for large scale. There are various reactors for example fluidized bed, transport bed, rotating cone, ablative, and vacuum. Fluidized and transport beds are accepted in thermal reaction design and known to produce high yield of oil. Numerous studies were done with different dimensions and capacities. The pyrolysis has been scaled up to commercial use as a result of the study.

Thangalazhy-Gopakumar et al. (2010) studied pyrolysis for pine wood to determine the best set point for the maximum oil yield. The author found that 450°C is the suitable set point of the pyrolysis experiment. Beyond this point the yield of oil decreased as the temperature increase. However, the author obtained more gas product from the process when the temperature increases. Gas production can be recirculated to the process and use as additional source of heat process. The recirculating gas product can helps increase product yield suggested by Park et al. (2008).

<u>2.4 Thermogravimetric Analysis</u>

Thermogravimetric analysis (TGA) is a method that is used to investigate the properties of materials as a function of temperature. The TGA measures and plots continuous graph as a function of temperature for example, mass loss and heat flow rate. Thermal decomposition is not only a first step of gasification or combustion process but it is also part of pyrolysis process (Rofiqul Islam et al., 2009). He also suggested that heat supply, total energy, and operation time are important design parameters for the pyrolysis process. A fundamental properties of a substance that can be determined and related to other properties (physical and chemical) is heat capacity. Enthalpies and entropies of transition can also be determined after obtain the heat capacity (Tong et al., 2007).

Basically, thermal properties of material can be determined by two methods, isothermal and non-isothermal using TGA measurements (Keuleers et al., 2002). Originally, solid state pyrolysis reaction can obtained from isothermal method analysis. Many experiments are required to be performed under isothermal condition and results are shown in term of non-isothermal during initial heating period until temperature reaches the desired point (Agrawal, 1992; White et al. 2011). Isothermal is time consuming due to the wide range of temperatures. The non-isothermal is more attractive because the temperature range of the experiment can be investigated directly (Agrawal, 1992; White et al. 2011).

Keuleers et al. (2002), used the modulated TGA non-isothermal method to determine the activation energy of $Mn(Urea)_2Cl_2$ by comparing the results with N-n-propyloxamide. It was used as a reference compound under the same experiment condition because the complexity of the decomposition. Ebrahimi-Kahrizsangi and Abbasi (2008) used the Coats-Redfern (CR) equation to investigate the reliability of the kinetic parameters of non-isothermal under different rate measurement. The CR method simulated the TGA curve of the reactions with different kinetic models, for example chemical, diffusion (Janders) and mixed mechanism, but the CR method cannot well-define the right reaction model. Later, Chen et al., (2006) proposed a single non-isothermal dynamic curve which can correctly described by several reaction models with a model-fitting approach. The activation energy is explained mathematically from the kinetic reaction curve of the property. According to this study, the activation energy increases linearly as the number of nth-order and Avrami-Erofeev reaction model increase. However the activation energies derived from fitting a single non-isothermal dynamic curve to nth-order and Avrami-Erofeev reaction model can be correlated through the activation energy of 1st order model (Chen et al., 2006).

CHAPTER 3

METHODOLOGY

3.1 Feedstock

According to Aylon et al. (2005), the reaction which occurs in during pyrolysis experiment is the endothermic reaction; the temperature in during the reaction was affected by the size of the particle. Oyedun et al. (2012) and Cuypers and Helsen (2011) agree that the smaller particle size will conduct the faster heat transfer and reduce the retention time during the experiment but small particle size will increase the power consumption during the experiment. On the other hand Seebauer et al. (1997), proposed that the larger particle size has shorter retention time due to the low porosity in the reactor. According to this experiment, size of the particle was control by using the commercial wood pellets which available in the market in order to the result of the experiment consistent. Hence the wood pellets which made from 100% pine wood was used as the feedstock as shown in figure 3.1. The size of the wood pellets feedstock is 5±0.05 mm. in diameter and 13±3 mm. in length. The wood pellets have been kept in the bag before the experiment to control the moisture content from the air transfer to the feedstock.

Figure 3.1 Wood pellets feedstock

3.2 Feedstock Analysis

Basically, if the chemical compositions of the particle are known the other properties of the particle can also be determined for example heating value, ash, and volatile etc. Sjostrom (1993) presented that fiber is the major composite of the wood and it contains about 40% of cellulose. He explained that the cellulose contains about 42.06% of carbon (CO_2), 6.06% of hydrogen (H_2), and 46.38% of oxygen (O_2) which can written in the form of $C_6H_{10}O_5$.

Thermogravimetric analysis (TGA) is the basic equipment which uses to investigate the thermal behavior of the sample. Skreiberg et al. (2011) said that the pyrolysis rate, heat and mass transfer, and mass lose kinetic rate also obtainable from TGA. Kim et al. (2010) investigated pyrolysis behavior of pine tree by using TGA which run under nitrogen (N_2) 20 mL/min mass flow rate under different heating rate of 5,10, 15, 20°C/min from 40°C to 800°C. At the same time Kim et al. also use Micro-tubing reactor to pyrolyse the sample. According to Kim et al. (2010), TGA experiment, the differential rate of conversion and $\frac{dX}{dt}$ are obtained from different heating rate. The highest peak contribute to the decomposition of cellulose and hemicellulose C (Müller-Hagendorn et al., 2003; Fisher et al., 2003; Kim and Agblevor, 2007; Park et al., 2009; and Kim et al., 2010) claimed that $\frac{dX}{dt}$ in the DTG curve increase respectively due to the heating rate. Skreiberg et al. (2011), Kim et al. (2010), and Hu et al. (2002) showed that the kinetic parameter can be obtained from TGA experiment. The activation energy which required during the experiment is about 241.17 kJ/mol from 20% conversion was calculated from Kim et al. Hence, SDT Q 600 from TA instrument (Figure 3.2 a) was used to investigate the material decomposition and thermal characteristic. Prepared sample was load into the ceramic pan as shown in figure 3.2 b about 5-15 mg. The sample pan was previously tare with the reference pan; this pan will keep empty the entire test as the reference (figure 3.2 c). According to pyrolysis experiment, N_2 was used as the atmosphere condition in the TGA to represent the absent of air in the pyrolysis. The sample was heated up with different heating rate 5, 10, and 20 °C/min from room temperature to 700°C to observe the point which mass has

insignificantly change during the pyrolysis . Then the set point and temperature range of pyrolysis experiment was selected. Then the air was applied to the experiment to determine the ash content in the sample.

(a)

(b)
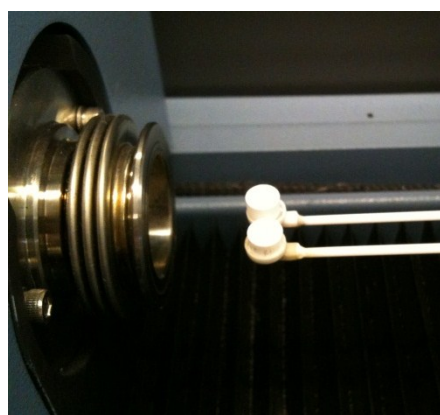
(c)

Figure 3.2 TGA instrument (a) SDT Q600 for TGA (TA Instruments, 2011), (b) Sample particle,

(c) TGA reference and sample pan

3.3 Pyrolysis Experiments

Pyrolysis experiment was performed by using the set up as illustrated in figure 3.3.

Figure 3.3 Pyrolysis diagram

4 sets of cartridge heater with 750 watt heating value were place into 10 litters of reactor as shown in figure 3.4a. Various loads of feed stock were loaded into the reactor. Then oven gasket and vacuum grease were used to seal the reactor. 2 outlets of copper tubes were connected to the top of the reactor lid which leads all gases and volatile matter to the condensing zone (figure 3.4b). 2 sets of thermocouple were place in the aluminum blocks inside the reactor and another was placed between the can and insulator. These thermocouples were connected to the monitor and controller in order to bring the temperature to the set point at 450°C. The wired heater was used as the outside heater which wrapped around the can to eliminate the possibility of gas to condense and the 1.5 inches of insulator was used to maintain the heat inside the reactor from transferring to the environment. Hence, the reactor was connected to electrical supply which stabilize the voltage by variac. The auto proportional-integral-derivative (PID) controller (CN7523, omega) and a solid state relay (SSR330DC25, omega) as shown in figure 3.5a and 3.5b were used in this experiment. While ramp the experiment up, data logging multimeter (Fluke 287) (figure 3.5c) was connected to the power line to observe the electrical consumption of the experiment.

After finish system set up in figure 3.6a, electrical was supply to the cartridge heaters about 82 Volt. Then the PID controllers will automatically control power supply to reach each set point. Various loads of wood pellets were experimented under the same condition and set point. Power consumption, amount of product, and retention time were recorded. The decomposition of feed stock started at a certain product, water and oil vapor respectively. The

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gas vapor and volatile escaped the reactor to the condensing towers through the copper tubes. The condenser columns were connected to the recirculating water chiller with the 0°C initial temperature in figure 3.6b and 3.7. Condensable gas and volatile which escaped the reactor through the copper tubes was condensed at the condensing tower area and flew down to the collector. Liquid products were collected at the round flask collector and separated later. Some of non-condensable gases will exhaust to environment at the top of the towers. Gas collector set with 1-liter flex foil bag (figure 3.5d and e) was installed at the top of the condenser. Then the gases were used in the gas characterization

(a)   (b)

Figure 3.4 Apparatus for pyrolysis experiment (a) Cartridges heater with 750 watt power,

(b) Round collector flask

(a)   (b)

(c)   (d)

(e)

Figure 3.5 Apparatus for pyrolysis experiment (a) PID controller (CN7523,Omega), (b) Solid-

state relay (SSR330DC25, Omega), (c) Multimeter (Fluke 287), (d) 1-liter FlexFoil bag (SKC),

(e) Plastic gas collector tube
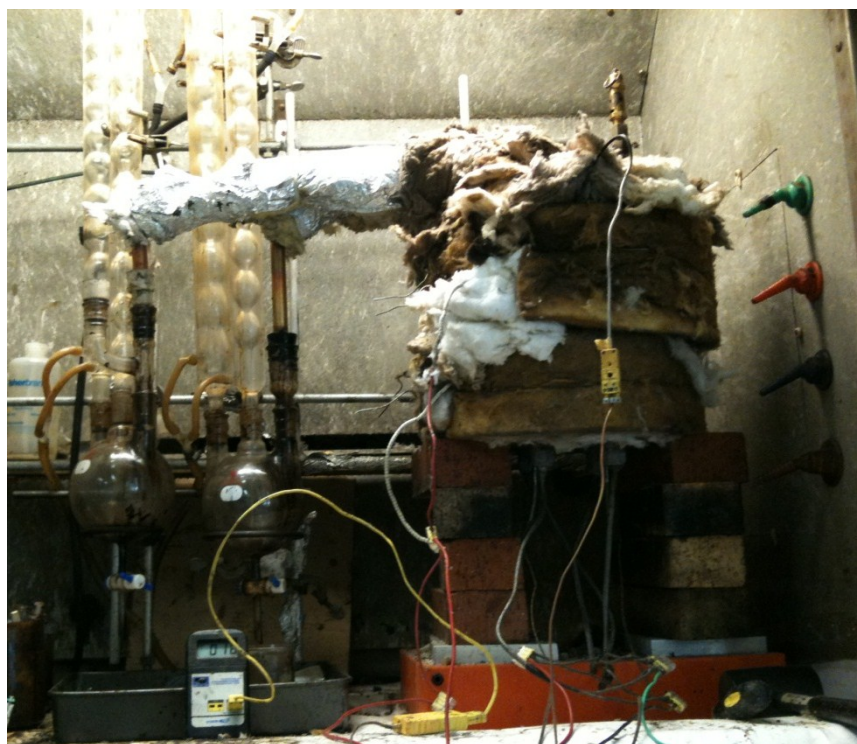
(a)

(b)

Figure 3.6 Pyrolysis experiment set up (a) Pyrolysis reactor with complete set up

(b) Recirculating water chiller

Gas Exhaust

Condensing Tower

Recirculating
water chiller

Multimeter

Reactor

Collector

Collector

Solid state relay

Power supply

PID Controller
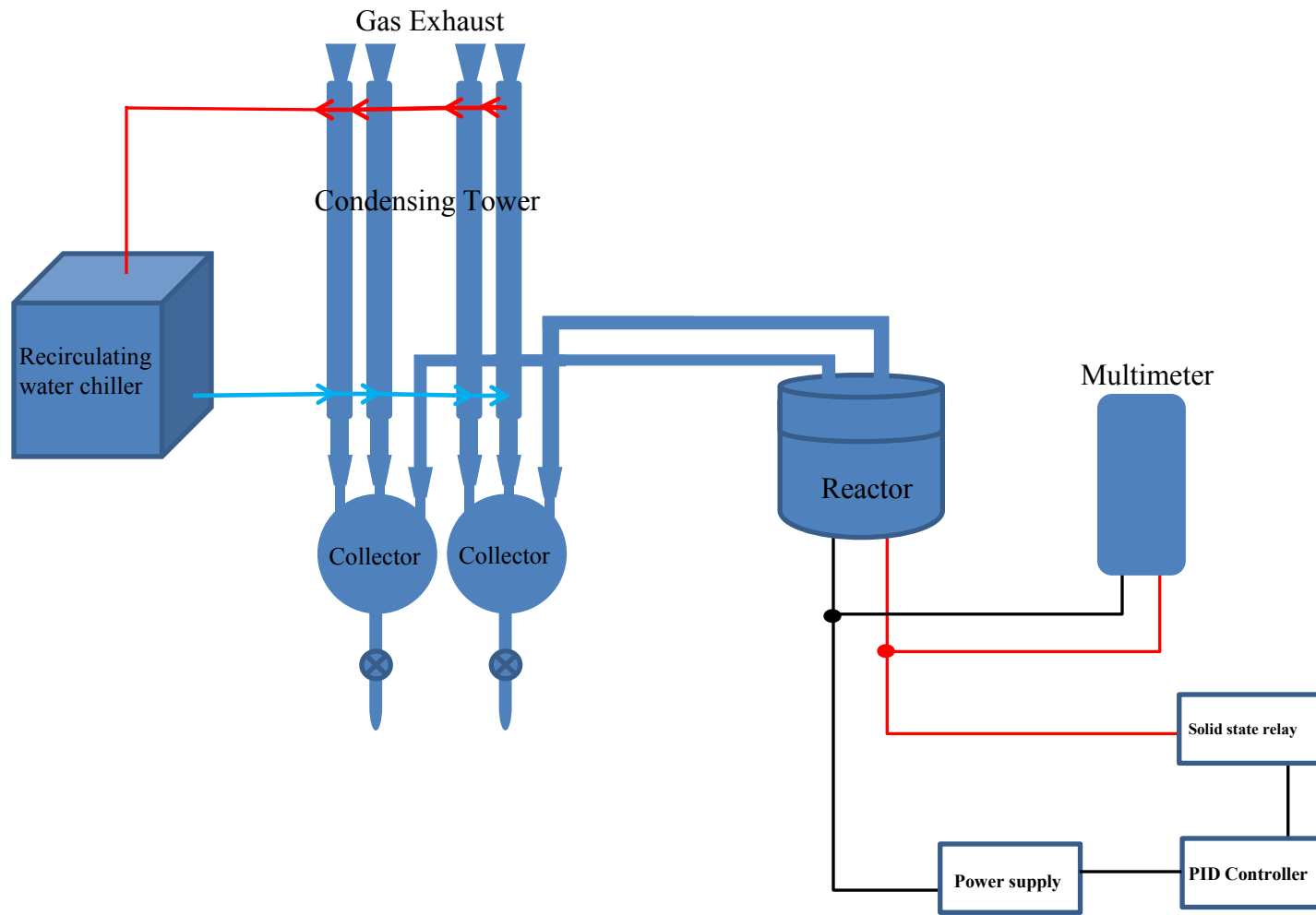
Figure 3.7 Pyrolysis system schematic diagrams

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<u>3.4 Oil Characterization</u>

The gas chromatography (GC) was used to analyses the composition and concentration of the mixture in both gas and liquid phase. GC basically operated under mobile and stationary phase. The mobile phase will carry the gas along the column, while the stationary phase is a packed or capillary column. The column will be used depend on the compound and purpose of the analyses. After sample was injected into the GC, different compound will travelling along and exist the column with different rate and time. The concentration peak of compounds is presented as thermal conductivity detector (TCD) or flame ionization detector (FID).

The GC which was utilized in this oil analysis experiment is

Model: SRI 8610C, FID, Figure 3.8

Carrier gas1: Helium (He) operated at 20 psi, 10 mL/min flow rate

Carrier gas2: Hydrogen (H_2) operated at 22 psi, 25 mL/min flow rate

Column type: Capillary column, from Restek corporation

Specification: 6m in length, 0.53 mm ID, 0.5 μm MXT ®-500 simulate distillation (cat.#70104) cold on column injection of Polywax® 655 in CS_2

Standard temperature as shown in Table 3.1 which was applied in this experiment is the ASTM D2887 (Standard test method for boiliang range distribution of petroleum fraction by gas chromatograph). Basically the GC uses the different in boiling point of substances. Different compounds boil at different temperature and time.

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Table 3.1 ASTM D2887 temperature program for oil analysis

Initial temperature, ^{o}C	Hold, min	Ramp, ^{o}C/min	Final temperature, ^{o}C
37	1	35	380
380	5	-50	39

Figure 3.8 SRI 8610C GC for oil analysis

Oil from pyrolysis experiment was separated to eliminate water and moisture content. Then 100 µL of fresh oil was drawn by auto pipette and injected in to a dram glass vial. The sample was diluted with 4 mL of toluene and only 1 µL was injected to the GC by a 5 µL microsyringe as shown in figure 3.9a and b.
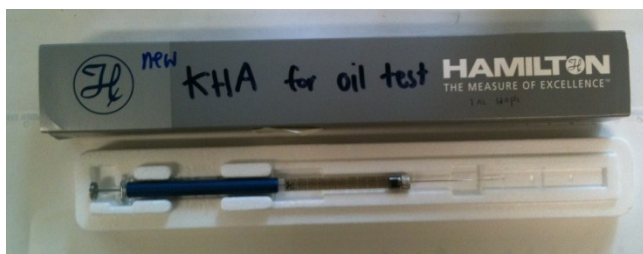
(a)   (b)

Figure 3.9 Apparatus for liquid characterization (a) Sample after dilution, (b) Hamilton 5 µL syringe

3.5 Gas Characterization

The same GC method which used to analyses oil produce was applied to gas. However, the different type of detector was required to use with gas. According to this experiment Thermal Conductivity Detector (TCD) as shown in figure 3.10a was the main GC apparatus to determine the composition of gas. Therefore, GC model: SRI 310C, TCD

Carrier gas: He operated at 7 psi, 10 mL/min flow rate

Column type: pack column from Restek corporation

Column: Shin Carbon ST 100/120 mesh (Cat #19809),

1 m in length with 1 mm ID Silcosteel® micro packed column

Isothermal temperature at 70^oC which hold for 50 minute was set as a temperature program. Then 1 mL of gas was drawn from the gas bag and injected to the GC by using gas tight syringe (figure 3.9b).

(a)   (b)

Figure 3.10 Apparatus for gas characterization (a) SRI 310C GC (b) SGE 0.5 mL gas tight syringe

3.6 Residue Characterization

TGA was introduced again to analyze the residue but the experiment was only run under nitrogen (N_2) atmosphere in order to investigate the volatile matter which remains in the residue.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Feedstock Analysis

Knowing the composition of the feedstock will help to understand and predict heating value and thermal properties. The analysis can be done experimentally by two method; proximate analysis and ultimate analysis. The ultimate analysis requires the specific and expensive equipment. On the other hand, proximate analysis can be obtained from the easy laboratory equipment said Erol et al. 2001.

4.1.1 Heating value

Basically, the heating value can be determined by using bomb calories meter. Ultimate or proximate analyses are another method which uses to determine heating value of the feedstock. The commercial wood pellets which were used during the experiment were glide in to 60 mesh size. Then wood pellets particle was put in TGA with the heating rate 10°C/min from room temperature to 100°C and hold for 10 minute to eliminate the moisture content in the sample. Then same heat rate was applied to the sample until the temperature reach 700°C. Fixed carbon and volatile matter which received from the TGA graph (figure 4.1) were used to estimate the heating value of the wood pellets as shown in table 4.1. The heating value can be determined from the equation 4.1. According to the accuracy analysis which was done by Erol et at. (2010) showed that the equation give the best accuracy of the result. On his conclusion showed that the equation gave only ±3 relative error which is the best result when compare with other equations.

Table 4.1 Proximate analysis of feedstock

Feedstock	%Moisture	%Volatile matter	%Fixed carbon	%Ash	HHV (MJ/kg)
Pine wood pellets	7.33	74.38	16.29	2	19.12

$$HHV= 13.0+0.392(FC)-0.00735(FC)^2-0.0231(As)+0.0149(VM) \qquad (4.1)$$

where FC, As, and VM are fixed carbon, ash, and volatile matter respectively. The heating value from the experiment proximate analysis was showed in the table 4.1. The same proximate analysis has been done by different authors as shown in table 4.2.
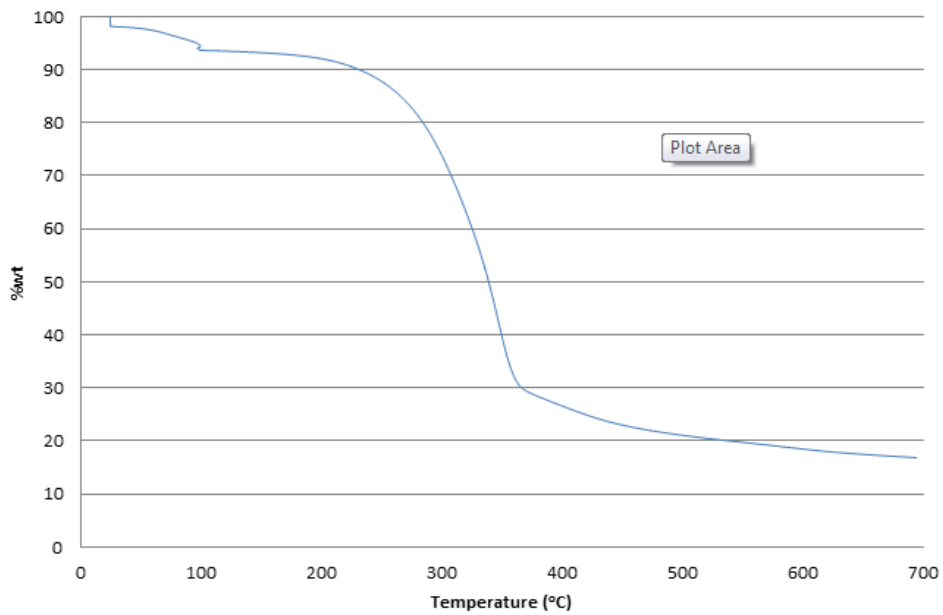
(a)
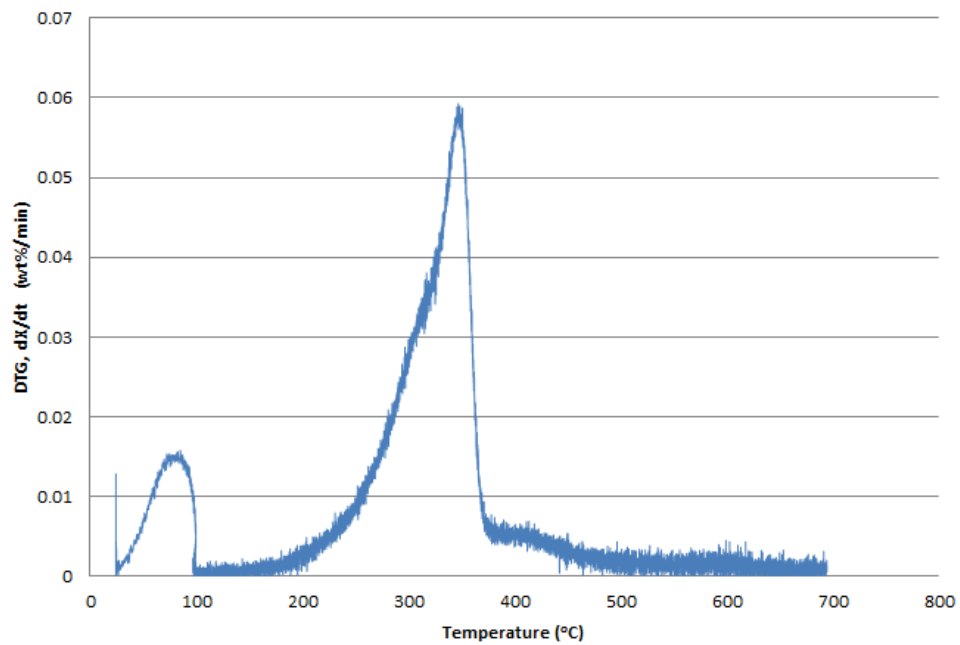
(b)

Figure 4.1 Plot of (a) Weight loss versus temperature, and (b) Rate of weight loss versus

temperature of the wood pellets under N$_2$ atmosphere at 10°C/min heating rate

Table 4.2 Proximate analysis of different pine wood from literature

Type of pine wood	HHV (MJ/Kg)	%Fixed carbon	%Volatiles	%Ash	%Moisture	Reference
Pine wood pellets	19.95	14.34	85.58	0.08	7	Skreiberg et al. (2011)
Pine saw dust	19.92	15.86	81.94	2.16	N/A	Chen et al. (2008)
Pine wood chip	N/A	60.32	15.08	10.77	13.83	Ryu et al. (2012)
Pine tree	20.0	N/A	N/A	0.9	4.09	Kim et al. (2012)
Torrefied loblolly pine	20.0	14.8	84.6	0.56	9.3	Meng et al. (2012)

4.1.2 Calorific requirement

The energy consumption or caloric requirement of the process plays an important role in the reactor's design, operation parameter specification, energy balance, and potential analysis for biomass pyrolysis, gasification, and combustion (He et al., 2006). According to He et al., 2006, Lauthouwers and Bellan, 2001, Janse et al., 2000, Jalan Sricastava, 1999, the caloric requirement can be determine from the equation (4.2)

$$Q = Cp,b \int mb\ dT + Cp,ch\ \int mch\ dT + Qp \qquad (4.2)$$

Where $C_{p,b}$ = specific heat of biomass (J/Kg-k)

$C_{p,ch}$ = specific heat of char (J/Kg-k)

Q_p = reaction heat of biomass

However, He et al.(2006) proposed that the range of pyrolysis is varied and the reaction take place continuously. Then the change in properties value should not be neglect. However, the specific heat and reaction heat is difficult to determine at high temperature. He et al. (2006) proposed that the heat requirement from the pyrolysis process can determine from the differential scanning calorimetry (DSC) curve measurement and sum with the reaction heat of the sample. Thermogravimetric differential scanning calorimetry (TG-DSC) was used to analyze the caloric requirement because the precision value of different mass change can be obtain as illustrated in figure 4.2. Another words the pyrolysis reaction would not occur if the heat available insufficient (Fantozzi et al., 2007)

Hence, overall heat capacity of the experiment can be determined according to the calorific analysis. Heat capacity of the product which is change as function of temperature was calculated by using heat flow and the heating rate. The heat capacity (Cp) of wood pellets from the experiment increased respectively to the temperature as illustrated in figure 4.3. The graph also showed that the Cp was highly changed around 350 to 450°C. Since sample was investigated and shown that the reaction is endothermic then the reaction heat will not present

in the system. Thus Cp value was used to determine the calorific requirement by substituted into equation 4.3.

$$\frac{Q}{m_{s,o}} = \frac{\int_0^f (m_s c_{p,s} \frac{dT}{dt} + m_s \dot{H}_p) dt}{m_{s,0}} \tag{4.3}$$

where ms = moss of sample during TG-DSC experiment (Kg)

      ms,0 = mass of sample at the beginning of TG-DSC experiment (Kg)

      cp,s = specific heat capacity of sample during TG-DSC experiment (KJ/Kg-$^{\circ}$C)

      $\dot{H}p$ = heat flow cause by reaction heat of biomass pyrolysis
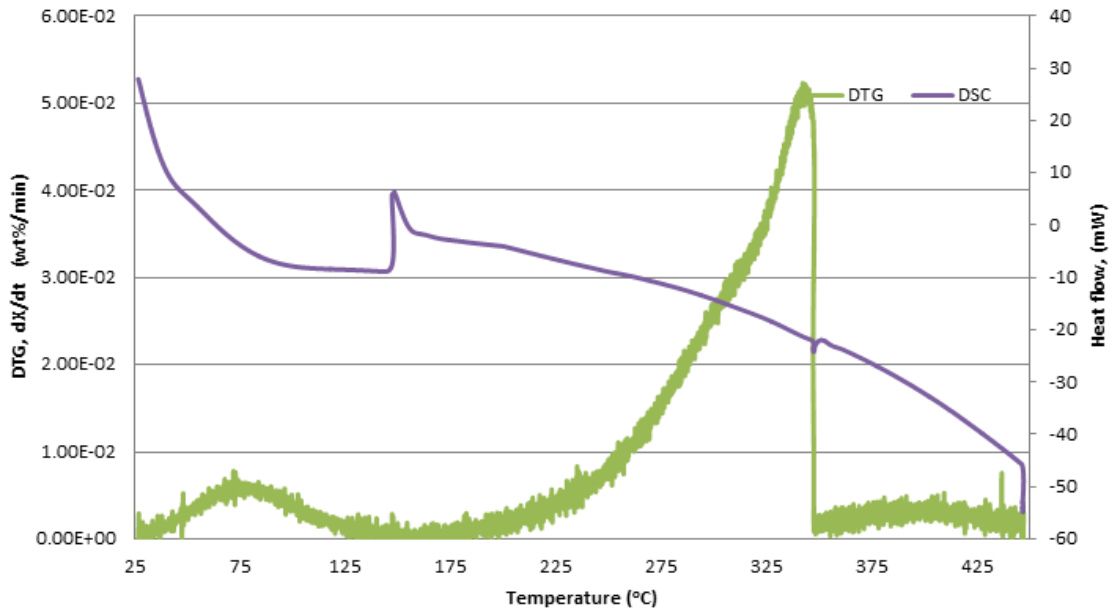
Figure 4.2 Comparison of DTG and DSC curve of wood pellets at pyrolysis condition
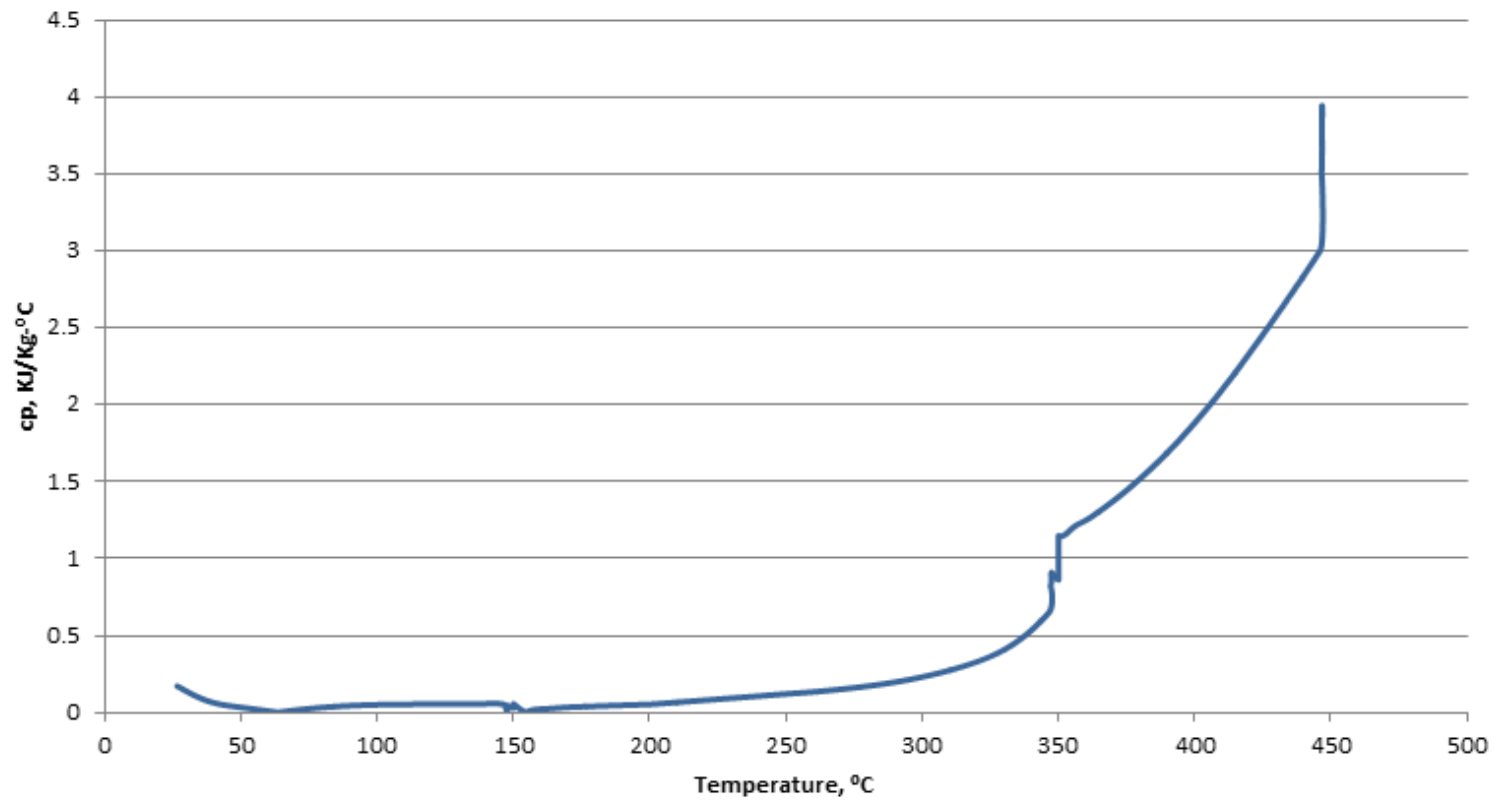
Figure 4.3 Plot of specific heat capacity (c_p) versus temperature of the wood pellets during the pyrolysis experiment

As a result of figure 4.2, endothermic process presented during whole degradation period. He et al. propose that the char tend to present more in the endothermic reaction than in exothermic reaction. The caloric requirement presents in figure 4.4.
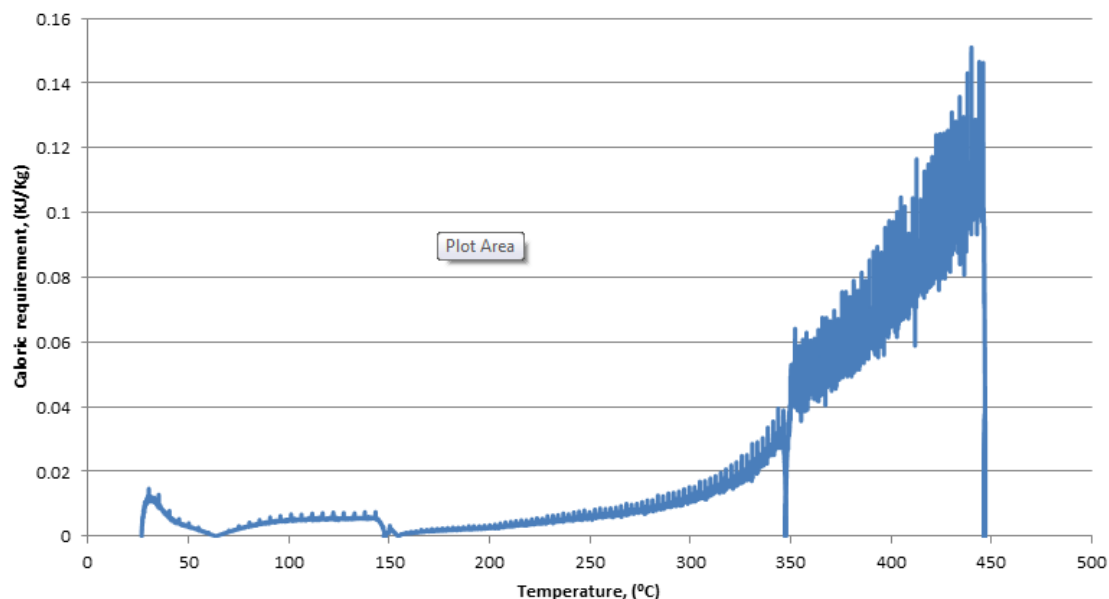
Figure 4.4 The calorific requirement of wood pellets by integration modified DSC

Then the graph was integrated to determine the total calorific requirement of the whole pyrolysis process. The graph showed that whole wood pellets pyrolysis needs only 289.84 KJ of energy is required per kilograms wood pellets of feedstock.

4.1.3 Chemical kinetics

The chemical kinetics of the process can also determine from TGA data. Kim et al. (2010) claimed that the investigation of characteristic and kinetics of pyrolysis feedstock will help to obtain helpful information of the fuel type (gas, oil, and char) which will generated from the process. According to this study, the degradation, characteristic and reaction mechanism of wood pellets can be understandable. Conversion X was obtained from TGA data can be calculated from equation 4.4.

$$X = \frac{Mo - Mt}{Mo - M\infty} \qquad\qquad (4.4)$$

where M_0 = initial mass of sample

M_t = mass of pyrolysis sample

M_∞ = the final residue mass

X = conversion factor

Different heating rate must be applied to experiment which perform by TGA (Leroy et al., 2006; Khawam and Flanagan, 2005; Skreiberge et al., 2011; Ebrahimi-Kahrizsangi and Abbasi, 2008). The heating rate 5, 10, and 20°C/min were used to perform the experiment as shown in the figure 4.5. Size of the DTG curves expands as the heat rate increase. The decomposition tends to increase respectively to the heat rate because more energy compensates the system and better heat transfer from the inside of the sample and the surrounding (Caballero et al. 1997). The significant decomposition temperature is between 200-450°C.
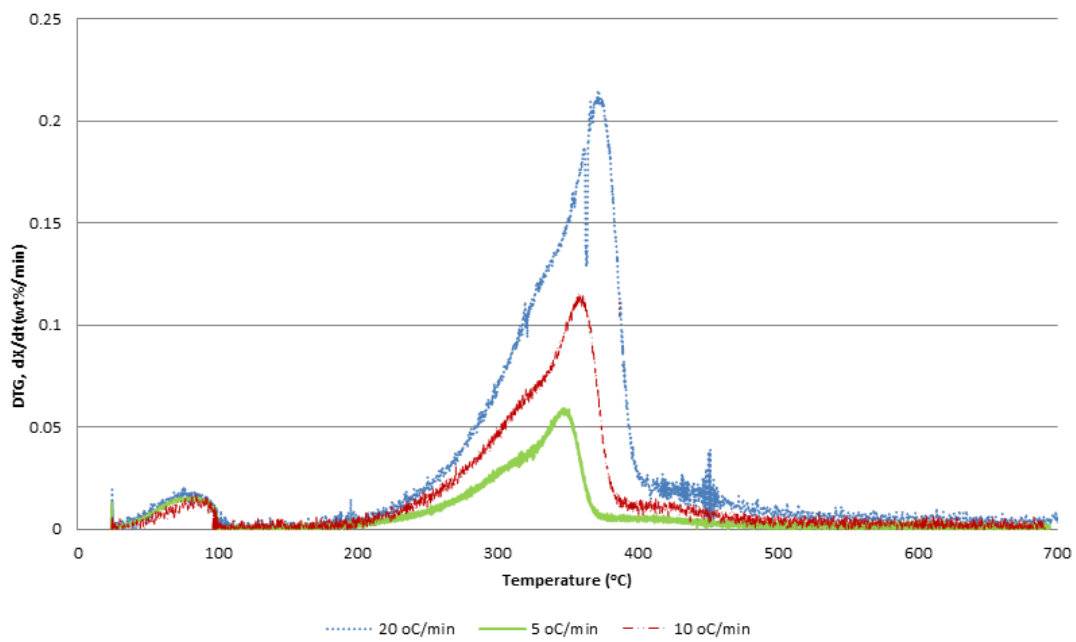
(a)
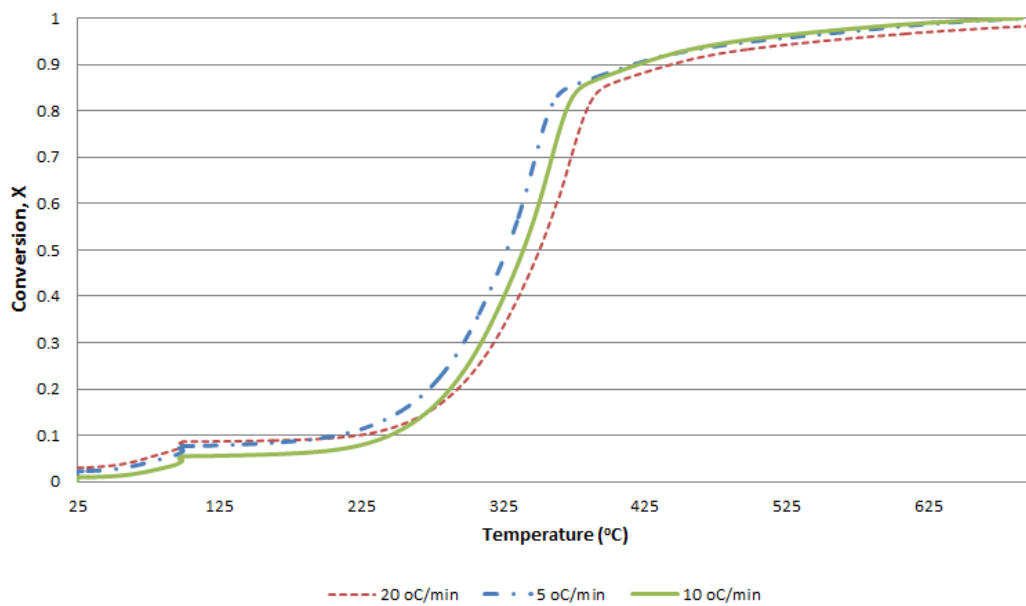
(b)

Figure 4.5 Plot of (a) DTG (b) TG illustrated the effect of wood pellets at different heating rate

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According to Vyazovkin (2000a, 2000b, 1997), the Arrhenius equation describes the rate constant as a step reaction and temperature. The kinetic of solid reaction may have mutated reactions and form (Brown et al., 2000 and Khawam and Flanagan, 2006). The thermal analysis method was used to determine the weight and enthalpic change of solid-state reaction said Khawam and Flanagan (2006). The empirical method was used to develop the Arrhenius equation. The theory was used only to determine the collision of gases and solution. But, later the equation was also used for solid-state kinetic (Khawam and Flanagan, 2006 and Galwey and Brown, 2002). Solid-state kinetics can be studied with thermal analytical method by measuring properties of sample while it is being heated, or held in a constant temperature. (Khawam and flannagan, 2006; Brown, 1998; 2001). However, El may et al. (2011) proposed that the Arrhenius equation working good in determination of mixture rubber in non-isothermal. Mostly, the kinetic is determined by the weight loss from the reaction by using TGA. Heat (exothermic or endothermic) can be measured by differential scanning calorimetry (DSC) or differential thermal analysis (DTA). Weight loss is converted into conversion factor (α), range from 0 to 1. The conversion fraction is measure from the experimental reaction as a function of temperature. The reaction activation energy is determined by applied isoconversional method or model free method, which can be done by grouping the pre-exponential factor (A) and put them into the intercept of linear equation the activation energy can be calculated by the slope (Khawam and Flanagan, 2006).

Arrhenius equation was introduced in the pyrolysis experiment in order to describe the chemical kinetic of the experiment as shown in equation 4.5.

$$Ki = Ai\ exp\left(-\frac{Ei}{RT}\right) \tag{4.5}$$

where Ki = pyrolysis rate constant (min⁻)

A = pre-exponential factor (s⁻)

Ei = activation energy (KJ/mol)

R= gas constant (8.314 J /mol-K)

T = absolute temperature (K)

The equation 4.5 was interpreted to suit TGA data. The differential method was used to determine pyrolysis chemical kinetic parameter (Kim and Agblevor, 2007; Maiti et al., 2007; Park et al., 2009) as equation 4.6.

$$\ln\left(\frac{dX}{dt}\right) = \ln(AX^n) - \frac{E}{RT} \tag{4.6}$$

Activation energy can be determined from the plot of $\ln(\frac{dX}{dt})$ versus $1/T$ (figure 4.6). The conversion range from 10 to 90% was applied to the equation. When slop of the graph use to determine $-\frac{E}{R}$ and the interception point use to determine $\ln AX^n$. When n orders are 0, 1, and 2 (Kim et al., 2010). Then pre-exponential factor (A) can obtained from equation 4.7

$$\ln(AX^n) = \ln A + n\ln(X) \tag{4.7}$$

The activation energy and pre-exponential factors were calculated as shown in table 4.3.

Table 4.3 Calculated kinetic parameter for the pyrolysis of wood pellets

Conversion factor (%)	Activation energy (KJ/mol)	Pre-exponential factor (A, $\frac{1}{min}$) Order of reaction		
		0th	1st	2nd
10	89.941	2.11×10^7	2.11×10^8	2.11×10^9
20	176.938	1.22×10^{15}	6.08×10^{15}	3.04×10^{16}
30	185.285	2.33×10^{15}	7.77×10^{15}	2.59×10^{16}
40	178.818	2.73×10^{14}	6.81×10^{14}	1.7×10^{15}
50	179.025	1.48×10^{14}	2.95×10^{14}	5.91×10^{14}
60	172.915	2.69×10^{13}	4.49×10^{13}	7.49×10^{13}
70	170.76	1.34×10^{13}	1.91×10^{13}	2.73×10^{13}
80	182.134	4.62×10^{13}	5.77×10^{13}	7.22×10^{13}
90	234.455	3.36×10^{15}	3.73×10^{15}	4.15×10^{15}
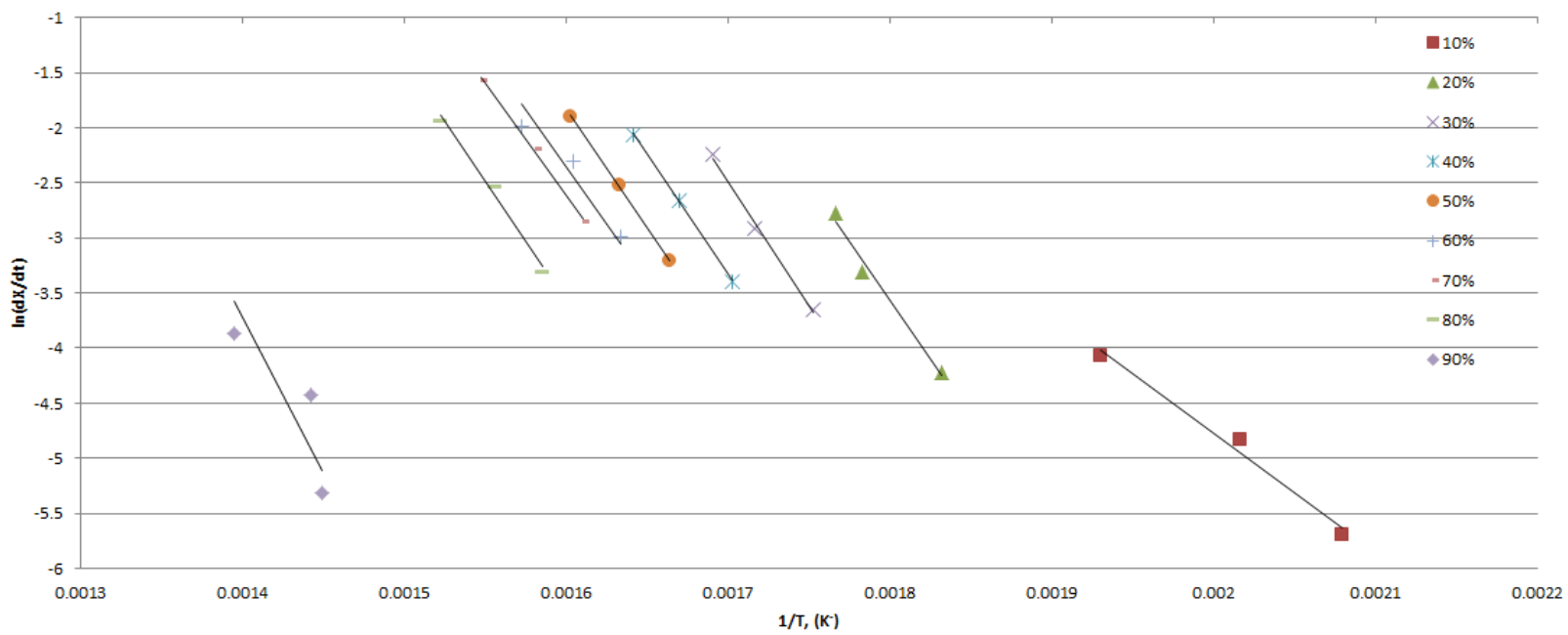
Figure 4.6 Plot of $\ln(\frac{dX}{dt})$ vs $\frac{1}{T}$ with heat rate of 5, 10, and 20 °C/min, the conversion values range from 10% to 90%

4.2 Pyrolysis

During the experiment, different loads of the biomass was used by varied from 4, 5, 6, and 7 lb to investigate the power consumption and combustible product. The chemical reaction which takes place during the pyrolysis process is difficult to explain. The scheme which was presented by Kaufopanos et al. (1991) was used in this experiment. Kaufopanos et al. (1991) explained that the biomass under pyrolysis reaction will decompose into volatiles, gases, and char. Under the same circumstance volatiles, gas, and char may re-decompose into volatile, gas, and char in different composition as shown in the figure 4.7.
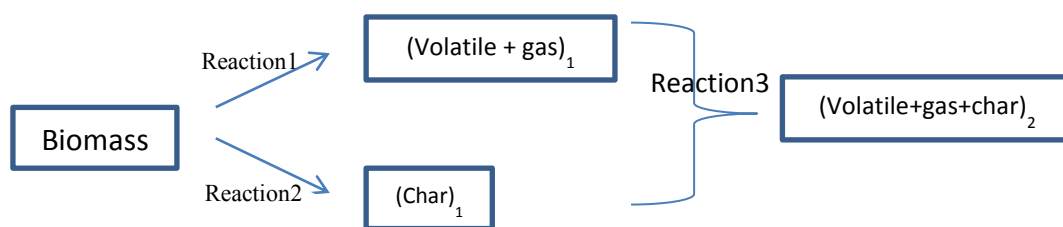
Figure 4.7 Kinetic scheme presented by Kaufopanos et al.

Final temperature of the experiment is needed to determine at the optimum point at the same heating rate. Bae et al. (2011), Jung et al. (2008), Park et al. (2009), Apaydin-Varol et al. (2007), and Wang et al. (2010) explained that the incomplete pyrolysis process at low temperature will increase the char product. However, this experiment will concern both product and energy consumption during the process. Wood pellets were tested with different final temperature to observe the products and the energy consumption during the experiment as illustrated in the figure 4.8. As a result of graph in figure 4.8, the final temperatue which suitable for the experiment is 450°C. The oil which produce during the pyrolysis experiment is the most concern product because the oil can be converted by the refinery process into the value able gasoline and disel fuel. Then the energy which use per grams oil can be determined as shown in the figure 4.9. Pyrolysis reactor consumes smallest amount of energy per grams of oil which is 34.03 KJ per grams oil.However if the pyrolysis was kept operating until temperature reach

500°C, the product was barly collected envent in the gas phase but the temperature was raising about 1°C/min. Until temerature reach about 530°C temperature hardly change from this point and the reaction could not identify.
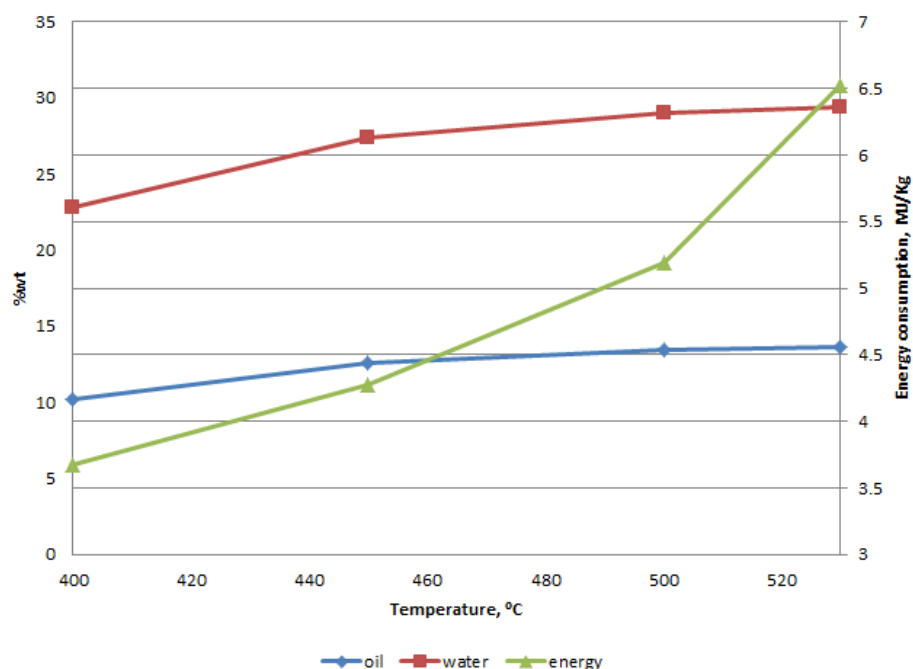
Figure 4.8 Percent pyrolysis product distribution of wood pellet and energy consumption versus temperature

After performed the experiment with different feedstock loads, products which were harvested and the energy consumption of the experiment presented in the table 4.4. Regarding to the experiment result, products (gas, water, and oil) increase as the load increase, also the electrical consumption. However, the retention time are indifferent no matter which load was put into the reactor. The same determination which used to select the final temperature was applied to determine the suitable load for the reactor.

On the other hand, residual (char), retention time of the experiment slightly decreases as the load increase and also the power consumption per kilogram of feed stock. Furthermore, liquid products from pyrolysis come out at certain range of temperature. Particularly, water will

condense first around 150-194°C, the oil will come out around 252-323°C and char is the final

product which need about 6 hours to cool down before able to unload (figure 4.10).
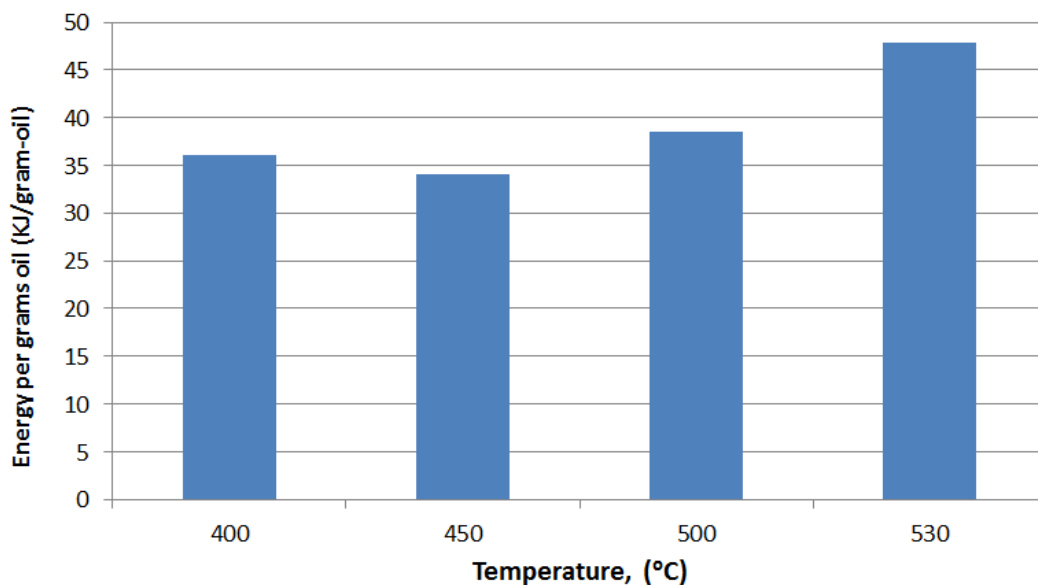
Figure 4.9 Show the amount of energy consumption per grams of oil at different temperature

set point

Table 4.4 Pyrolysis product distribution of wood pellets at different load

Load (lb)	Products (%wt)			
	% Water	%Bio-oil	%Residue	%Gas[a]
4 (1.81kg)	38.02	9.82	32.35	19.81
5 (2.27kg)	34.92	8.82	31.56	24.7
6 (2.72kg)	37.32	7.93	31.27	23.48
7 (3.18kg)	33.51	8.79	31.57	26.12

Note: [a] percent gas production obtained by difference.

| (a) | (b) | (c) |
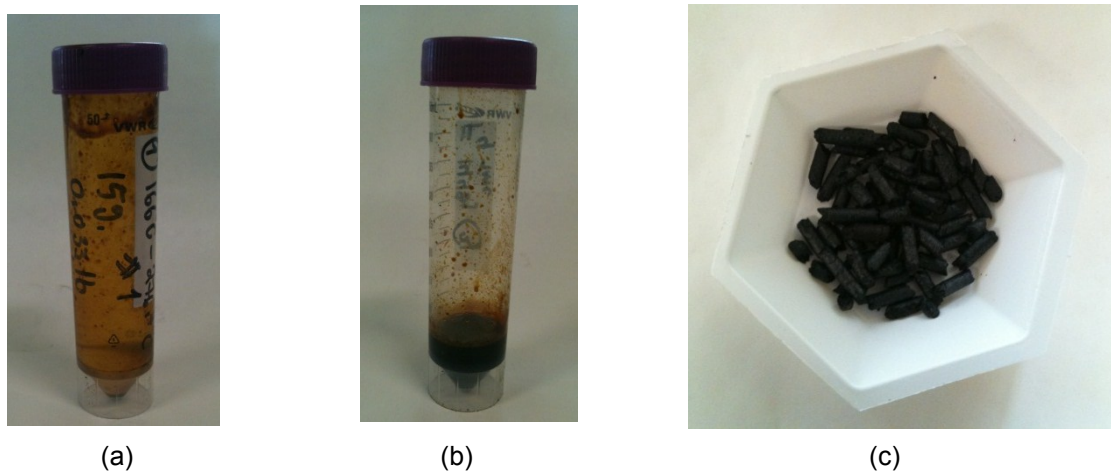
Figure 4.10 Pyrolysis products (a) Water, phase (b) Bio-oil, and (c) Char

4.3 Oil Characterization

The composition of bio-oil from wood pellets pyrolysis at temperature set point $450^{\circ}C$, analyzed by using GC illustrated in the figure 4.12. The graph illustrated the group of peak during 1.5- 5 and 6-9 minute retention time. According to the ASTM 2887 standard as shown in figure 4.13 and the data set from the table 4.5, the major compound of the bio-oil wood pellets should contain with C_{11}-C_{16} and C_{24}-C_{36}. The boiling point of the compounds are from 196-287 and 391-$507^{\circ}C$ respectively. Moreover, the simulation distillation which presented by Reis-Vasco et al. (2000), Xavier et al. (2011), Cassel et al. (2009), can be used as simulation the product after the oil distillation in the refinery process. The right distillation method must be applied depend on the oil. The simulation method is another alternative way which used to estimate the product and method which will perform (Cassel and Vargas, 2006). Basically, GC will separate product in the boiling range from C_5 to C_{120} but GC which was performed during this experiment can separate in the range of C_9 to C_{44}. The detectable temperature range is depending on the standard which used with the GC.

This simulation interprets the GC data and present in the simulation curve form. As a result of the different in boiling point range of each compound and retention time then the curve can plot as illustrated in figure 4.11. Xavier et al. (2010) said that the oil is considered as a

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single compound when use in the mass balance. Then the mass transfer of oil will consider as one single mass throughout the process.
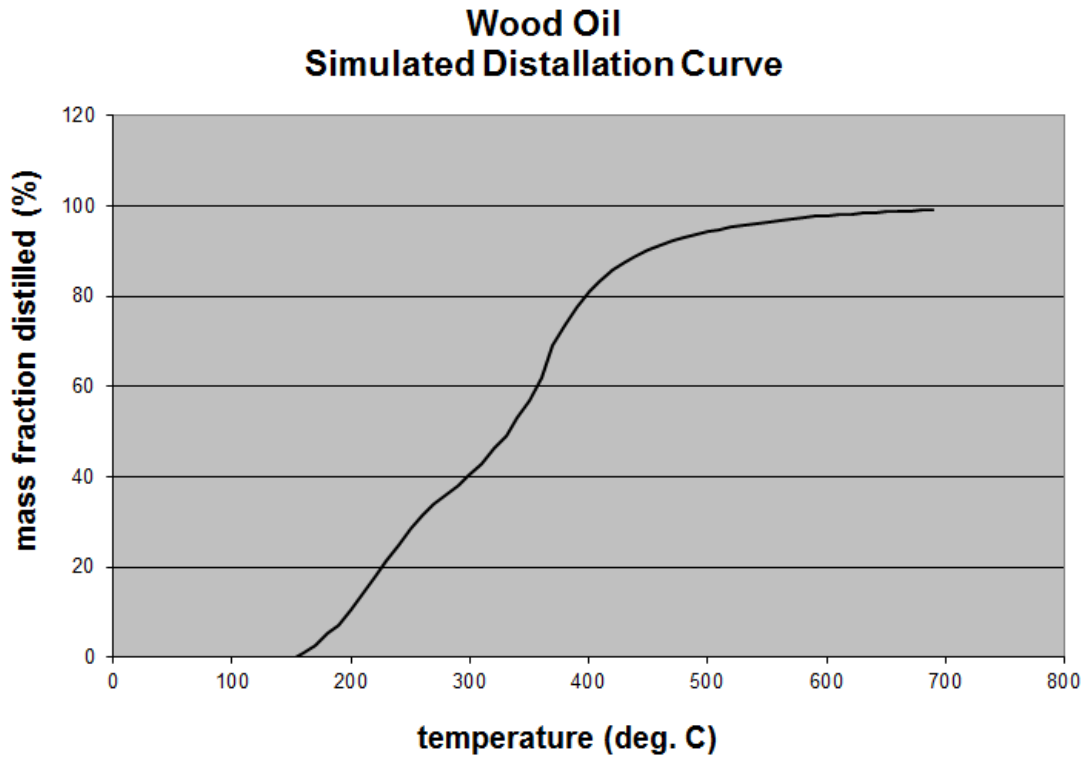
Figure 4.11 Simulation distillation of wood pellets bio-oil
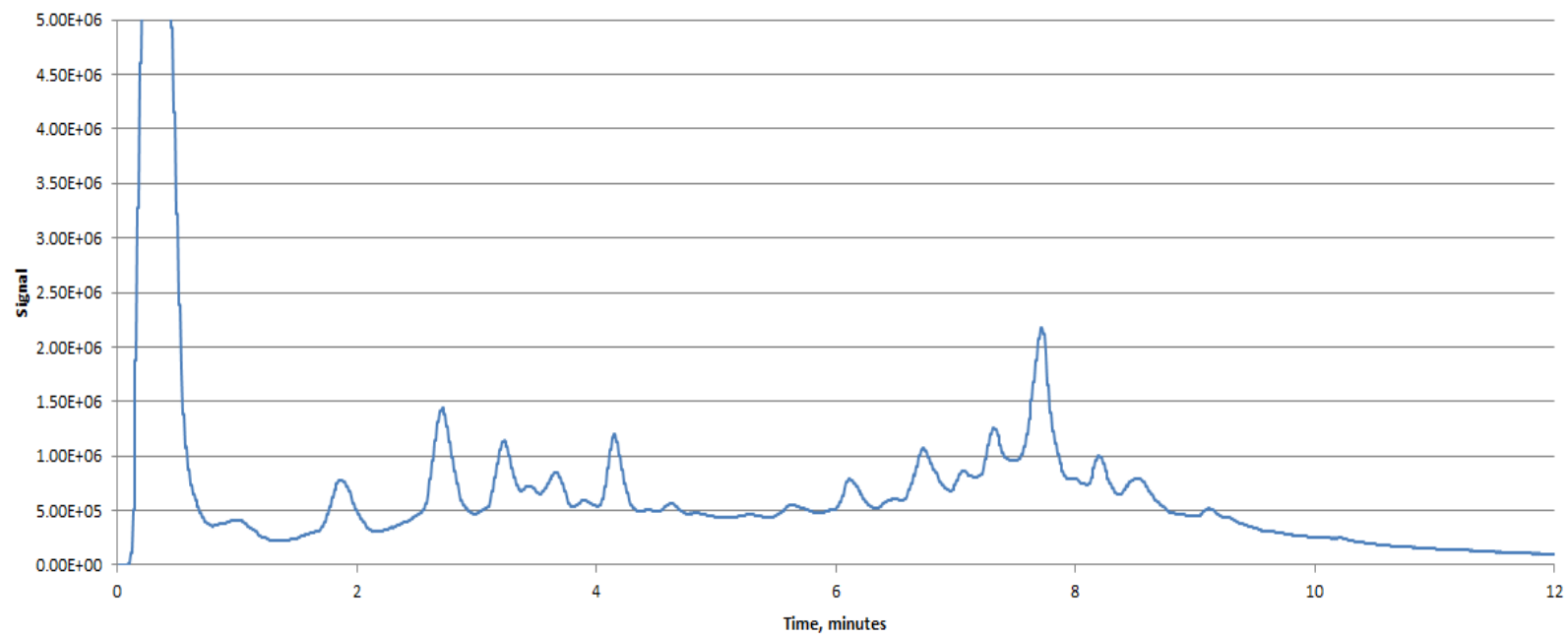
Figure 4.12 The gas chromatography of wood pellets bio-oil from wood pellets pyrolysis at temperature 450°C
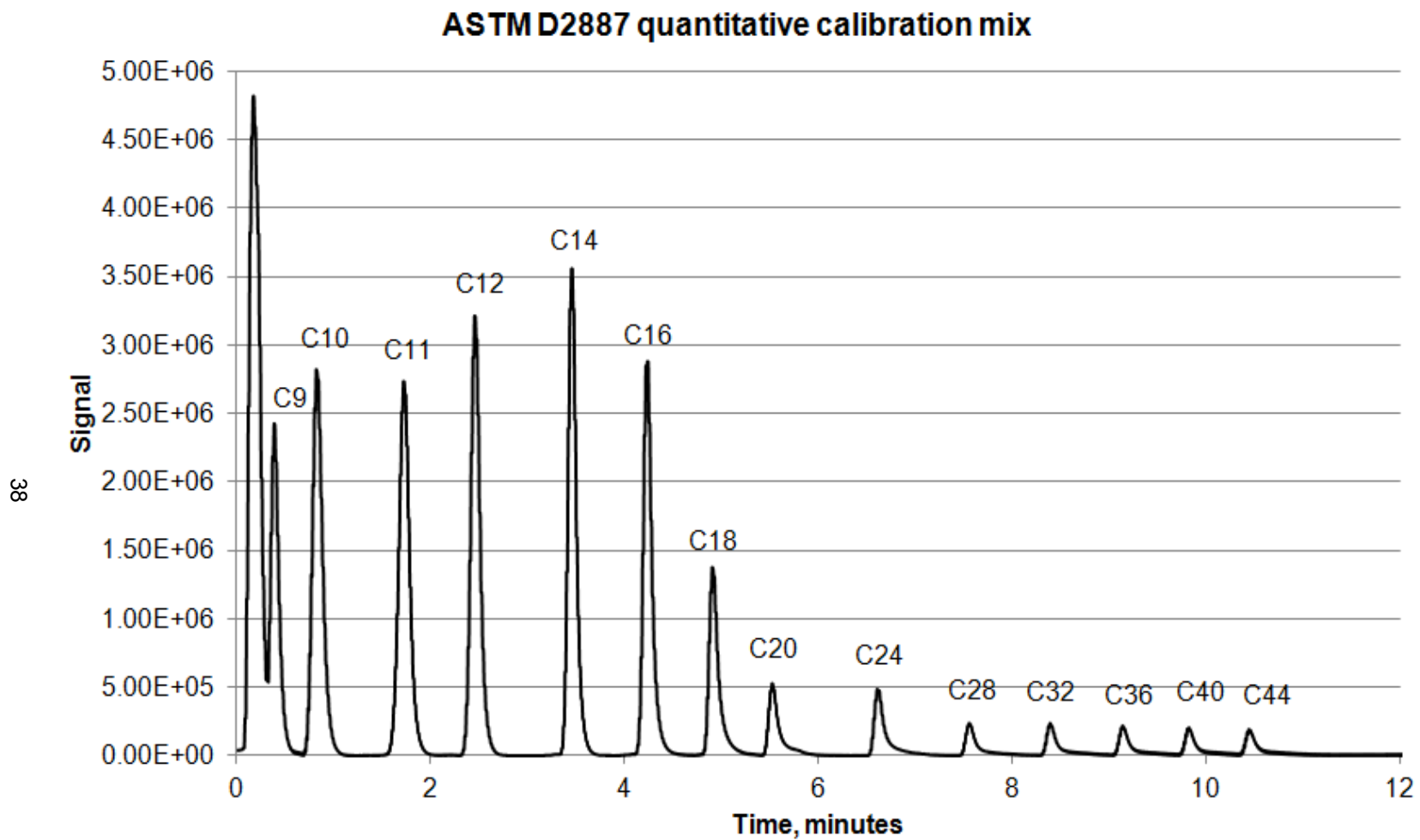
Figure 4.13 Gas chromatography of ASTM D2887 quantitative calibration mix

Table 4.5 Boiling point and retention time of standard components

Name	Formula	Temperature, °C	Time, minute
Nonane	C_9H_{20}	151	0.400
Decane	$C_{10}H_{22}$	174	0.816
Undecane	$C_{11}H_{24}$	196	1.716
Dodecane	$C_{12}H_{26}$	216	2.450
Tetradecane	$C_{14}H_{30}$	253	3.450
Hexadecane	$C_{16}H_{34}$	287	4.233
Octadecane	$C_{18}H_{38}$	317	4.900
Eicosane	$C_{20}H_{38}$	359	5.516
Tetracosane	$C_{24}H_{50}$	391	5.600
Octacosane	$C_{28}H_{58}$	408	7.550
Dotriacontane	$C_{32}H_{66}$	450	8.383
Hexatriacontane	$C_{36}H_{74}$	507	9.133
Tetracontane	$C_{40}H_{82}$	525	9.816
Tetratetracontane	$C_{44}H_{90}$	547	10.433

Product which report from the distillation curve can present in the temperature range from 150-200, 200-260, 260-340, 340-430, 430-570, and 570-700°C which are heavy naphtha, kerosene, gas oil, light vacuum gas oil (light VGO), heavy vacuum gas oil (heavy VGO), and Vacuum resident respectively. The simulation estimates that the bio-oil from wood pellets pyrolysis contain about 7.6% of heavy naphtha, 21.4% of kerosene, 20.1% of gas oil, 36.1 of light VGO, 11.0% of heavy VGO, and 2.9% of vacuum residue. Regarding to the estimation result, the heavy VGO, the gas oil and light VGO can convert into gasoline and diesel fuel respectively in the further process. The NMRs result also confirm that the bio-oil from the wood

pellets pyrolysis contain the aliphatic hydrocarbon which is the composition of the gasoline. The aromatic hydrocarbon also found in this bio-oil about 6.6-8.0 ppm.

4.4 Gas characterization

CO, CO_2, and CH_4 were analyzed the result as shown in the figure 4.14 and table 4.6. The gas was collected at a certain time during the reaction period. The gas was collected in the range 350-400, 400-450, and 450-500°C. The gas was not able to collect before 350°C due the condensing process and insufficient pressure. From the analysis showed that the majority of gases in the wood pellets pyrolysis are CO_2, CO, and CH_4 respectively. However, Wang et al. (2007) proposed that H_2 can be observed between temperature around 400-600°C due to the poly condensation of the free radical released during pyrolysis. According to this experiment, H_2 was undetectable event in the high temperature period. Moreover, no gas compounds presented in GC result after temperature go beyond 500°C. Hence, the heating value of gas can be calculated by using equation 4.8.

$$HHV_{gas} = HHV_{CO}*\%wt_{CO} + HHV_{CH4}*\%wt_{CH4} \qquad (4.8)$$

Table 4.6 Gas product distribution of wood pellets pyrolysis

Temperature range	Gas production,%wt		
(^{o}C)	CO	CH_4	CO_2
350-400	18-28	0	71-81
400-450	28	1.3-1.5	69-70
450-500	27-30	8.5-12.5	57-61
Estimate HHV (MJ/Kg)	4.89		
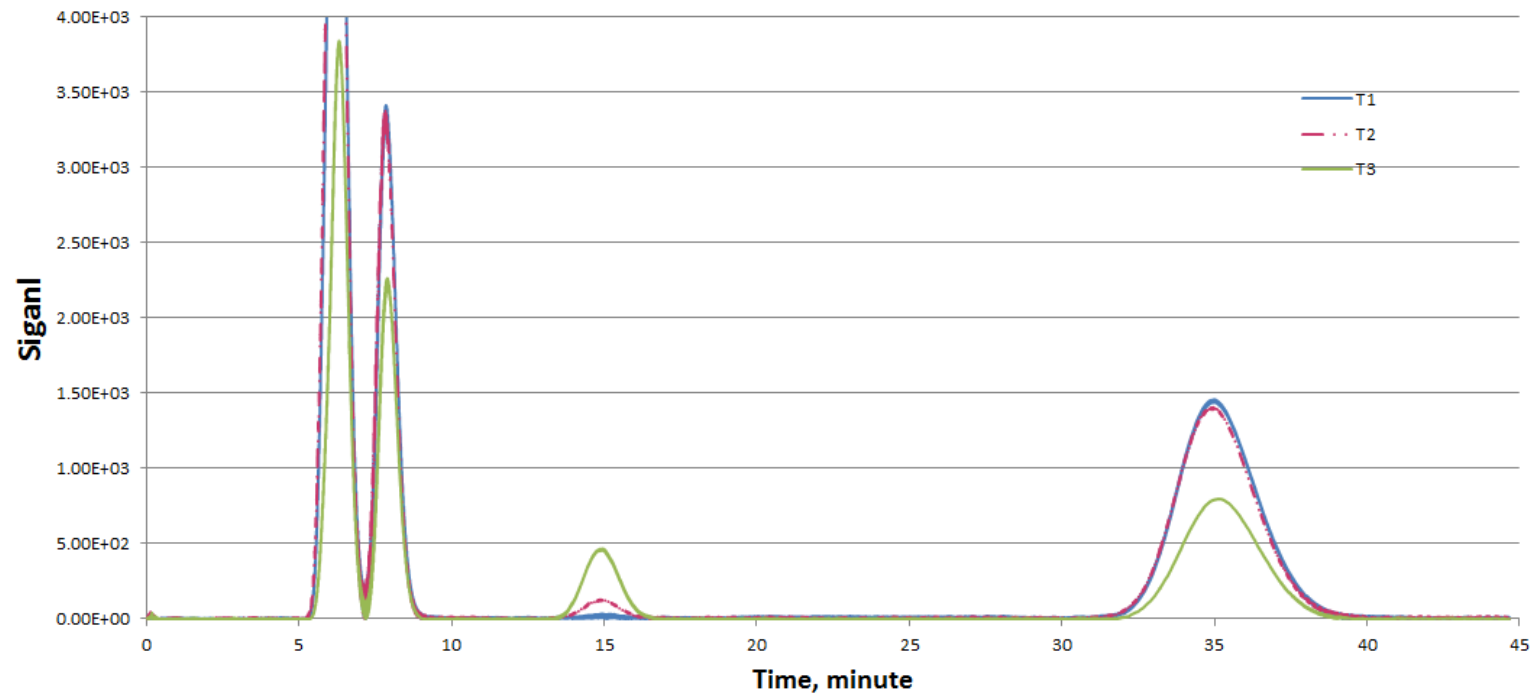
Figure 4.14 Example of gas chromatograph product

4.5 Residue characterization

The same proximate analysis method as feedstock characterization was also used to determine the heating value of the char residue of the feedstock. The equation 4.9 which proposed by Parikh et al. (2005) was used to estimate the heating value of char residue form the pyrolysis process.

$$HHV_{char} = 0.3536(FC) + 0.1559(VM) - 0.0078(Ad) \qquad (4.9)$$

Ahmaruzzaman (2008) also confirmed that the equation will give about 3% error when compare with his experimental data.The heating value which obtained from the calculation (table 4.7) also agreed with experimental data of Thangalazhy-Gopakumar et al. (2010). The heating value of product increase as a result of the increase of carbon and (carbon+hydrogen) (Demirbas,2004). Demirbas also suggested that heating value will increase when eliminate the water from char.

Table 4.7 Proximate analysis of char product from pyrolysis process

Sample	%Moisture	%Volatile matter	%Fixed carbon	%Ash	HHV (MJ/kg)
Char	10	12	66	2	25.54

CHAPTER 5

ENERGY BALANCE

Energy supply plays important role in pyrolysis experiment because sufficient amount of energy must supplies to the pyrolysis to create the reaction (Fantozzi, 2007). According to the first law of thermodynamics which is known as the conservation of the energy, is the fundamental explanation of this experiment. The first law of thermodynamics stated that energy can be neither created nor destroyed during a process, it can only change form. Hence, the feedstock energy, course estimate about 20 MJ/kg was not the main energy of reaction under nitrogen atmosphere because the endothermic behavior of process. Unlike the reaction under air atmosphere, the wood pellets release the energy as a result of the exothermic process. Then chemical reaction under pyrolysis condition turns the energy of the wood pellets into energy of products, such as gases, bio-char, and bio-oil, by suing the external energy from electricity to create the reaction. The first law of thermodynamics not only used to determine the efficiency of pyrolysis thermal conversion system but also energy balance of the system. The energy balance was studied to determine the efficiency of the thermal conversion process of pyrolysis reactor. The efficiency of thermal conversion process is the ratio between the energy required by the system at minimum loses or no loses condition versus the real energy supplied to the system. The energy balance diagram of the pyrolysis experiment is shown in figure 5.1. According to figure 5.1, pyrolysis process obtained energy input from the two sources first is the energy input from the electricity and second source is energy from the feedstock.
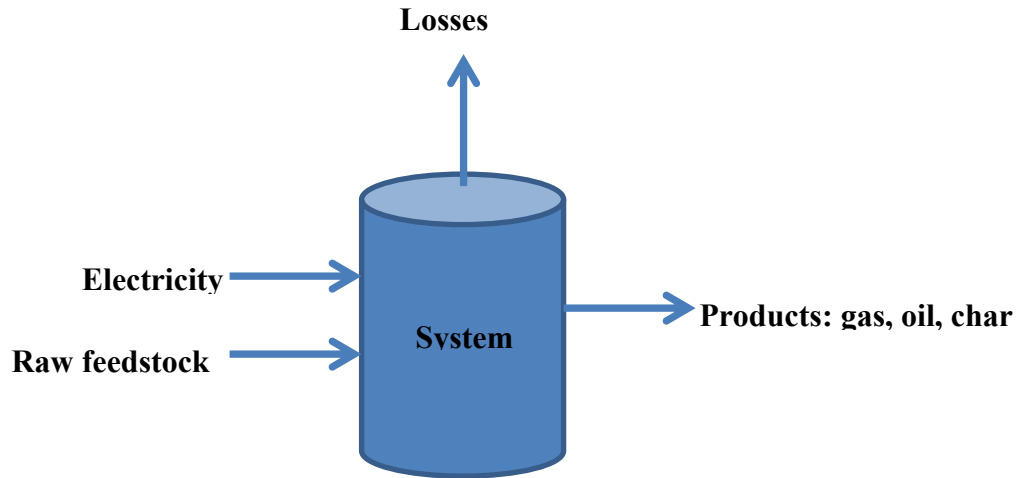
Figure 5.1 Energy balance diagram

The electricity was supplied to the system continuously from room temperature until temperature reached the final temperature at 450°C by suing the PID controller. The PID controller works according to the temperature set point program which programed by the user, the solid state relay which connected to the controller control temperature inside pyrolysis reactor by sent signal to the cartridge heaters. At this point Fluke 287 multimeter was connected to system circuit in order to record the energy usage of the system. The power supplied of system can be recorded as illustrated in figure 5.2. After that, the real energy consumption can be determined by integrated the area of the graph by using equation5.1.

$$E_{Electricity} = \int V_{meter} I \, dt \qquad (5.1)$$

when   I= W_{heater}/V_{heater}

W_{heater} = watt power which obtain from heater specification

V_{heater} = voltage of heater which give highest watt power

V_{meter} = voltage of real system which obtain from Fluke 287 multimeter

t = retention time of the system
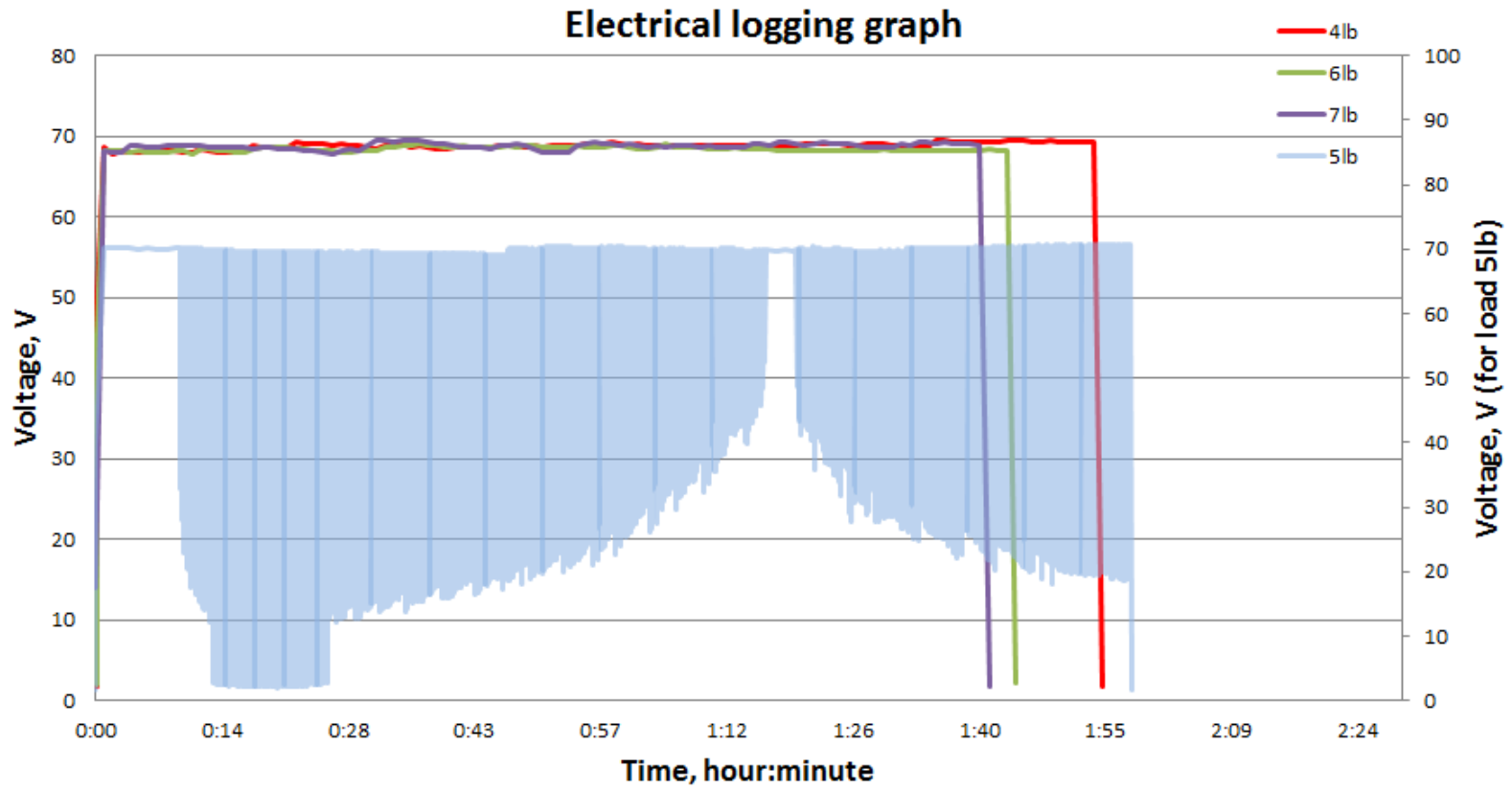
Figure 5.2 The electrical logging data of the 4, 5, 6, and 7lb wood pellets load

However, electrical input would not completely convert into the thermal energy due to losses. Losses can be determined from the energy balance equations present in equation 5.2.

$$Q_B + Q_E = Q_{oil} + Q_{Char} + Q_{gas} + Q_{exp} + Q_{loss} \qquad (5.2)$$

where Q_B = energy value of biomass

Q_E = electrical energy

Q_{oil} = energy value of bio-oil

Q_{char} = energy value of bio-char

Q_{gas} = energy value of gases

Q_{loss} = energy loss

Basically, losses took place in many areas for example loss due to the heat transfer, loss due to enthalpy change, and loss due to initial startup. However, the loss due to the initial startup was quite huge when compared with the electrical input of the system because the electricity needed to heat up the metal part of the reactor from room temperature until it reach final temperature at 450°C. The metal part of reactor composed with aluminum, stainless steel, and copper with total weight about 10 kilograms. By using following equation 5.3, then the heat loss due to the initial warm up can be determined.

$$Q = CpAl \int mAldT + Cpcu \int mcudT + Cpsteel \int msteeldT \qquad (5.3)$$

where Cp_{Al} = heat capacity of aluminum

Cp_{cu} = heat capacity of copper

Cp_{steel} = heat capacity of stainless steel

m = weight of metal part of reactor (aluminum, copper, and stainless steel)

dT = temperature different (room temperature and final temperature at 450°C)

As a result of calculation showed that about 80 percent of electrical energy was used in the constant initial startup of the reactor no matter how much the load of feedstock in the experiment.

First law of thermodynamics not only used to determine the energy balance of system but also used to determine thermal conversion of system by compare between the minimum energy requirement of the system and the real electrical consumption as show in the figure 5.3.
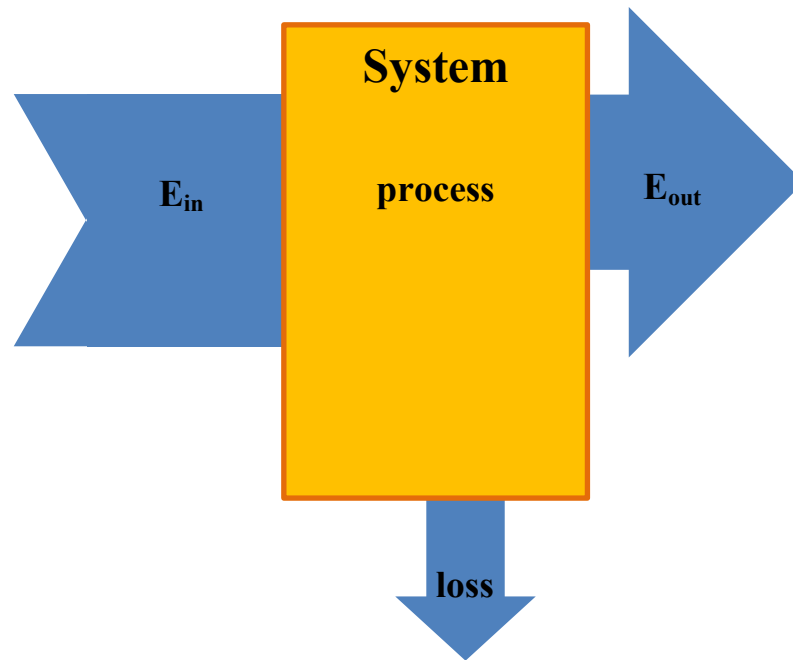
Figure 5.3 Energy diagram of the system

According to the diagram, the energy input of the system was from the electricity, energy output was the energy of products, and loss was the different from system. However, the calorific requirement of system was determine from the previous chapter by using TGA. Then the calorific requirement can be assumed as the minimum input of the system and the different between the electrical input and calorific requirement is the loss of the system. Hence, the efficiency can be determined by using equation 5.4.

$$\eta_{th} = \frac{E_{out}}{E_{in}} = 1 - \frac{E_{loss}}{E_{in}} \tag{5.4}$$

After determine the efficiency of system by using the previous equation, result showed that efficiency of system is around 4 – 8 percent because the huge amount of initial warm up reduced the efficiency of system as showed in table 5.1.

Then economic value of system should be determined to know whether system is worth developing in the future by using EROI value.The energy return on energy invested (EROI), the factor which is used to measure the strength of the energy supply technique. EROI is the most important parameter to describe the overall life cycle efficiency of power supply technique (Weißbach et al., 2013).The concept of EROI is the ratio between energy delivered against the energy required in process can be describe as followed equation (Brandenberger et al.,2013; Atlason and Unnthorsson, 2013; and Weißbach et al., 2013)

$$EROI = \frac{Usable\ energy}{Energy\ expended} \qquad (5.5)$$

Atlason and Unnthorsson (2013) proposed that the equation seems straightforward at the beginning but it is more complex whether to include as the numerator and denominator such as the energy used during transportation process, product producing, and producing machine so on. According to this experiment, only electrical supply at reactor was counted as the energy expended of system. EROI value of experiment also showed in table 5.1. EROI value can tell liability of system. When EROI value is smaller or equal to 1, means that the system cannot use as a power generator because it works as a heat sink. The bigger of EROI number, the higher possibility to invest in pyrolysis wood pellets.

Table 5.1 Energy inputs, output, thermal efficiency, and EROI of the wood pellets pyrolysis system

Load of feedstock (lb.)	Energy input (MJ)	Energy requirement (MJ)	Initial energy warm up (MJ)	Energy output (products) (MJ)				η_{th} (%)	EROI
				Bio-oil	Gas	Char	Total		
4	11.76	0.53		3.03	1.93	15.34	20.30	4.5	1.73
5	10.18	0.66	8.57	3.54	2.74	18.28	24.56	6.5	2.41
6	10.67	0.79		4.03	3.78	19.92	27.73	7.4	2.60
7	10.41	0.92		5.31	4.06	28.10	37.46	8.8	3.60

CHAPTER 6

CONCLUSIONS AND RECOMENDATION

6.1 Conclusion

- According to this study, the optimum temperature for wood pellets pyrolysis is 450°C. However, at this temperature set point did not give the maximum yields of oil but it consumed minimum energy per grams of oil.

- The activation energy of the wood pellets pyrolysis can be determined by the differential method. The activation energy ranged between 89.9 and 234.45 KJ/mol depend on the conversion range during the analysis.

- The calorific requirement of the reaction determined by using TGA experiment was about 289.84 KJ/Kg.

- According to heat transfer from overall system then the conversion efficiency of the system is about 4.4-8.8%.

- However, 5 lb. load gives the maximum mass balance but 7 lb. load give both maximum in efficiency and the energy return on the energy invested because some energy was used to warm the metal part or the reactor up.

6.2 Recommendation

- The conversion efficiency of the pyrolysis reactor should be improved. Reduce heat transfer from the pyrolysis reactor is the major concern in order to obtain better thermal efficiency.

- Reduce the energy expend due to the system warm up by using continuous system.

- Reduce the surface area per volume ratio in order to increase thermal efficiency of system.

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BIOGRAPHICAL INFORMATION

Pawarat Bootpakdeetam was born on the 30th July 1985 in an educator family. She grew up in Surin, Thailand. She was study primary school at Anubarn Surin School. After that she continued her study at Sirindhorn School until she finished grade 12. Then she pursued and received her bachelor degree in mechanical engineering from Kasetsart University, Bangkok, Thailand, in March 2007. After her graduated, she was working as a sale engineer in public company before decided to quit and continue her master degree study. In 2011, she continued her Master Degree in Mechanical Engineer at The University of Texas at Arlington, Texas, USA.