PYROLYSIS OF AGRICULTURAL WASTE: EFFECT OF TEMPERATURE AND HEATING RATE

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ABSTRACT

Due to the depleting of non-renewable source energy (fossil fuel) and increases of environmental pollution, a search of sustainable alternative has gained significant attention. This involves the conversion of biomass from palm waste which are empty fruit bunch (EFB) and palm oil fiber (POF) to produce fuel gas, solid and bio-oil through pyrolysis. However the yield of products depends on some parameter. This research was carried out to study the effect of temperature and heating rate to the yield of products. The pyrolysis process was carried out using Quartz Glass Reactor in lab scale electrical tubular furnace. Preliminary analysis was conducted using thermo gravimetric analyzer (TGA) to determine the volatile matter and moisture content. From the result of TGA, it is found that POF contain more volatile matter in comparison of EFB. The CHNS analyzer also used to know the percentage of carbon, hydrogen, nitrogen and sulfur contained in the sample. The experiment was conducted to study the effect of temperature by varies the temperature to 400 ^oC, 500 ^oC, 600 ^oC and 700 ^oC and study the effect of heating rate by changing to 10 ^oC/min and 100 ^oC/min. The result showed that yield of bio-oil for both sample reaches maximum at 500 ^oC and decreases as the temperature increased. The yield of bio-oil increase from 55.7 wt% at 400 ^oC to 69.20 wt% 500 ^oC for EFB, while for POF the yield increase from 77.30 wt% at 400 ^oC to 89.10 wt% 500 ^oC For the fuel gas yield, the yield was seems to indirectly proportional with yield of bio-oil. When the yield of bio-oil increase the yield of fuel gas decreases and vice versa. For the solid yield, EFB and POF proved that yield of solid was decrease by the increases of temperature. It can be found that, the solid product produce 26 wt% and 65 wt% at 400 ^oC. Meanwhile, at 800 ^oC, only 10 wt% and 15 wt% solid product was found for EFB and POF. For study the effect of heating rate of EFB and POF, the result shows that yield of bio-oil high at high heating rate while the yield of fuel gas and solid was low at high heating rate. The highest bio-oil produced by both sample were 56 wt% and 89 wt%. The functional group and chemical compositions present in the bio-oil at optimum conditions were identified by using Gas chromatography Mass Spectrometry (GC-MS). From analysis, it is shown that bio-oil contains complex compound mostly from groups of phenol, alcohol, ketones, furans, and carboxylic acid.

ABSTRAK

Disebabkan oleh kekurangan punca tenaga yang tidak boleh diperbaharui (minyak fosil) dan pencemaran persekitaran, pelbagai cara untuk menggantikan sumber-sumber tersebut sedang giat dijalankan. Salah satunya ialah dari pertukaran tenaga dari biojisim dari kelapa sawit iaitu gentian kelapa sawit (POF) dan buah kelapa sawit kosong (EFB) melalui proses pirolisis untuk menghasilkan minyak bio, petrol gas dan pepejal. Kajian ini adalah bertujuan untuk mempelajari kesan suhu dan kadar pemanasan terhadap komposisi produk. Proses pirolisis dijalankan menggunakan Gelas Quartz Reaktor di dalam tungku tiub pembakaran. Analisa menggunakan termo gravimetric analisis (TGA) untuk mengetahui kewapan dan kandungan kelembapan telah dijalankan. CHNS analisis juga dijalankan untuk mengetahui peratus karbon, hydrogen, nitrogen dan sulfur yang terdapat di dalam bahan. Eksperimen telah dijalankan untuk mengkaji kesan haba dengan mempelbagaikan suhu kepada 400 ^{o}C, 500 ^{o}C, 600 ^{o}C and 700 ^{o}C dan mempelajari kesan kadar pemanasan dengan menukar kepada 10 ^{o}C/min and 100 ^{o}C/min. Hasil dari kajian menunjukkan bahawa komposisi minyak bio mencapai kadar maksimum pada suhu 500 ^{o}C dan ianya menurun jika pemanasan diteruskan. Komposisi minyak bio untuk kedua-dua sampel meningkat dari 55.7 wt% pada suhu 400 ^{o}C kepada 69.20 wt% di suhu 500 ^{o}C untuk EFB manakala untuk POF, komposisi minyak bio meningkat dari 77.30 wt% pada suhu 400 ^{o}C kepada 89.10 wt% pada suhu 500 ^{o}C.. Bagi komposisi pepejal, EFB and POF telah membuktikan bahawa komposisinya akan berkurang dengan kenaikan suhu. Di dapati, pepejal terhasil sebanyak 26 wt% dan 65 wt% pada suhu 400 ^{o}C. Manakala pada suhu 800 ^{o}C, hanya 10 wt% dan 15 wt% pepejal yang dapat dihasilkan oleh EFB dan POF. Manakala bagi kajian kesan kadar pemanasan pula, hasil telah menunujukkan bahawa komposisi minyak bio meningkat dengan kadar pemanasan yang tinggi manakala petrol gas dan pepejal pula sebaliknya bagi kedua-dua bahan. Komposisi minyak bio tertinggi yang dihasilkan pada 100 ^{o}C/min bagi EFB dan POF ialah 56 wt% dan 89 wt%. Minyak bio yang telah dihasilkan telah dianalisa untuk mengetahui kumpulan berfungsi didalamnya menggunakan Gas Chromatography Mass Spectrometry (GC-MS) dan didapati bahawa minyak bio mengandungi sebatian kompleks kebanyakannya dari kumpulan fenol, alcohol, keton, furans, asid karbosilik dan struktur karbonik.

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LIST OF SYMBOLS

^{o}C	Degree of celsius
<	Less than
%	Percent
μ	Micro
cm	Centimetre
g	gram
min	Minute
mm	millimetre
ml	millilitre
psi	unit of pressure

LIST OF ABBREVIATIONS

BTG	Biomass technology group
CO	Carbon monoxide
CO_2	Carbon dioxide
EFB	Empty fruit bunch
GC-MS	Gas chromatography mass spectrometry
H_2O	Water
OD	Outside diameter
POF	Palm oil Fibre
TGA	Thermogravimetric analyzer
TG	Thermo gravimetry

1 INTRODUCTION

1.1 Introduction

The non-renewable (fuel fossil) source from underground is depleting, so particularly, many developing country try to find a way to find another renewable supply so that they not too reliable on one non-renewable sources. Biomass is one of the renewable sources that can be substitute fossil fuel to generate energy. The uses of biomass are not only helping them to reduce the uses of fossil fuel but also environmental friendly.

Biomass can come from agricultural waste; everything that involves or used from agriculture that specified waste form it that used for agriculture activities. Biomass also include definitions include harvested forest timber, contaminated waste wood, municipal solid waste and tires that are unsustainably. Environmental groups make a conclude that excludes burning garbage and limits biomass to sources such as forest-related harvesting residue, landscaping and right-of-way trimmings and agricultural crops and crop by products also categorized as biomass. Biomass is not a new technology, in fact it have been developed many years before. However, in Malaysia this technologies just developed by an addition concluded in the 9th Malaysia plan (Mohd, 2009)

Malaysia takes an initiative to make many more research and try as many as possible samples that can be used as the biomass energy consumption. Main contributor of biomass in Malaysia is come from palm oil which are using Empty fruit Brunches (EFB) and palm oil fibre because Malaysia is the one of the largest palm oil producing countries, which about 30M ton of palm oil wastes generate each year (Yang, et.al. 2006). The biomass waste is used to produce energy for power and fertilizer purposes. There are more than 270 palm oil mills operating in Malaysia that utilize mainly fiber and partly shell in their boilers as fuel to generate power and steam required (Suhaimi, 2012).

Figure 1.1: The abundance of palm oil biomass (Ahmad et.al., 2009)

Pyrolysis is the thermal decomposition of fuel into liquid, gases and solid in the absence of oxygen. The end of pyrolysis and the composition of the gases are dependent on several parameters including temperature, biomass species, particle size, heating rate, operating pressure and reactor configurations as well as adding of catalyst (Yang,et. al. 2006). However, temperature and heating rate is the most important parameters that will affect the yield of the bio-oil products

1.2 Objectives

The objective of this research is to study the effect of tempearature and heating rate in the process of pyrolysis of agricultural waste from palm oil industry.

1.3 Scope of this research

This pyrolysis was carried out by using Palm oil fiber (POF) and Empty fruit bunch (EFB) as the feedstock. This is because both of it are low priced and abandoned material from palm oil milling process (Azizan, et.al., 2009). The influence of temperature and heating rate of the pyrolysis was studied. The temperature was varied from 400 ^{o}C to 700 ^{o}C, while the heating rate was 10 ^{o}C/min and 100 ^{o}C /min. The experiment will be conducted by using Quartz Glass Reactor. The gas product from the experiment was analyzed by using Gas Analyzer while the liquid product from the pyrolysis will be analyzed by using GC-MS.

1.4 Significant and Rationale

Biomass pyrolysis is not a new technologies but the importance of this technologies nowadays has become more crucial since crude oil become depleted and the environmental concern of global warming. Many researches had been conduction about the usefulness of pyrolysis and proven that this technology is worthy to be developed.

In this project, EFB and POF will be used as feedstock. Rationale of using these as sample of biomass is because it is the most waste in palm oil industry compared to others waste.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 is the introduction on non-renewable, renewable source of energy, biomass and its types. The sample that used in this research is from palm oil waste. There was an elaboration on the development of palm oil industries in Malaysia. This chapter also covered the objective, the scope, significant and rationale.

Chapter 2 gives a review on the biomass definition and the explanation of how biomass was produced. There also the description of the types of biomass that available from many kinds of agricultural waste. The understanding of biomass was further by explaining the application of biomass and how its processes to convert into source of energy. Then, there is also an explanation on the pyrolysis including the types of pyrolysis, pyrolysis reactors and parameter that will affect the yield of products.

Chapter 3 is an explanation on the method of pyrolysis experiment. First of all, the flow of the methodology that has been done in this experiment is discussed. The description of each step from the sample preparation until the data analysis is explained. All the analyses parameters are also described.

Chapter 4 l shows the result and discussion from the experimental procedure. The results from biomass solidacterisation and pyrolysis are discussed in detail. The effect of temperature and heating rate of pyrolysis are also explained in this chapter.

Chapter 5 is all about the conclusion and future work that can be done to improve this research.

2 LITERATURE REVIEW

2.1 Overview

This paper present the experimental study of the effect of temperature and heating rate towards biomass by using pyrolysis method. Biomass is a renewable resource that use as the substitution for the fossil fuel to be the energy sources. The advantage of biomass as source of energy are can decrease the pollution which mean more environmental friendly and

2.2 Biomass

Biomass is an organic matter that used as renewable resources of energy which come from wood, solid waste, municipal waste and crops. Chemical formula for the biomass is CxHyOz which mean that carbon, hydrogen and oxygen are the major molecules that exists in the biomass.

Biomass is produced by plants as a result of photosynthesis; some of the energy in the sunlight is converted into the chemical energy that binds various atoms to form carbohydrate molecules. Then, the energy produce will be passed on herbivores (animals that eat plants) and people that eat them. This is the evidence that biomass is the renewable sources that always can be produce and always exist. (Mohd, 2009).

In Malaysia, biomass is the most sources that potentially to generate energy. Most of sources of biomass in Malaysia are from agricultural wastes which are from oil palms waste, rice husks and fruit waste. Major contribution of biomass in Malaysia is from oil palms waste (including shell, fibre and empty fruit brunch (EFB) because Malaysia is productivity from different type of agriculture waste is shown in Table 2.1.

Table 2.1: Energy productivity for different type of agricultural waste from Ninth Malaysia plan (Ghani, et.al. 2009)

Agricultural waste	**Energy productivity (million boe/ year)**
Oil palms	88.7
Paddy plants	29.5
Rubber trees	11.54
Coconut trees	28.21
Sugarcane	80.33
Logging	54.9

In this table, it showed that the biggest energy productivity is the oil palms. The energy comes from biomass of empty fruit bunches of palm oil, the shell and its fibre. It follows with sugarcane waste which is from its baggase.

2.3 Biomass Applications

The world energy demand on biomass is increasing. Energy produce by biomass can be used for many things either directly or indirectly. Directly biomass consuming is for burning wood and heating cooking and indirectly biomass consumed by changing it to liquid and gaseous fuel and use for mobile applications (Fletcher,et.al., 2004).

Kenya, a country that have severe problem of deforestation; they used waste from deforestation to produce biomass and used for heating and cooking. Figure 2.1 shows how Kenya people use agriculture waste for cooking (Practical Action)

Figure 2.1: Agriculture waste using for cooking (Practical Action)

Biomass that change to ethanol and biodiesel also been used in transportation system. Most of European country maintains plans for large-scale production in case of an emergency (Wood Gas as Engine Fuel). Biomass fuel, said tends to be cheaper than fossil fuel (Oracle Thinkquest Education Foundation). In fact, the use of energy from biomass is also said to be environmentally friendly. This is because, before the biomass processing technologies are introduced, it is thrown away and cause pollution.

2.4 Biomass conversion

Biomass fuels and residue can be converted to energy via thermal, biological and physical processes. Each process area is described with the greatest emphasis on the technologies that are attracting the most attention in the research, demonstration and commercial. The three main thermal processes available for converting biomass to a more useful energy form are combustion, gasification and pyrolysis.

Combustion to produce thermal energy is the traditional way of using biomass, which is what humans have been doing since they discovered fire. Combustion process converts a solid fuel into gaseous product of combustion through high temperature oxidation reactions. (Zinoviev, et.al.,2007). The generation of hot gaseous will converted into steam and usually use in the power plant as the source of energy for steam turbine. However, the energy that have been converted have the low efficiency and inconvenient for the large power plant.

Gasification is the heating of biomass into synthesis gas (syngas, a mixture of hydrogen and carbon monoxide) in an environment with limited oxygen. The main production of gasification is gaseous. The gaseous product divided into two which are the lower energy gas and medium energy gas. The lower energy y gas will use sources of energy of engines while for the medium energy gas is use as fuel gas and converted to methane.

Pyrolysis is the chemical breakdown of a substance under extremely high temperature without absence of oxygen. The products from pyrolysis process are gas, hydrocarbons (liquid) and solid (Suhaimi, 2012).the gasification is actually the extension of temperature from gasification method to produce other products than gaseous. The function of gaseous product from pyrolysis usually as same as gasification while for the liquid it usually use fuel and distillates. The conclusion of biomass conversion is showed in Figure 2.2.

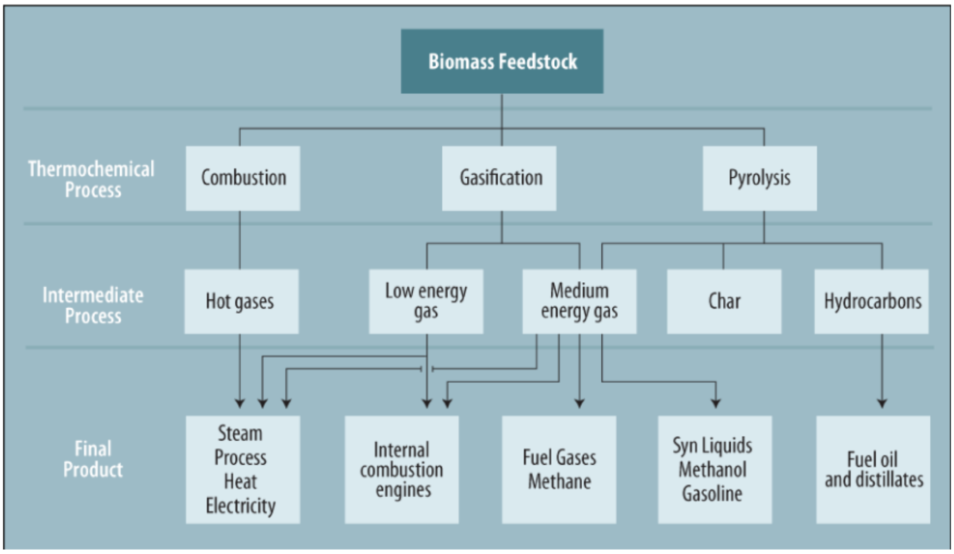

Figure 2.2: Conclusion of biomass conversion (Zinoviev, et.al., 2007)

2.5 Pyrolysis

Pyrolysis can be divided into two types which are slow pyrolysis and fast pyrolysis. Slow pyrolysis produces more solid and gases product which are gases, solid and tar. Slow pyrolysis is done by use slow biomass heating rate with low temperature. The lower temperature regime of decomposition of biomass showed mainly H_2O, CO_2 and CO were evolved. The fast pyrolysis process produces more on liquid which called as bio-oil. Fast pyrolysis experiment be conduct in high temperature and high heating rate. However, currently most research is focusing on maximizing the yield of liquid product (fast pyrolysis) as opposed to solid. The liquid pyrolytic product can be easily stored and transported, readily upgraded and refined to produce high quality fuels and may contain chemical in economically recoverable amounts (Ozcimen and Karaosmanoglu,2003) Fast pyrolysis liquid yield can be until 80% while the rest is the solid and other material.

The overall reaction involve in fast pyrolysis in Figure 2.3. Biomass reacts in the reactor with the high temperature and low pressure and then move to transient oxygenated fragments. Fragmentation involved depolymerization of the biomass to anhydro-glucose compounds and other light combustible volatiles (Sadaka and Eng, 2012).

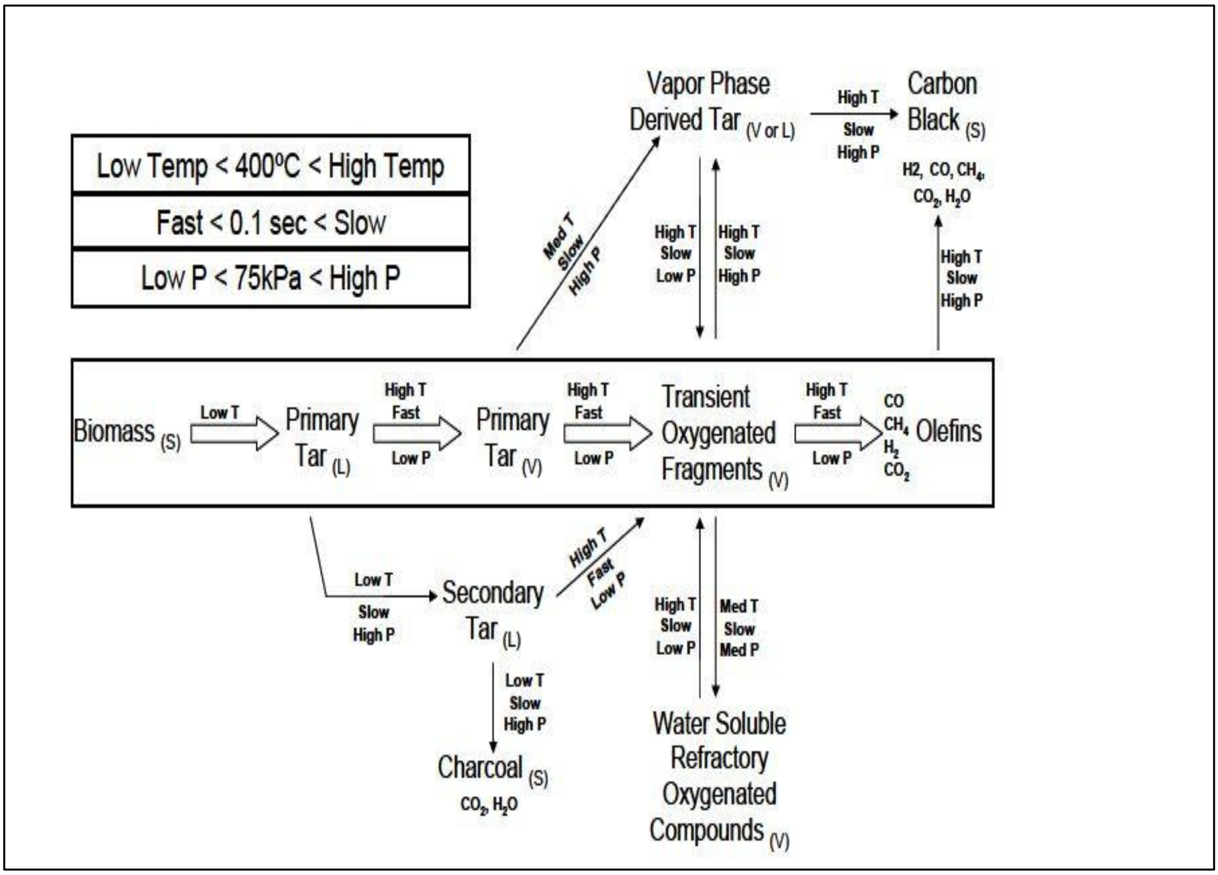

Figure 2.3: Reaction of fast pyrolysis (Sadaka and Peng, 2012)

Fast pyrolysis also has its own stage. On the first stage, the biomass will be heated at high temperature and low pressure and produce tar as primary product. If the heating is extended the yield of result will volatile and produce gas as the main product.

2.6 Pyrolysis Reactors

The thermochemical conversion processes under consideration are interrelated. Pyrolysis is known to be a precursor to both gasification and combustion. As a consequence, it is not necessary to develop or manufacture a reactor specifically for analysis of biomass pyrolytic reactions. Suitable reactors are those already outlined in the previous chapter on gasification, e.g., fixed bed, fluidized bed, entrained flow and suspension flow reactors.

2.6.1 Bubbling Fluidized bed Pyrolyzers

Compared to other types of reactors, fluidized beds are simpler to design and construct. They have several advantages including good gas solids contact, excellent heat transfer solidacteristics, better temperature control, and large heat storage capacity. Fluidized bed pyrolyzers give good consistent performance with high liquid yield of typically 60-75 wt% (Sadaka & Eng, 2012).

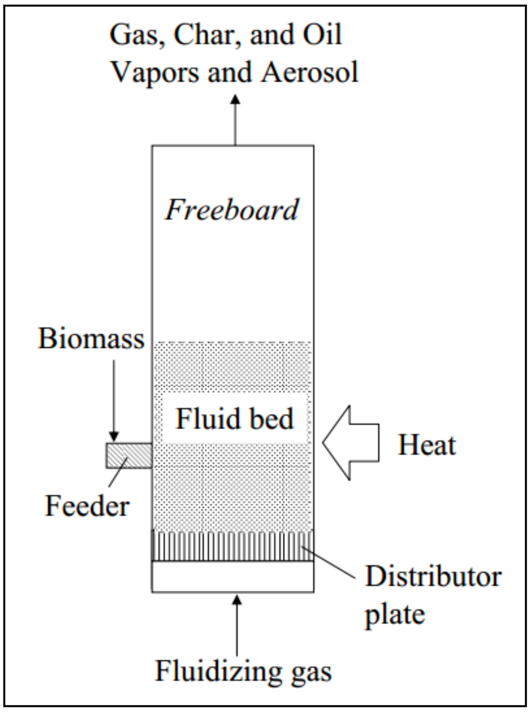

Figure 2.4: Bubbling fluidized bed pyrolyzer (Sadaka & Eng, 2012)

Commercial plants have multiple stages collection systems including de-misters, although aerosol capture is extremely difficult. Since the pyrolysis process is endothermic, external heating was needed. However, heat transfer to bed at large-scales of operation has to be considered carefully due to scale-up limitations of different method of heat transfer. Fluidized bed pyrolyzers include the following equipment: feeder, fluid bed, distributor plate and freeboard.

2.6.2 Circulating fluid Beds and Transported bed

Circulating fluidized bed pyrolyzers have same solidacter as bubbling bed pyrolyzers excluding that the residence time for solid and vapours is the faster. Compared to bubbling fluidized bed pyrolyzers, vapour and solid excape faster due to higher gas velocities. (Sadaka, 2012). The inability to maintain uniform radial temperature profiles and to avoid local slagging problems makes the bubbling bed pyrolyzer unsuitaible for large installations. (Li et.al., 2004)

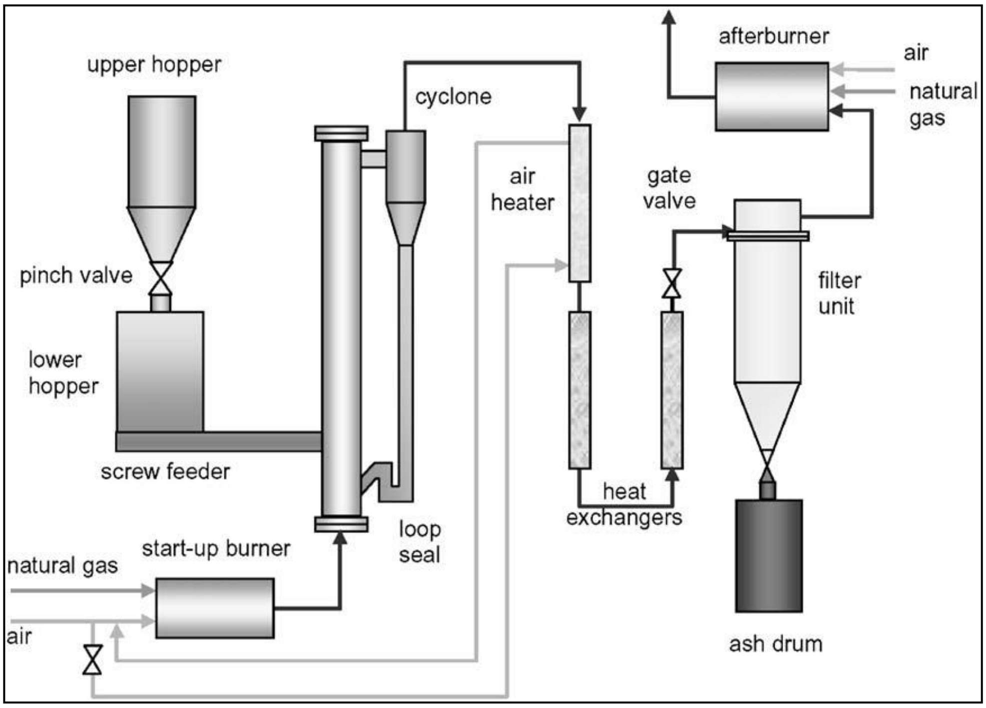

Figure 2.5: Circulating fluid beds and transported bed (Li et.al., 2004)

2.6.3 Rotating Cone Pyrolyzer

Rotating Cone pyrolyzer was a new reactor design for fast pyrolysis that was developed by Biomass Technology Group (BTG) in the Netherland. In a rotating cone pyrolyzer, sand and biomass are transported by centrifugal forces. Sand is to avoid fouling the cone wall and to enhance heat transfer. However, there are some of disadvantages of this pyrolyzer. This pyrolyzer required very small particle size and hard to scale up (Christopher, 2013)

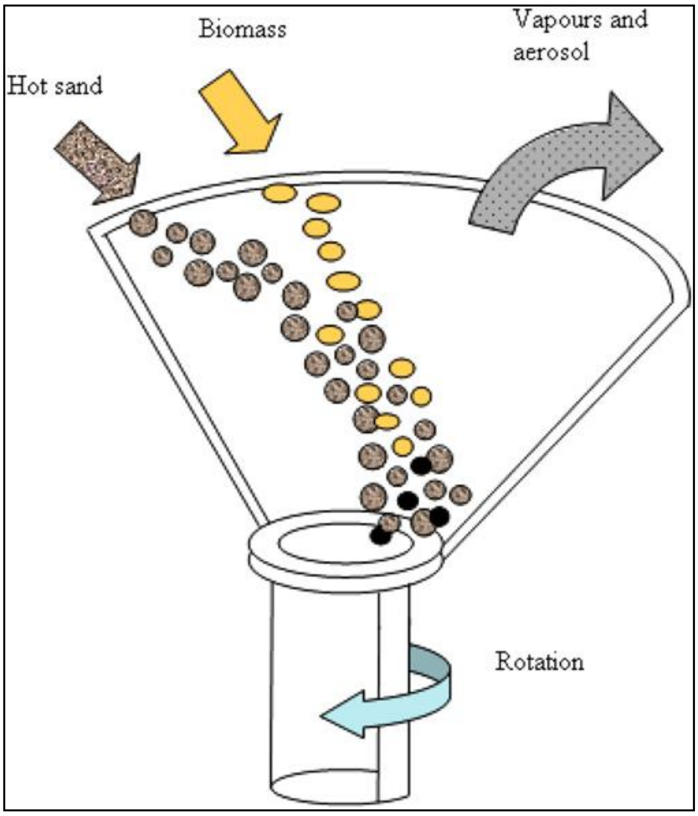

Figure 2.6: Rotating cone pyrolyzer (Ishak, 2012)

2.7 Effect of Temperature

Temperature is one of the most important parameters that determine the optimum yield of products from biomass. The pyrolysis rate increases with temperature, that can be determined by weight loss, evolution rate of primary volatile product or simultaneous measurement of density and temperature profiles in the pyrolyzing solid (Sadaka and Eng P, 2012). According to Bridgwater (2003), the optimum temperature for the pyrolysis is depending on the type of the pyrolysis itself. In his study, fast pyrolysis recorded 500 ^{o}C as the optimum temperature for the optimum yield with by-products bio oil while slow pyrolysis recorded at 400-450 ^{o}C as the optimum temperature for the optimum yield of with by-products gases hydrocarbons.

However, study has showed that different samples have different optimum temperature to achieve the highest yield of products. Onay (2006), in his study has done research on pyrolysis by using safflower seed as feedstock. According to his study, at temperature 500, 550 or 600 ^{o}C, the oil yield reaching maximum at 54 wt% for all heating rate. Figure 2.3 shows the result relation between percentage of yield and temperature in his study.

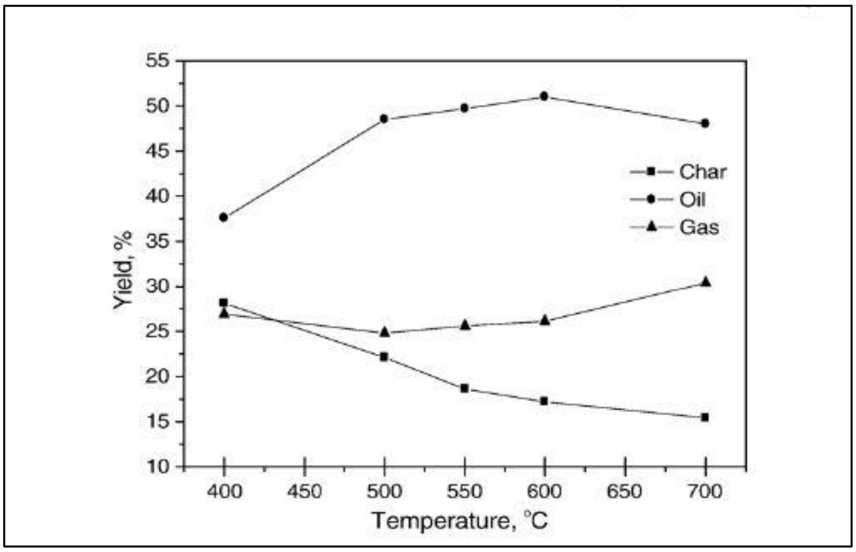

Figure 2.7: The relationship between percentage of yield and temperature (Onay, 2006)