MODELLING AND SIMULATION OF BIO-OIL PRODUCTION FROM PALM OIL BIOMASS VIA FAST PYROLYSIS USING ASPEN PLUS

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LIST OF ABBREVIATIONS

CAGR	Compound Annual Growth Rate
CH_4	Methane
C_2H_4	Ethylene
C_2H_6	Ethane
C_3H_6	Propylene
C_3H_8	Propane
CO	Carbon monoxide
CO_2	Carbon dioxide
EFB	Empty Fruit Bunch
H_2	Hydrogen
MF	Mesocarp Fiber
MPOB	Malaysian Palm Oil Board
PKS	Palm Kernel Shell
POME	Palm Oil Mill Effluent

PEMODELAN DAN SIMULASI PENGELUARAN BIO-MINYAK DARI BIOMAS MINYAK PALM MELALUI PIROLISIS PANTAS MENGGUNAKAN ASPEN PLUS

ABSTRAK

Peningkatan penggunaan tenaga, sumber bahan bakar yang terbatas, kebergantungan besar kepada bahan bakar fosil, dan pelepasan gas rumah hijau telah menyebabkan peningkatan penyelidikan dalam bidang sumber tenaga yang dapat diperbaharui. Sumber tenaga boleh diperbaharui adalah pilihan terbaik untuk memenuhi permintaan tenaga semasa dan mengurangkan kebergantungan kepada bahan bakar fosil. Dalam kajian ini, tiga biojisim minyak sawit, iaitu tandan buah kosong (EFB), serat mesokarp (MF), dan tempurung inti sawit (PKS) dioptimumkan untuk pengeluaran bio-minyak melalui pirolisis cepat. Proses pemodelan dan simulasi dilakukan menggunakan ASPEN PLUS V10.0. Simulasi merangkumi bahagian pra-rawatan, bahagian pirolisis pantas, pemisahan pepejal gas, dan bahagian penapisan minyak bio. Model yang dikembangkan berjaya disahkan dengan data eksperimen yang diperoleh dari literatur. Kemudian, kesan keadaan operasi seperti suhu pirolisis dan masa tinggal semasa pirolisis pantas biojisim kelapa sawit diperiksa untuk memaksimumkan hasil produk minyak bio. Berdasarkan hasilnya, hasil maksimum minyak bio untuk EFB, MF, dan PKS masing-masing adalah 56.46 wt.% berat, 47.39 wt.% berat, dan 44.03% berat, diperoleh pada suhu 550 °C untuk masa tinggal bersamaan 2 saat . PKS mencapai hasil bio-arang dan gas tertinggi iaitu 49.77 wt.% berat dan 37.21 wt.% berat pada suhu 450 °C dan 600 °C, masing-masing kerana kandungan ligninnya yang tinggi. Hasil yang diperoleh dalam kajian ini selaras dengan hasil eksperimen yang terdapat dalam literatur. Oleh itu, model yang dikembangkan dapat digunakan untuk mengoptimumkan proses pirolisis cepat untuk sumber biojisim yang berlainan tanpa perlu melakukan penyelidikan eksperimen yang kompleks. Model sedemikian akan memberikan sumbangan yang besar terhadap peningkatan dan intensifikasi pirolisis biojisim.

MODELLING AND SIMULATION OF BIO-OIL PRODUCTION FROM PALM OIL BIOMASS VIA FAST PYROLYSIS USING ASPEN PLUS

ABSTRACT

The increase in energy consumption, limited fuel resources, massive dependency on fossil fuels, and greenhouse gas emission has resulted in increased research development on renewable energy sources. Renewable energy is the best option for meeting the current energy demands and reduce the dependence on fossil fuels. In this final year project, three palm oil biomass, namely empty fruit bunches (EFB), mesocarp fibre (MF), and palm kernel shell (PKS) were optimized to produce bio-oil via fast pyrolysis. Process modelling and simulation were carried out using ASPEN PLUS V10.0. The simulation includes pre-treatment, fast pyrolysis section, gas-solid separation, and bio-oil refining section. The model developed was successfully validated with the experimental data obtained from literature. Then, the effect of pyrolysis temperature and residence time during the fast pyrolysis of oil palm biomass were studied to maximize the yield of bio-oil product. Based on the results, the maximum bio-oil yields for EFB, MF, and PKS were 56.46 wt.%, 47.39 wt.%, and 44.03 wt.%, respectively, obtained at a temperature of 550 °C and residence time of 2 s. PKS achieved the highest biochar and gas yield of 49.77 wt.% and 37.21 wt.% at 450 °C and 600 °C, respectively due to its high lignin content. The obtained yields in this study are consistent with experimental results found in the literatures. Therefore, the model developed can be used to optimize fast pyrolysis process for different biomass sources without the need to perform complex experimental investigations. Such model will make an important contribution on the improvement and intensification of fast pyrolysis of biomass.

CHAPTER 1
INTRODUCTION

Chapter 1 introduces the overview of this research and significance of utilization of oil palm biomass in Malaysia for the production of biofuel. In general, this chapter summarizes the research background of oil palm biomass and various thermochemical conversion technologies such as gasification, combustion, and pyrolysis for energy production from oil palm biomass, the problem statement, and the objectives of this research.

1.1   Research Background

Due to an increasing environmental awareness and the growing need to decrease dependence on fossil fuel-based energy sources, much attention has been paid in using clean, renewable energy. Renewable energies are of growing importance in addressing environmental concerns over the use of fossil fuels and their contribution to greenhouse effect. Many governments, business, industries, and individuals around the world have begun to wake up to the need for more renewable energy. Biomass is among the main renewable energy sources as it plays an essential role in both environmental protection as well as in economic development. Biomass can be utilized for generation of electricity, process heating in industries, as well as for household heating.

The biomass and waste-to-energy technologies investments was around 11.2 billion U.S. dollars in 2019 as illustrated in the **Figure 1.1** (McCrone, et al., 2020). Furthermore, the waste to energy market value reached 35.1 billion U.S. dollars in 2019. The market value is projected to reach 50.1 billion U.S. dollars by 2027, increasing at a compound annual growth rate (CAGR) of 4.6 percent from 2020 to 2027 (Choudhary, 2020). This shows that biomass is increasingly turning into one of the world's most widely utilized energy source, with many developing nations having significant agriculture sectors generating up to 40-50% of their overall energy from biomass (Ward, et al., 2014)
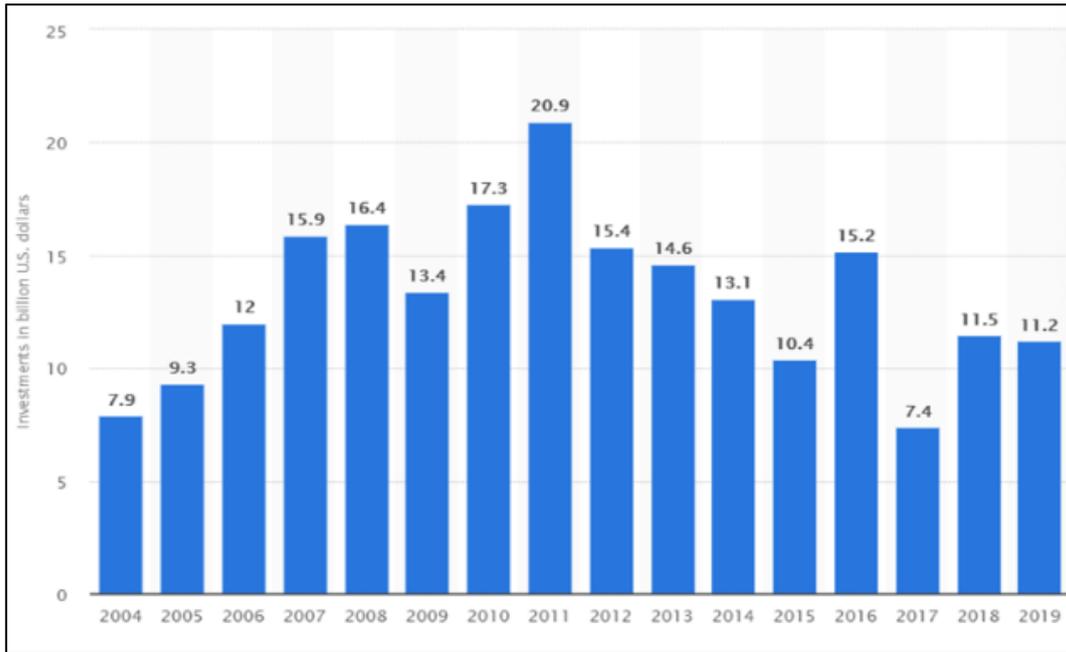
Figure 1.1 The investment in biomass and waste-to-energy technologies worldwide between 2004 and 2019 (McCrone, et al., 2020)

Malaysia being the second largest producer of oil palm in the world, the oil palm industry is the major biomass source in Malaysia, and the supply is abundant. According to Malaysian Palm Oil Board (MPOB), there are approximately 5.9 million hectares of oil palm planted areas nationwide at the end of 2019 as shown in the **Table 1.1**. This contributes over 85.5% of the overall total lignocellulosic biomass production in Malaysia (Umar, et al., 2013). The country's oil palm industry generates about 90 million tonnes of lignocellulosic biomass which includes empty fruit bunch (EFB), mesocarp fibre (MF), and palm kernel shell (PKS). Due to huge quantities of biomass produced from palm oil, Malaysia has the potential of utilizing the biomass as renewable energy source.

Table 1.1 Malaysia oil palm plantation areas as of December 2019 (hectares)
(Malaysian Palm Oil Board, 2019)

STATE	MATURE (HA)	%	IMMATURE (HA)	%	TOTAL (HA)	%
JOHOR	694,097	91.5	64,439	8.5	758,535	12.9
KEDAH	81,794	90.2	8,927	9.8	90,721	1.5
KELANTAN	127,221	74.2	44,124	25.8	171,345	2.9
MELAKA	52,083	90.8	5,257	9.2	57,340	1.0
NEGERI SEMBILAN	170,970	90.5	18,009	9.5	188,979	3.2
PAHANG	668,236	87.0	100,161	13.0	768,397	13.0
PERAK	363,813	89.3	43,790	10.7	407,603	6.9
PERLIS	842	94.5	49	5.5	891	0.0
P.PINANG	13,445	97.4	355	2.6	13,800	0.2
SELANGOR	117,558	90.0	13,112	10.0	130,671	2.2
TERENGGANU	153,656	85.0	27,065	15.0	180,721	3.1
PENINSULAR MALAYSIA	**2,443,715**	**88.3**	**325,288**	**11.7**	**2,769,003**	**46.9**
SABAH	1,353,812	87.7	190,669	12.3	1,544,481	26.18
SARAWAK	1,419,295	89.5	167,378	10.5	1,586,673	26.9
SABAH & SARAWAK	**2,773,107**	**88.6**	**358,047**	**11.4**	**3,131,154**	**53.1**
MALAYSIA	**5,216,822**	**88.4**	**683,335**	**11.6**	**5,900,157**	**100.0**

Energy production from oil palm biomass covers a broad range of processes which stretches from thermochemical, biochemical, to physico-mechanical processes producing different forms of energy. The category of thermochemical conversion methods includes pyrolysis, combustion, and gasification. Densification and shedding were categorized under physical conversion methods while fermentation and anaerobic digestion falls under biological conversion methods. Thermochemical conversion processes require high input energy than other processes, but they are desirable due to their high process yield, large scale production, short reaction time, liquid products with higher energy densities, and capable of converting different type of biomass wastes (Kurnia, et al., 2016).

Basically, thermochemical conversion processes involves the use of high-temperature to break the bonds of organic matter and reform these intermediate products into biochar, syngas, and bio-oil (Corona, et al., 2016). Gasification which falls into this category, involve thermal degradation of biomass in an oxygen-deficient environment which occurs at a temperature of around 500-1300 °C to produce a fuel gas. In gasification, the biomass is broken

down into the mixture of produced gas so called synthesis gas (syngas) which consists of methane (CH_4), hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO).

Unlike gasification, combustion involves high-temperature conversion of waste usually around 700-1400 °C on the presence of oxygen to produce thermal energy and flue gas consisting of carbon dioxide and water. Combustion has the advantage of utilizing existing plants as they are employing a commercially and well-developed available technology. However, because of the presence of high moisture content in biomass feedstock direct combustion of biomass can cause considerably air pollution or haze (Awalludin, et al., 2015). Besides that, due to presence of alkali compound in biomass feedstock agglomeration and ash fouling are common problem (Relacionados & Melissari, 2014).

Pyrolysis is highly promising for the conversion of waste into liquid fuels, biochar, and useful gas. In contrast to combustion, pyrolysis is not exothermic, and it involves thermal decomposition of organic matter at a temperature around 500°C-800°C without the presence of oxygen to produce products such as bio-oil, charcoal, and fuel gas. Pyrolysis breaks down large hydrocarbon molecules of lignocellulosic biomass into smaller hydrocarbon molecules. The most common types of pyrolysis technique are fast pyrolysis and slow pyrolysis. In fast pyrolysis, the biomass is rapidly heated at a temperature around 500 °C with high heating rate (10-200 °C/s) to produce bio-oil product whereas in slow pyrolysis the biomass is heated at a controlled temperature with low heating rate (0.1–1 °C/s) under gas residence time of around 5 to 30 min to produce char/solid products (Corona, et al., 2016). **Table 1.2** shows the comparisons of different thermochemical conversion technologies for conversion of biomass to bioenergy.

Table 1.2 Comparative of thermochemical processes (Corona, et al., 2016)

Process	Temperature (°C)	Pressure (MPa)	Products
Combustion	700-1400	0.1	Thermal energy
Pyrolysis	500-800	0.1	Biochar Gas Bio-oil
Gasification	500-1300	0.1	Syngas

Among the various thermochemical conversion processes, pyrolysis has shown a lot of potential when used to convert biomass to liquid fuels because it gives bio-oil products of better quality and highest liquid yield up to 75 wt.% on a dry-feed basis compared to other techniques (Guillain M, 2009; Bridgwater T, 2006). Various factors such as type of biomass, heating rate, gas flow rate, final temperature, particle size and holding time plays an important role on the production and composition of pyrolysis product (Mimmo T, 2014; Paethanom A, 2012). In order to maximize the yield of bio-oil products, factors such as low temperature, high heating rate, and short gas residence time are employed whereas to increase the yield of biogas, high temperature, low heating rate, and long gas residence time process is preferred (Demirbas, 2004). **Figure 1.2** shows the utilization of products of the three main thermochemical processes (pyrolysis, gasification, and combustion) available for the conversion of biomass to renewable energy.
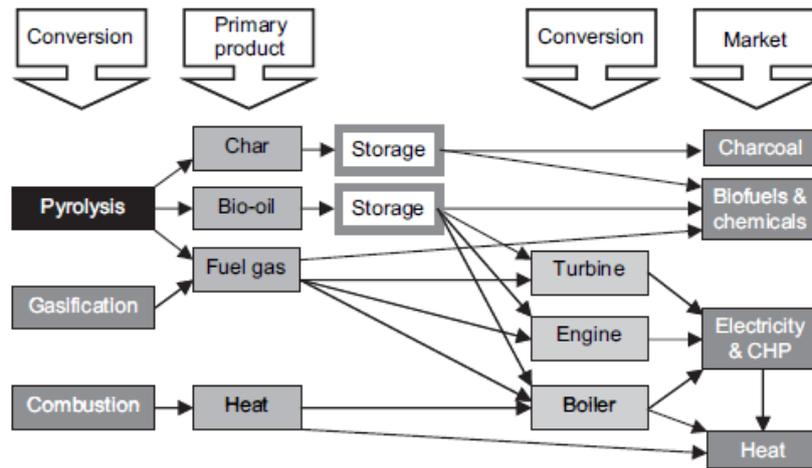
Figure 1.2 Utilization of products of the three main thermochemical processes (Bridgwater, 2012)

In this present study, fast pyrolysis was used to produce bio-oil from three main oil palm biomass namely empty fruit bunches (EFB), mesocarp fibre (MF), and palm kernel shell (PKS). Fast pyrolysis requires high heating rates and short residence time in the absence of oxygen to produce bio-oil, biogas, and char (Ward, et al., 2014). The bio-oil product yield from the oil palm biomass can be optimized by controlling the fast pyrolysis operating conditions such as the pyrolysis temperature and residence time (Mabrouki, et al., 2015). Modelling and simulation are a good option to optimize the pyrolysis operating conditions and to perform economic analysis on different oil palm biomass compared to having a time-consuming and costly experimental study. Thus, the main focus of this study is to improve the performance of fast pyrolysis process design using three different oil palm biomasses (EFB, MF, and PKS) by optimizing the operating conditions. Advanced System for Process Engineering (ASPEN PLUS) is an important simulation tool to optimize and analyse the performance of chemical processes is used to perform modelling and simulation of the fast pyrolysis process design in order to maximize the bio-oil product yield of the three different oil palm residues (EFB, MF and PKS). With this, we can utilize the amount of oil palm biomass produced in the palm oil industry and bring fast pyrolysis technologies to the forefront in providing sustainable solution for both economic growth and environmental protection.

1.2 Problem Statement

During the past two decades the control of consumption of energy has been a major challenge for sustainable development. The increase in energy consumption, limited fuel resources, massive dependency on fossil fuels, air pollution and greenhouse gas emission has resulted in increased research development on renewable energy sources. In the past few years, much attention has been focused on utilizing lignocellulosic biomass to produce biofuels, as they are eco-friendly, sustainable, affordable, and capable of competing with fossil fuel. Malaysia is currently the world's second-biggest producer of palm oil, the oil palm industry is the main biomass source in Malaysia, and the supply is abundant. Therefore, it is very important that the oil palm biomass can be utilized for both protection of the environment and economic development. Fast pyrolysis is very promising due to its highest yield and quality of bio-oil product compared to other techniques. There are several factors that plays a significant role on the production and composition of pyrolysis product such as type of oil palm biomass, final temperature, heating rate, gas flow rate, particle size and holding time. The main challenge to new researchers is to identify the optimum operating condition during the fast pyrolysis of different oil palm biomass to maximize the yield of bio-oil product. In this study, the yield of bio-oil product from oil palm biomass is optimized by controlling the main operating conditions such as type of oil palm biomass, pyrolysis reactor temperature and residence time. Since the experimental work is complex, costly, and time-consuming adding together with the current crisis of COVID-19 pandemic, modelling and simulation gives a better alternative to optimize the fast pyrolysis operating conditions by using the chemical properties from proximate and ultimate analysis data from literatures. The ASPEN PLUS V10.0 will be used to perform modelling and simulation to optimize efficient operating conditions on fast pyrolysis process design. Due to enormous amounts of oil palm waste produced in Malaysia,

it is anticipated that this study will bring oil palm fast pyrolysis processes to the forefront and offer a sustainable solution on utilising the oil palm biomass as a source of renewable energy.

1.3   Research Objectives

The main objectives of this research study are:

i.   To develop the model for bio-oil production from oil palm biomass via fast pyrolysis by using ASPEN PLUS V10.0.

ii.   To validate the developed model using published data of the experimental investigation obtained from literatures.

iii.   To perform simulation and optimization by using ASPEN PLUS V10.0 for fast pyrolysis operating parameters (pyrolysis reactor temperature and residence time) using three different oil palm residues namely empty fruit bunch (EFB), mesocarp fibre (MF) and palm kernel shell (PKS) and identifying the operation conditions for optimum bio-oil yield.

CHAPTER 2
LITERATURE REVIEW

Chapter 2 presents the literature review and previous discoveries of oil palm biomass in Malaysia. The chemical compositions of oil palm biomass were reviewed, and the current management scenario of oil palm waste in Malaysia were discussed. Furthermore, the principle of pyrolysis of biomass and the optimum operational condition and yield obtained from previous literatures to maximize the bio-oil product were reviewed. Lastly, various applications of pyrolysis products were briefly discussed.

2.1   Oil Palm Biomass

Malaysia has around 457 palm oil mills as of October 2020, processing approximately 117 million tons of fresh fruit bunch (Malaysian Palm Oil Board, 2020). For each kg of oil palm produced, there are nearly 4 kg of dry biomass generated (Ng, et al., 2012). The main biomass generated from palm oil extraction mills are empty fruit bunches (EFB), mesocarp fibres (MF), and palm kernel shells (PKS) as shown in the **Figure 2.1**. EFB and MF are produced when the fresh fruit bunches of oil palm biomass are pressurized cooked and stripped during the process of extraction of oil whereas the PKS are obtained after separating nuts from their kernels during the extraction of palm kernel oil and crude palm oil (Awalludin, et al., 2015).

Figure 2.1 Oil Palm Biomass wastes from palm oil mills (A)Empty fruit bunches (EFB), (B)Mesocarp fibre and (C)Palm kernel shells (Awalludin, et al., 2015).

2.2   Chemical Composition of Oil Palm Biomass

The main chemical constituents of oil palm biomass consist of cellulose, hemicellulose, and lignin. Usually, they constitute around 85–90 % of the oil pam biomass while inorganic minerals and other organic extractives constitute the rest (Pasangulapati, et al., 2012). These polymers are linked with each other, and their relevant content in oil palm biomass varies with the type of oil palm biomass. The lignocellulosic contents of EFB, MF and PKS were tabulated in **Table 2.1**.

Table 2.1 Lignocellulosic contents of palm oil wastes (Abnisa, et al., 2013).

Type of oil palm wastes	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Empty fruit bunches	51.2	22.5	21.3
Mesocarp fibre	23.7	30.5	27.3
Palm kernel shell	27.7	21.6	44

From **Table 2.1**, it was observed that EFB has high cellulose content compared to MF and PKS, whereas a high hemicellulose content was found in MF. Furthermore, PKS was observed to achieve the highest lignin content. Various researchers have investigated the pyrolysis of biomass components at different temperature conditions to produce bio-oil, biochar, and non-condensable gases. Zhao, et al., (2017) studied pyrolysis of three main biomass components (cellulose, hemicellulose and, lignin) in a tube furnace at 300-700 °C. From their investigation, the author reported that among the three components, cellulose always yielded more bio-oil (47.77-64.70 %) in the temperature range of 400-700 °C followed by hemicellulose (28.62-41.44 %) and lignin (18.13-34.31 %). Compared to cellulose and hemicellulose, lignin is the most thermally resistant component due to its complex structure

which comprises of network of cross-linked aromatic molecules that are very difficult to decompose and have high thermal stability (Stefanidis, et al., 2014).

2.2.1   Cellulose

Cellulose is the most abundant organic compound on Earth with molecular formula of $(C_6H_{10}O_5)_n$. It is a polysaccharide comprising of linear chain of up to about 10000 of $\beta(1\rightarrow4)$ linked D-glucose units (Crawford, 1981). Cellulose is very fibrous, crystalline, and rigid due to its conformation which strongly favors hydrogen bonding between cellulose molecules (Meneses, et al., 2017). It has a stable structure and mechanically robust which makes it insoluble in water and resistant to depolymerization. **Figure 2.2** illustrate the chemical structure of cellulose.
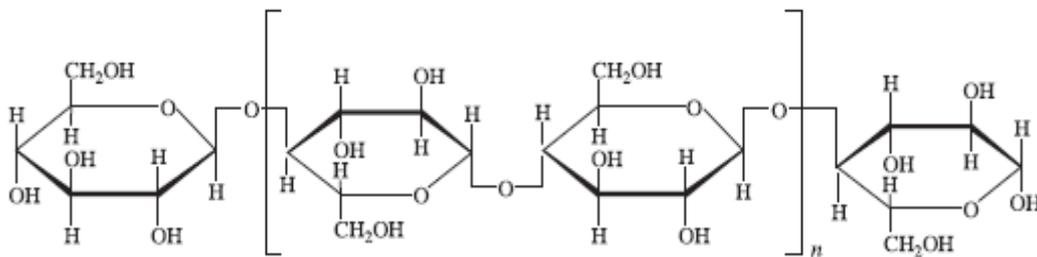
Figure 2.2 Chemical structure of cellulose (Alam, et al., 2014)

When cellulose is heated at a temperature above 350 °C during pyrolysis it decomposes to form char, vapors, aerosols, and gases such as carbon dioxide (Mettler, et al., 2012). The vapors produced can be condensed to form bio-oil at a temperature around 500 °C (Czernik & Bridgwater, 2004). Raud, et al.,(2014) reported that, high cellulose content in oil palm biomass is important condition for the production of bio-oil. This is because cellulose can easily undergo thermal decomposition to produce bio-oil.

2.2.2   Hemicellulose

Hemicellulose are polysaccharides that are chemically associated with cellulose with generic formula of $(C_5H_8O_4)_n$. They are characterized into four groups namely as xylans, mannans, mixed linkage β-glucans and xyloglucans (Heinze, 2005). Their backbones consist of β-(1→4)-linked major sugar units and unlike cellulose which is unbranched, hemicellulose is a branched polymer. **Figure 2.3** illustrate the chemical structure of hemicellulose.
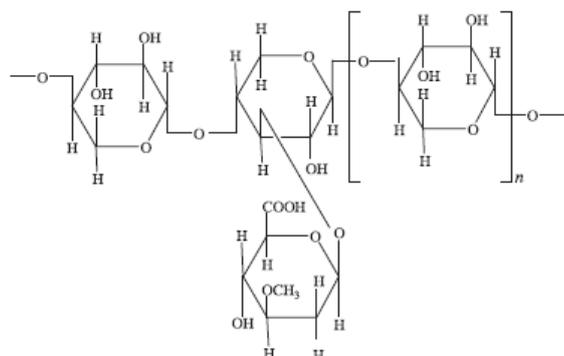
Figure 2.3 Chemical structure of hemicellulose (Alam, et al., 2014)

Hemicellulose has low degree of polymerization compared to cellulose and are easily hydrolyzed in alkali or dilute acids. Unlike cellulose which is strong, crystalline, and resistant to hydrolysis, hemicellulose has a random and amorphous structure with very little strength (Yu, et al., 2017). During pyrolysis, the degradation of hemicellulose starts at lower temperature approximately 200–260 °C and it results more volatile, less chars and less tars than cellulose (Abnisa, et al., 2013).

2.2.3   Lignin

Lignin is a complex three-dimensional polymer consisting of 4-propenyl-2-methoxy phenol, 4-propenyl phenol and 4-propenyl-2.5-dimethoxyl phenol (Meneses, et al., 2017). **Figure 2.4** illustrate the chemical structure of lignin. Lignin is the third most abundant chemical constituent of oil palm biomass and is very important in the formation of cell wall as

they support the structure of the plant by providing resistance to the microbial attack and impermeability (Hendriks & Zeeman, 2009). It ties all other constituents of oil palm biomass which make the biomass water insoluble and harder to degrade. Chang & Holtzapple,(2000) reported that, high lignin content in oil palm biomass led to low digestibility of the biomass. Reason for this is that thermal decomposition of lignin is much more difficult compared to that of cellulose and hemicellulose. The pyrolysis of biomass with high lignin content generally leads to high yield of solid char (Akhtar & Amin, 2012).

Figure 2.4 Chemical structure of lignin (Mahmood, et al., 2018)

2.3   Current Management Scenario of Oil Palm Biomass

Malaysia produces huge amount of oil palm residues from oil palm production. Broad research in alternative uses of the by-products is going on. Usually, the oil palm biomass produced is either disposed on landfills, converted to fertilizers, or utilized as animal feed (Mahmud K.N., 2020). In Malaysia, a number of methods have been broadly used by the oil palm industries to improve the sustainability of the industry in agreement with agriculture practices, codes of practices and environmental regulations. Conventionally, composting technique has been widely applied to recycle oil palm biomass in most oil palm plantations in Malaysia as its relatively simple and inexpensive. Additionally, around 77% of palm oil mills

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in Malaysia use combustion or combined heat and power (CHP) systems to generate electricity whereas only 5% of the industries use gasification for power generation (Hamzah, et al., 2019). The main challenge that the oil palm industries are facing in achieving sustainable development is the handling of oil palm biomass wastes in compliance with environmental regulations for instance the Environmental Quality Act (EQA) 1974. Therefore, more research should be done on this field to find more sustainable ways of utilizing the oil palm biomass for both environmental protection as well as economic development.

2.4   Pyrolysis Principle

Pyrolysis involves thermal decomposition of organic matter at a temperature around 500°C-800°C in the absence of oxygen. The chemical reaction involved during pyrolysis of biomass constituents (cellulose, hemicellulose, and lignin) are very complex and comprises of multiple steps. The final product of pyrolysis of biomass consists of biochar, bio-oil, and non-condensable gases. **Figure 2.5** shows the degradation pathways for pyrolysis of cellulose, hemicellulose, and lignin.
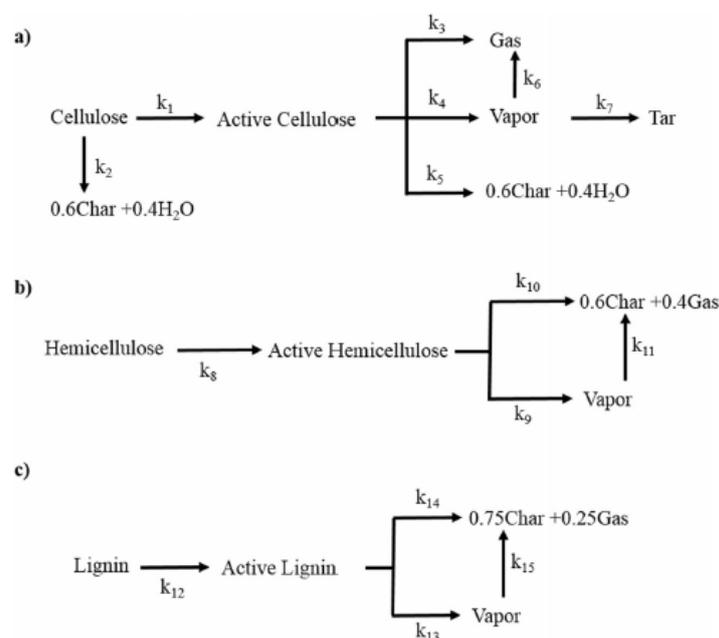
Figure 2.5 Degradation pathways for pyrolysis of (a) cellulose, (b) hemicellulose, and (c) lignin (Thu, et al., 2020).

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The organic compounds present within the biomass begins to decompose at a temperature of around 350–550°C and it can continue until 700–800°C in the absence of oxygen (Bridgwater & Peacocke, 2000). Pyrolysis breaks down large hydrocarbon molecules of biomass into smaller hydrocarbon molecules, that are released from the process stream as solid char, non-condensable gases, and condensable vapors (tars and oils). The final product depends on pyrolysis operating conditions such as reactor temperature, residence time, heating rate, size of feed particles, and gas flow rate. **Figure 2.6** illustrates the decomposition process of biomass constituents at different temperature.
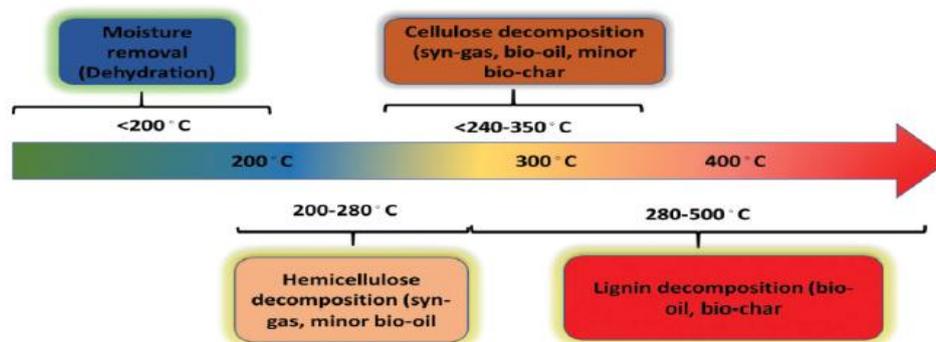
Figure 2.6 Decomposition of biomass constituents at different temperature (Zaman, et al., 2017).

The pyrolysis process of biomass to produce bio-oil, biochar and gaseous products includes pre-treatment (drying and size reduction), thermal decomposition (pyrolysis reactor), gas-solid separation (cyclone), condensation and collection of the bio-oil product were shown in **Figure 2.7**. The pre-treatment of biomass includes drying and grinding. The biomass sample is usually dried to less than 10% water using a drum drying unit to minimize the water content in the bio-oil product (Zaman, et al., 2017). After the drying procedure, the biomass is introduced into the grinder for size reduction prior to being fed into the reactor. The sample is then fed into the pyrolysis reactor whereby the biomass is heated to a temperature of around 500-800 °C in the absence of air to produce char, vapours, aerosols, and gases. Followed by that, is the separation of solid char from the pyrolysis gas stream using cyclone separator unit. Then the pyrolysis gas stream is condensed to obtain bio-oil product which then enters the

separator that separates the syngas and bio-oil. The bio-oil product is stored to preserve the oil compounds to achieve a high yield and good quality.
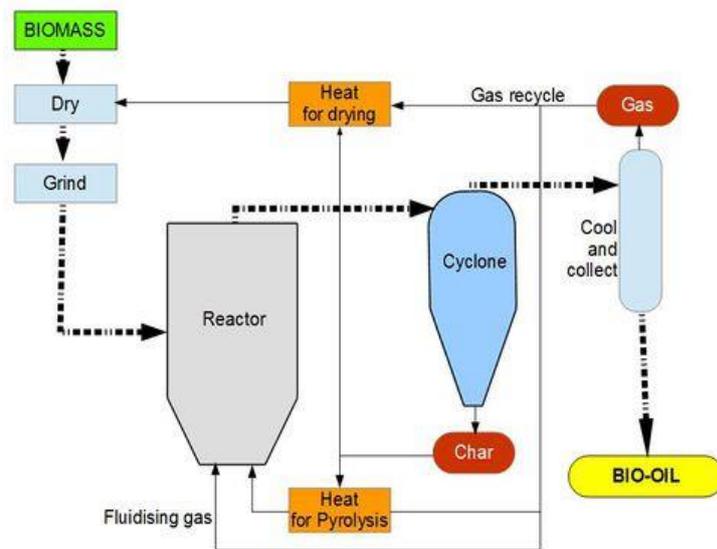
Figure 2.7 Pyrolysis process of biomass (INTEC, 2015)

2.5   Types of Pyrolysis

The most common types of pyrolysis technique are fast pyrolysis and slow pyrolysis which are classified based on their heating rates.

2.5.1   Slow Pyrolysis

In slow pyrolysis, the biomass is heated at a controlled temperature of around 400 °C with low heating rate (0.1–1 °C/s) under residence time of around 5 to 30 min mainly to produce char/solid products (Corona, et al., 2016). Due to long gas residence time, the gas phase products have sufficient time to react continuously with each other to form charcoal (Bahng, et al., 2009).

2.5.2   Fast Pyrolysis

In recent years, several studies have been extensively conducted on the conversion of biomass to produce bio-oil via fast pyrolysis. Fast pyrolysis has attracted more attention due to its highest yield and quality of bio-oil product produced with a minimum of gas and char

compared to other techniques. It occurs at high temperature of around 500 °C with high heating rate (10-200 °C/s) under short residence time (few seconds or less) to form vapours, aerosols, and charcoal (Corona, et al., 2016). The short gas residence time is employed intentionally to prevent the decomposed products to undergo re-polymerization. When the product is rapidly cooled and condensed, a dark brown mobile liquid is formed with half heating value compared to that of conventional fuel oil (Bioenergy, 2021).

2.6   Products of Pyrolysis of Oil Palm Biomass

Fast pyrolysis offers the effective use of oil palm biomass to produce bio-oil, biochar, and gaseous product as shown in **Figure 2.8**. The first product produced during fast pyrolysis is biochar. Demirbas, (2004) reported that, high biochar is produced when the pyrolysis is carried out at low heating rate, low temperature, and long vapor residence time. The second main product produced is bio-oil. The yield of bio-oil from oil palm biomass can be maximized by employing high heating rate and short vapor residence time (Demirbas, 2004). The third main product produced are the non-condensable gaseous products consisting mainly of hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), and traces of ethylene (C_2H_4), ethane (C_2H_6), propylene (C_3H_6) and propane (C_3H_8) (Mahmud K.N., 2020). The yield of syngas is favored by high temperature, low heating rate and long gas residence time (Demirbas, 2004).

Figure 2.8 Products of Pyrolysis of Oil Palm Biomass (Kabir, et al., 2015)

2.6.1   Biochar

Char is a solid residue present on the pyrolysis vapors product and is removed by cyclone separation. It contains high percentage of carbon, small amounts of oxygen and hydrogen, and inorganic compounds that were present in the original oil pam biomass (Pattiya, 2018). Nevertheless, some small amount of it that passes through the cyclones is present in the bio-oil product which exacerbate the instability problem and accelerate aging (Bridgwater, 2012). Char can be utilized as a solid fuel to power boilers therefore it is considered as a valuable by-product.

2.6.2   Bio-oil

The bio-oil product from fast pyrolysis is obtained after the gaseous products consist of aerosols, true vapors and non-condensable gases from pyrolysis reactor are cooled rapidly to minimize secondary reactions resulting from condensation of the true vapors (Bridgwater, 2012). The bio-oil produced is dark brown in color and its composition consists of complicated mixture of water, fine chars, and compounds (monomers, oligomers, and polymers) resulting from cellulose, hemicellulose, and lignin components of biomass. These includes alcohols furans, ketones, aldehydes, sugars, acids, syringols, guaiacols, phenols, esters and multifunctional compounds, such as hydroxyaldehydes, hydroxyketones, and hydroxyacetic acids (Pattiya, 2018).

The application of bio-oil produced as a fuel in turbines or engines is challenging due to its unfavorable properties such as high viscosity, high oxygen content, acidity, instability during storage and high water content (Czernik & Bridgwater, 2004). The organic acids which come from biopolymer degradation cause the bio-oil to have a pH of about 2.5 which can results corrosion of pipes and containers used to store the bio-oil. Therefore, materials that are corrosion-resistant such as stainless steel or polyolefin are required (Xu, et al., 2018).

Depending on the nature of the biomass, the high oxygen content of bio-oil (45–50 wt.%) results to many problems such as low heating value, poor miscibility with hydrocarbons, and poor thermal stability (Xu, et al., 2018). The water content in the bio-oil product is around 15-30 wt% depending on the operating conditions and biomass feedstock moisture content. High water content in the bio-oil produced is not desirable as it leads to lower flame temperature and heating value, also it decreases the efficiency of combustion and delays ignition. Therefore, drying of biomass feedstock is crucial as it helps to reduce the water content on the bio-oil product.

To overcome the undesired properties, the bio-oil can be upgraded by physical and chemical methods to give higher quality biofuel that can be used as transportation fuels. The physical upgrading methods includes filtration to remove particulates, blending the bio-oil product with solvents and additives to improve its flash point, miscibility, boiling range and reduce viscosity (Bridgwater, 2013). The chemical upgrading methods includes hydrocracking and hydrotreating of bio-oil product to displace oxygen atom by hydrogen as well as to lower the molecular weights (Xu, et al., 2018). Hydrotreating and hydrocracking chemical upgrading methods are very promising approaches for industrial processing of bio-oil product into transportation fuels because they are at engineering stage in the development.

2.6.3   Non-condensable Gases

Non-condensable gases produced from heating of oil palm biomass during fast pyrolysis consists of CO_2, CO, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8. Furthermore, if the bio-oil collection system is not 100% efficient several light volatile components such as toluene, benzene, pentane, acetaldehyde, and xylenes may be present in the gaseous stream (Pattiya, 2018). The fast pyrolysis gaseous products contain a substantial amount of valuable combustible gases such as CO_2, H_2 and CH_4 which can be used for fuel purposes in the industrial combustion process to provide process heat as reported by Bridgwater, (1994).

2.7   Fast Pyrolysis Optimum Operating Conditions and Yield

Various biomass feedstocks have been studied over the years to determine the optimal conditions to produce higher bio-oil product yield.

2.7.1   Experimental Investigations

Sukiran, et al., (2016) carried out the fast pyrolysis of empty fruit bunch (EFB), trunk, frond, and palm kernel shell (PKS) using fluidized bed reactor by varying several process parameters that affect the yield of bio-oil product such as pyrolysis temperature and particle size. The range of temperature used was 400-600 °C and particle size of $< 90 - 180$ µm for EFB and 107-125 µm for trunk, frond and PKS. Based on the results, the maximum bio-oil yield was 43.5 wt.% obtained using EFB having particle size of 107-125 µm at the pyrolysis temperature of 500 °C while the lowest yield was from PKS (18.9 wt.%). The yields of bio-oil for trunk and frond were 29.4 wt.% and 25.7 wt.%, respectively.

Additionally, Sukiran, et al., (2018) also investigated the impact of different washings on the yield of resulting bio-oil products from fast pyrolysis of empty fruit bunches (EFB) using a fluidized bed reactor at 500 °C with particle size ranging from $< 90 - 180$ µm. Three types of pre-treatment were performed. These pre-treatments of the sample included washing with NaOH (0.1M), H_2SO_4 (0.1M), and distilled water. The reported results showed that EFB without washing pre-treatment gave 47.4 wt.% bio-oil yield while the EFB washed with H_2SO_4 shows the maximum bio-oil yield of 55.6 wt.% followed by EFB washed with distilled water (52.8 wt.%) whereas EFB washed with NaOH gave the lowest yield of 24.3 wt.%. Recently, Sutrisno & Hidayat (2018) studied the effect of temperature and heating rate of fast pyrolysis process on empty fruit bunch using bench scale tubular furnace reactor to produce bio-oil product. They found out the maximum bio-oil yield produced was 44.5% at a temperature of 450 °C and heating rate of 10 °C/min. The bio-oil products were mainly composed of aldehydes, acids, ketones, alcohols, oligomers, phenols, and ketones.

Ogunkanmi, et al., (2018) investigated the effect of particle size and pyrolysis temperature on bio-oil yield of palm kernel shells (PKS) using fixed bed reactor. The maximum bio-oil yield was 38.67 wt.% at 450 °C for a feed particle size of 1.18mm. This reported bio-oil product yield for PKS was consistent with that reported by Ahmad, et al., (2014) 38.4 wt.% using fixed bed reactor at 450°C with a heating rate of 50 °C min^{-1} and a nitrogen sweep gas flow rate of 50 ml min^{-1}. Kabir, et al., (2018) carried out pyrolysis of oil palm mesocarp fiber catalysed with a steel slag derived zeolite (FAU-SL) in a fixed bed reactor at 450 °C, 550 °C, and 600 °C. Based on the results, the maximum bio-oil yield of 47 wt.% was achieved at 550 °C.

2.7.2 Modelling and Simulation Investigations

Although, several studies have been conducted to investigate the effect of operating conditions on the bio-oil product yield, major investigations focus on the experimental results. There are very few studies that integrates process modelling and simulation results which is very crucial for development of efficient fast pyrolysis process. Mabrouki, et al., (2015) performed optimization of bio-oil production from the fast pyrolysis of palm shell, empty fruit brunch and mesocarp fibre using SuperPro Designer (SPD) software. Operating conditions such as pyrolysis reactor temperature and residence time were examined. The model showed that, the maximum bio-oil yield of 46.75 wt.% is obtained for empty fruit brunch, while mesocarp fibre and palm shell produce a yield of 45.05 wt.% and 36.65 wt.% respectively. Furthermore, from their results a temperature of 550 °C and a residence time of 0.5 s was suitable for obtaining maximum bio-oil product yield.

Ward, et al., (2014) developed computational fluid dynamics (CFD) model and perform simulation of four different biomass, namely wood, birch, pine chips, and shredded green waste using ASPEN PLUS V10.0 to increase the yields of pyrolysis products such as bio-oil, biochar, and syngas as a function of pyrolysis temperature, and physical and chemical

properties of biomass. Based on their results, the highest yield of bio-oil is achieved by shredded green waste (58.01 wt.%), followed by birch (43.10 wt.%), while wood and pine chips achieve a yield of 42.97 wt.% and 42.77 wt.% respectively. The high yield for shredded green waste were obtained due to its high cellulose and low moisture content. Therefore, shredded green waste was recommended as a potential biomass for bio-oil production compared to other mentioned biomass via fast pyrolysis.

Modelling and simulation are very crucial for understanding of the thermo-chemical reaction mechanism as well as optimizing efficient and economic fast pyrolysis process design rather than having a costly and time-consuming experimental study (Ward, et al., 2014). After taking into account all of these factors it is required to do more research for further development and improvement of the modelling and simulation in this area. **Table 2.2** summarizes the main results from selected literature. Therefore, the main focus of this study is to improve the performance of the fast pyrolysis process with oil palm biomass as a function of operating conditions such as pyrolysis reactor temperature and residence time and to identify the operation condition during the fast pyrolysis of different oil palm biomass (EFB, MF and PKS) for optimum bio-oil yield. Modelling and simulations of bio-oil production from fast pyrolysis of oil palm biomass is done using ASPEN PLUS V10.0. The ASPEN PLUS can optimize the operating conditions such as pyrolysis temperature and residence time, also it can calculate the pyrolysis yield by obtaining chemical properties from ultimate and proximate analysis test values from literatures.

Table 2.2 Summary of optimal conditions and yields reported in recent literatures for production of bio-oil via fast pyrolysis of biomass.

Biomass types	Optimal conditions	Bio-oil yield	Reactor type	References
Empty Fruit Bunches Trunk Fronds Palm Kernel Shell	Temperature = 500 °C Feed particle size = 107-125 μm	43.5 wt.% 29.4 wt.% 25.7 wt.% 18.9 wt.%	Fluidized bed reactor	(Sukiran, et al., 2016)
Empty Fruit Bunches	Temperature = 450 °C Heating rate = 10 °C/min	Without washing = 47.4 wt.% Washed with H_2SO_4 = 55.6 wt.% Washed with NaOH = 24.3 wt.%. Washed with distilled water = 52.8 wt.%	Fluidized bed reactor	(Sukiran, et al., 2018)
Empty Fruit Bunches	Temperature = 450 °C Heating rate of 10 °C/min	44.5%	Bench scale tubular furnace reactor	(Sutrisno & Hidayat, 2018)
Palm Kernel Shells	Temperature = 450 °C Feed particle size = 1.18 mm	38.67 wt.%	Fixed bed reactor	(Ogunkanmi, et al., 2018)
Mesocarp Fibre	Temperature = 550 °C	47 wt.%	Fixed bed reactor	(Kabir, et al., 2018)
Empty Fruit Bunches Mesocarp Fibre Palm Kernel Shells	Temperature = 550 °C Residence time = 0.5s	46.75 wt.% 45.05 wt.% 36.65 wt.%	Fluidized bed reactor	(Mabrouki, et al., 2015)
Shredded green waste Birch Wood Pine chips	Temperature = 500 °C Feed particle size = 1 mm	58.01 wt.% 43.10 wt.% 42.97 wt.% 42.77 wt.%	Fluidized bed reactor	(Ward, et al., 2014)

2.8   Application of Pyrolysis Products

The bio-oil produced from pyrolysis has high energy density than the raw biomass. It can be easily stored, handled, and transported (Shrivastava, et al., 2020). The bio-oil product can be utilized directly as a fuel in a turbine, boiler or an engine for heat and electricity production. It can also be upgraded to produce gasoline and diesel that can be used as a transport fuel (Bridgwater, 1999). Another use of bio-oil is the production of chemicals through recovery. These chemicals include hydroxyacetaldehyde, polyphenols, fertilisers, and a wide variety of flavours for the food processing industry (Bridgwater, 1999). **Figure 2.9** summarizes the possibilities for bio-oil applications. The biochar and gas produced during pyrolysis can be utilized as biofuels for power or heat generation for use in pyrolysis or other processes (Shrivastava, et al., 2020).
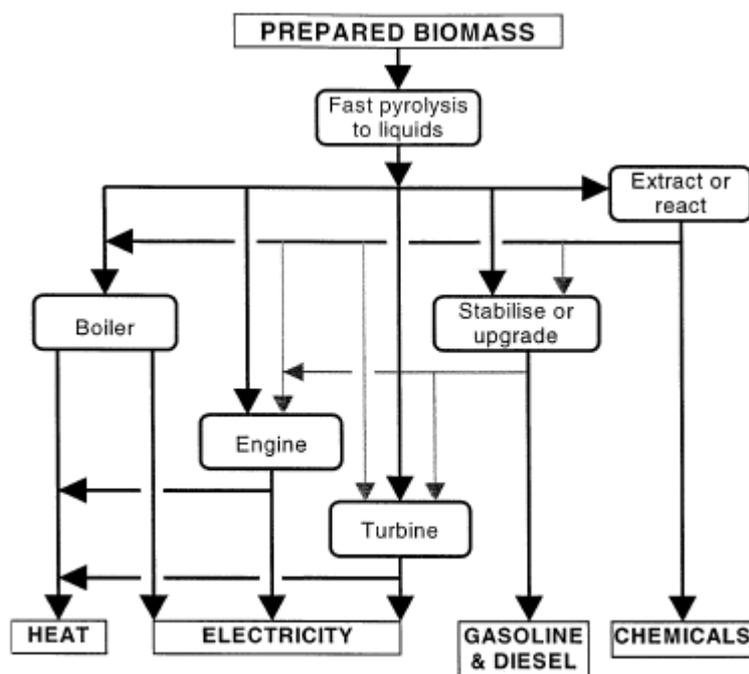
Figure 2.9 Applications of bio-oil (Bridgwater, 1999)