THE PRODUCTION OF BIO OIL THROUGH BATCH PYROLYSIS PROCESS

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ABSTRACT

Energy demand is increasing continuously due to rapid growth in population and industrialization development. The major energy demand is provided from the conventional energy sources such as coal, oil, natural gas, etc. Two major problems, which every country is facing with these conventional fuels, are depletion of fossil fuels and deterioration of environment. Pyrolysis of biomass will be one of the alternative ways to encounter this problem. The pyrolysis of palm-oil industrial waste was investigated in a static batch reactor is. The effect of pyrolysis parameter on the product yields and composition were investigated. PKS was pyrolysed at moderate range of temperatures of 200˚C, 300˚C, 400˚C, 500˚C and 600˚C. The effects of various temperatures towards the yield of pyrolysis process of palm kernels were investigated. The compositions and properties of the pyrolytic oils and solid chars are determined with respect to pyrolysis temperatures. The static batch reactor shows that the temperature of 400 ˚C gives the highest percentage of PKS bio-oil yield which attributes to 37.2 %. EFB with sample length of L < 1 mm, 1-5 mm, 5-10 mm, L > 10 mm were pyrolysed at constant temperature of 400 ˚C. The highest yield of the bio oil for the empty fruit bunches is obtained at the range of length between 5-10 mm whish attribute to 39.525 wt%. Preliminary experiment was conducted using thermogravimetric analyzer (TGA) to determine the volatility, ash content, moisture and fixed carbon. The functional groups of the product which is bio oil are identified by using Fourier Transform infrared spectrometer (FTIR). The chemical characterization studies show that the bio oil obtained from the palm kernels has the potential to be a valuable source renewable fuel and as feedstock for specialty of chemicals.

ABSTRAK

Permintaan terhadap tenaga terus meningkat kesan perkembangan pesat populasi dunia dan pembangunan industry. Bekalan utama tenaga adalah datang daripada sumber seperti arang batu, minyak mentah, gas asli dan sebagainya. Dua masalah utama yang biasa dihadapi oleh semua negara berkenaan sumber tenaga ini adalah berkenan bekalan sumber bahan api fosil yang semakin berkurangan dan kesan buruknyer terhadap alam sekitar. Pyrolisis biomass adalah salah satu dari cara alternatif bagi mengatasi masalah ini. Pyrolisis terhadap sisa industry kelapa sawit telah dijalankan menggunakan "static batch" reaktor. Kesan parameter pyrolisis terhadap hasil pyrolisis dan komposisinya telah dikaji. Proses pyrolisis terhadap tempurung kelapa sawit telah dijalankan pada suhu 200^0C, 300^0C 400^0C, 500^0C dan 600^0C. Kandungan dan sifat minyak pyrolitik dan arang yang terbentuk telah dikenal pasti. Kajian yang dijalankan menunjukkan bahawa pada suhu 400^0C telah memberi peratusan penghasilan mimyak tertinggi iaitu sebanyak 37.2 %. EFB dengan saiz sampel L < 1 mm, 1-5 mm, 5-10 mm, L > 10 mm telah di pyrolysis pada suhu tetap iaitu pada 400 ^{0}C. Kajian yang dijalankan menunjukkan bahawa pada saiz 5-10 mm telah memberi peratusan penghasilan mimyak tertinggi iaitu sebanyak 39.525 wt%. Ujikaji awal yang dijalankan terhadap tempurung kelapa sawit menggunakan thermogravimetric analyzer (TGA) adalah bertujuan untuk menentukan kemeruapan, kuantiti abu dan kelembapan tempurung kelapa sawit yang digunakan dalam eksperimen. Manakala kumpulan berfungsi untuk minyak yang dihasilkan telah diuji menggunakan Fourier Transform Infrared (FTIR).Sifat-sifat kimia yang dikaji menunjukan bahawa minyak yang terhasil berpotensi menjadi bahan api dan boleh dijadikan bahan mentah bagi penghasilan bahan kimia.

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g	-	gram
s	-	second
° C	-	degree calcius
mol/g	-	mole per gram
wt%	-	weight percentage
mm	-	millimeter
mg/l	-	milligram per liter
%	-	percentage
mg/MJ	-	milligram per Mega Joule
mg/m^3	-	milligram per meter cubic
in	-	inch
psig	-	pressure gauge
MJ/kg	-	Mega Joule per kilogram
MJ/m^3	-	Mega Joule per meter cubic
cm	-	centimeter
ml/min	-	milliliter per minute
wt%	-	weight percentage
cm^3/min	-	centimeter cubic per liter
mg/l	-	milligram per liter

CHAPTER 1

INTRODUCTION

1.1 Introduction

As energy demand is increasing continuously due to speedy development in population and industrialization, the development of energy sources is not keeping pace with spiraling consumption. Developed countries are also finding it difficult to compensate even after increasing the energy production multifold due to growth pressure. The major energy demand is compensated from conventional energy sources such as coal, oil, natural gas, etc. Two major problems, which every country is facing with these conventional fuels [Saxena R.C. et al., 2009] Firstly, these energy sources are at the verge of getting extinct. World's oil reserves are estimated to get depleted by 2050. Secondly, energy extraction from these conventional fuels causes pollution. It is well known that SO_2 emission produced by burning fossil fuels is the major cause of acid rain. Globally, increase in emissions rates of greenhouse gases, i.e., CO_2 present a threat to the world climate. As an estimate in the year 2000, over 20 million metric tons of CO_2 were expected to be released in the atmosphere every year [Putun A.E. et al, 2001, Bridgewater A.V. et al, 2003]. If this trend continues, some extreme natural calamities are expected such as excessive rainfall and consequent floods, droughts and local imbalance.

Presently, there is utmost need of alternative energy resources which are cheap, renewable and do not cause pollution. Therefore, attention is being given to alternate and renewable sources such as solar, wind, thermal, hydroelectric, biomass, etc.

Biomass is organic material made from plants and animals. Biomass contains stored energy from the sun. Plants absorb the sun's energy in a process called photosynthesis. The chemical energy in plants gets passed on to animals and people that eat them. Biomass is a renewable energy source because we can always grow more trees and crops, and waste will always exist. Some examples of biomass fuels are wood, crops, manure, and some garbage [Annual Energy Review*, 2006*]. Biomass is part of the carbon cycle, where carbon in the air is converted into a biological matter using photosynthesis.

Biomass is a renewable source of fuel, as plants or trees specifically grown to produce biomass can be replaced, and don't take long to grow. Biomass is seen as more environmentally friendly and longer lasting than traditional fossil fuels. Biomass has another significant advantage over fossil fuels in that plants suitable for producing biomass and bio-fuel can be grown almost anywhere in the world. Fossil fuels like petrol or gas and other traditional fuel types are only produced in certain areas of the world, but biomass can be created anywhere.

In Malaysia, Biomass resources are available from palm oil plantations, forestry and wood industry, rice husk and several other agricultural sources and agro-industries. Presently the largest fraction (about 90%) of solid biomass fuels is used (ineffectively) as a boiler fuel in palm oil industry, but also to some extent (about 10%) in wood industries, rice mills, sugar mills etc. The largest and most easily available biomass resources originate from the country's palm oil industries. The oil palm industry in Malaysia started 80 years ago in a modest way. Today it is the largest in agricultural plantation sector, exceeding rubber plantation by more than double in area planted. In

terms of hectare, the total area under oil palm cultivation is over 2.65 million hectares producing over 8 million tonnes of oil annually.

The oil consists of only 10% of the total biomes produced in the plantation. The remainder consists of huge amount of lignocellulosic materials such as oil palm fronds, trunks, empty fruit bunches and mesocarp remains. The conventional method of burning these residues often create environmental problems in that it generates severe air pollution and is prohibited by the Environment Protection Act. In abiding by the regulations, these residues are becoming expensive to dispose. This residue is the larges biomass resource in Malaysia. Malaysia therefore has a great potential in turning its abundant supply of oil palm industry by-products into value-added products. Palm oil mills are not evenly distributed throughout Malaysia. 42% of the planted area is in Western Malaysia, while 58% is located in Peninsular Malaysia. The 5 states with the highest planted area cover 85% of the country total [Anders Evald et al., 2005].

Pyrolysis is the thermal decomposition of organic materials in the absence of oxygen or any other reagents, to produce a solid residue, known as char, a liquid fraction and gases such as hydrogen, carbon monoxide and dioxide and methane.[E. Kantarelis et al.2008]. In the pyrolysis process the heavier hydrocarbons are cracked giving rise to lighter ones; these are the greatest interest as their heating values are higher. Bio-oil is a complex mixture, highly-oxygenated with a great number of large size molecules, which nearly involve all species of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, carboxylic acids and alcohols. The biochar product is carbon-rich and a potential solid biofuel.

Pyrolysis has been widely used for utilizing waste biomass materials such as waste textiles [Miranda et al., 2007], waste tires [Shen et al., 2007], used automobile lubricating oils [Kim and Kim, 2000], waste cottons [Isci and Demirer, 2007], forestry and agricultural wastes [Lapuerta et al., 2007; Cao et al., 2004]. In this study we

investigate the effect of temperature and pyrolysis characteristic to obtain valuable information about bio-fuels that can be potentially generated by pyrolysis. The process of pyrolysis is accomplished by heating the samples under non-oxidizing conditions in order to produce solid, liquid and gaseous products using static batch reactor. The functional group of the product which is bio oil were identified by using FTIR .The chemical characterization studies showed that the bio oil obtained from palm kernel shell might be a potentially valuable source as renewable fuel and chemical feedstock.

1.2 Problem Statement

The using of renewable energy such as biomass as an alternative for fossil fuel will help to prevent environment pollution and green house effect. Although biomass contains carbon and the generation of energy out of this fuel releases CO_2, this CO_2 is also taken out of the atmosphere during growth of the plant. In contrast to the carbon in fossil fuels the carbon in biomass has a cycle period from plant to the atmosphere and back of between one and some tens of years. The using of renewable energy will also decrease the depending on fossil fuel as primary energy source in our daily life That is very important because these energy sources are at the verge of getting extinct. World's oil reserves are estimated to get depleted by 2050.

Pyrolysis is widely use to convert the stored energy from the sun (biomass) into useful product which is bio-oil, but it is difficult to get high yield of the liquid product and it efficiencies which is either the production is worth with the energy use for conversion process. The pyrolysis on this study will be carried out using static batch reactor and electric tubular furnace. By determining and justifying the product, as bio oil. We can declare that the process that been developed is functioning and have a potential to be commercialize. Temperature and sample size played major role in determining the fraction of yield of bio-oil, bio-gas and char production. In this study we

need to determine the optimum temperature and sample size that will produce the higher yield of bio-oil product.

1.3 Objective of Research

To study the production of bio oil trough batch pyrolysis process on palm kernel shell and empty fruit bunch.

1.4 The Scope of Research

To achieve the objective, scopes have been identified in this research. The scopes of this research are listed as below:

1. The pyrolysis of palm oil waste was investigated in a static batch reactor.
2. The effect of temperature to a pyrolysis process of palm kernel shell was investigated with constant overall particle size of 1mm diameter. The study had been conducted at moderate temperature 200^0C, 300^0C, 400^0C, 500^0C and 600^0C.
3. The effect of sample size to a pyrolysis of empty fruit bunch was investigated with constant temperature of 400 ^{0}C. The study had been conducted for sample length of L < 1 mm, 1-5 mm, 5-10 mm, L > 10 mm.
4. The composition and properties of the pyrolytic oils and solid char were determined to justified and validate the batch pyrolysis process that been used.

CHAPTER 2

LITERATURE STUDY

2.1 Biomass Background

Biomass comprises all the living matter present on earth. It is derived from growing plants including algae, trees and crops or from animal manure [Bridgewater, 1999]. The biomass resources are the organic matters in which the solar energy is stored in chemical bonds. It generally consists of carbon, hydrogen, oxygen and nitrogen. Sulfur is also present in minor proportions. Some biomass also consist significant amounts of inorganic species. Plants, via photosynthesis, produce carbohydrates which form the building blocks of biomass [Demirbas, 2001]. Biomass contains stored energy from the sun. Plants absorb the sun's energy in a process called photosynthesis. The chemical energy in plants gets passed on to animals and people that eat them. Biomass is a renewable energy source because we can always grow more trees and crops, and waste will always exist. Some examples of biomass fuels are wood, crops, manure, and some garbage.

Biomass is part of the carbon cycle, where carbon in the air is converted into a biological matter using photosynthesis. Biomass is a renewable source of fuel, as plants or trees specifically grown to produce biomass can be replaced, and don't take long to grow. Biomass is seen as more environmentally friendly and longer lasting than traditional fossil fuels. Biomass has another significant advantage over fossil fuels in that plants suitable for producing biomass and bio-fuel can be grown almost anywhere in

the world. Fossil fuels like petrol or gas and other traditional fuel types are only produced in certain areas of the world, but biomass can be created anywhere.

Biomass is one of the most important potential sources of renewable energy in Malaysia. Biomass resources are available from palm oil plantations, forestry and wood industry, rice husk and several other agricultural sources and agro-industries. Presently the largest fraction (about 90%) of solid biomass fuels is used (ineffectively) as a boiler fuel in palm oil industry, but also to some extent (about 10%) in wood industries, rice mills, sugar mills etc. [Anders Evald et al., 2005] The present utilization of solid biomass fuels takes place in industries, that have direct access to the biomass, and who are used to handling large volumes of the products.

2.2 Biomass Utilization

Biomass has always been a major source of energy for mankind from ancient times. Presently, it contributes around 10–14% of the world's energy supply [Putun AE, et al., 2001]. Biomass can be converted into three main types of products:

1. Electrical/heat energy.
2. Fuel for transport sector.
3. Feedstock for chemicals.

Traditionally, biomass had been utilized through direct combustion. Burning biomass produces pollutants including dust and the acid rain gases such as sulfur dioxide and nitrogen oxides but the sulfur dioxide produced is 90% less than that is produced by burning coal. The quantities of atmospheric pollution produced are insignificant compared to other pollution sources. Biomass usage as a source of energy is of interest due to the following envisaged benefits:

1. Biomass is a renewable, potentially sustainable and relatively environmentally friendly source of energy.

2. A huge array of diverse materials, frequently stereo chemically defined, are available from the biomass giving the user many new structural features to exploit [Bozell Joseph J, 1999].

3. Increased use of biomass would extend the lifetime of diminishing crude oil supplies.

4. Biomass fuels have negligible sulfur content and, therefore, do not contribute to sulfur dioxide emissions that cause acid rain.

5. The combustion of biomass produces less ash than coal combustion and the ash produced can be used as a soil additive on farms, etc.

6. The combustion of agricultural and forestry residues and municipal solid wastes (MSW) for energy production is an effective use of waste products that reduces the significant problem of waste disposal, particularly in municipal areas.

7. Biomass is a domestic resource which is not subject to world price fluctuations or the supply uncertainties as of imported fuels.

8. Biomass provides a clean, renewable energy source that could improve our environment, economy and energy securities [Othmer K, 1980].

9. Biomass usage could be a way to prevent more carbon dioxide production in the atmosphere as it does not increase the atmospheric carbon dioxide level.

Biomass can be used in many ways to obtain energy. Most of the biomass energy is consumed in domestic purposes and by wood-related industries. It is burned by direct combustion to produce steam that drives the turbine or generator to produce electricity. Gasifiers are used to convert biomass into a combustible gas which is then used to drive a high efficiency, combined cycle gas turbine. Biomass is converted to pyrolysis oil by

heating. Pyrolysis oil is easier to store and transport than solid biomass material and is burned like petroleum to generate electricity.

2.3 Biomass Resources

Biomass can be obtained from various sources. These categories are mentioned below. Wastes: This category comprises wastes from agricultural production, process waste from agro industries, crop residues, etc. Standing forests: This comprises various intermediate products and residual wastes of different nature. Energy crops: This energy crop includes various edible and non-edible crops. Biomass resources that can be used for energy production cover a wide range of materials which can be categorized in two ways, namely, modern biomass and traditional biomass. Modern biomass usually involves large-scale uses and aims to substitute for conventional energy sources. Traditional biomass is generally confined to developing countries and small-scale uses [White LP, Plasket LG, 1981].

In Malaysia, the largest and most easily available biomass resources originate from the country's palm oil industries. Generally the available resources are already in use, either as an industrial raw material, for food/feed purposes or for energy. However the utilization schemes are not in all cases very efficient and some resources could be made available through acceptable changes in current practices:

1. Empty fruit bunches (EFB) account for a potential of 75 PJ, almost all currently disposed of in the plantations.

2. Palm kernel shells (PKS) account for a potential of 66 PJ, about half of which is already in use as in-mill fuel.

3. Palm oil mill efficiency improvements can release significant resources for other uses such as increased electricity production.

The main products are off course not exactly available for a biomass energy market, but a quantification of the different resources is rele vant for perspective and comparison:

Table 2.1: Energy potential 2003 in main products, byproducts and residues from palm oil Industry [MPOB].

				Product volume		**Heating value**		**Total potential**	
	Abr.	**Mois.**	**Fraction**	**Product**	**Dry Mat.**	**LHV as is**	**LHV DM**	**LHV as is**	**LHV as is**
		% m.c.	**of FFB**	**1000 ton/year**	**1000 ton/year**	**GJ/ton**	**GJ/ton**	**PJ**	**TOE**
Fresh fruit bunches	FFB	50.5%	100.0%	67610	33487	12.4	27,6	840	20077
Empty fruit bunches	EFB	67.0%	21.1%	14293	4717	4.3	18,0	61[1]	1468
Mesocarp fibers		37.0%	12.7%	8600	5418	11.1	19,0	95	2274
Kernel shells	PKS	12.0%	5.7%	3833	3373	17.3	20,0	66	1586
Kernels	PK	12.7%	5.4%	3624	3164	21.1	24,5	76	1824
Crude Palm Oil	CPO	0.1%	19.8%	13353	13340	39.3	39,4	525	12548
Effluent	POME	93.0%	60.0%	40566	2840		17,0	26[2]	618
Total					**32851**			**850**	**20318**

1. Energy potential is based on the very moist 67% m.c. EFB from the palm oil mill. Due to reduced water content, the resource in processed EFB at 45% m.c. is higher, app. 75 PJ.

2. Energy potential in effluent is based on potential production of biogas, app. 28 m3/1000 l POME and app. 23 MJ/m3 LHV for the gas.

Palm oil mills are not evenly distributed throughout Malaysia. Figure 2.1 shows the localization of palm oil plantations in the country. 42% of the planted area is in Western Malaysia, while 58% is located in Peninsular Malaysia. The 5 states with the highest planted area cover 85% of the country total. Figure 2.2 show the relative distribution of planted area in the most important states in Malaysia.

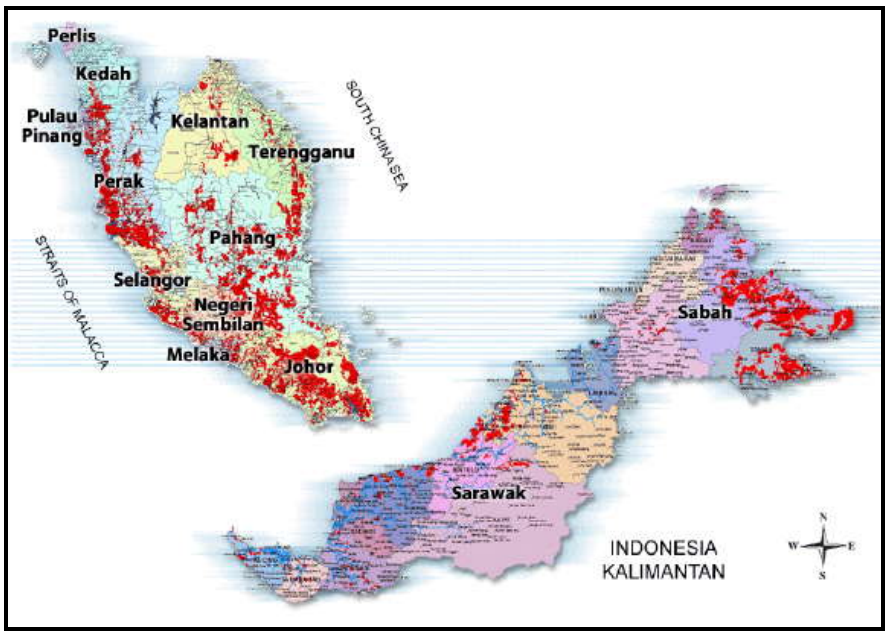

Figure 2.1: Distribution of palm oil plantations in Malaysia.

[MPOB, 2003]

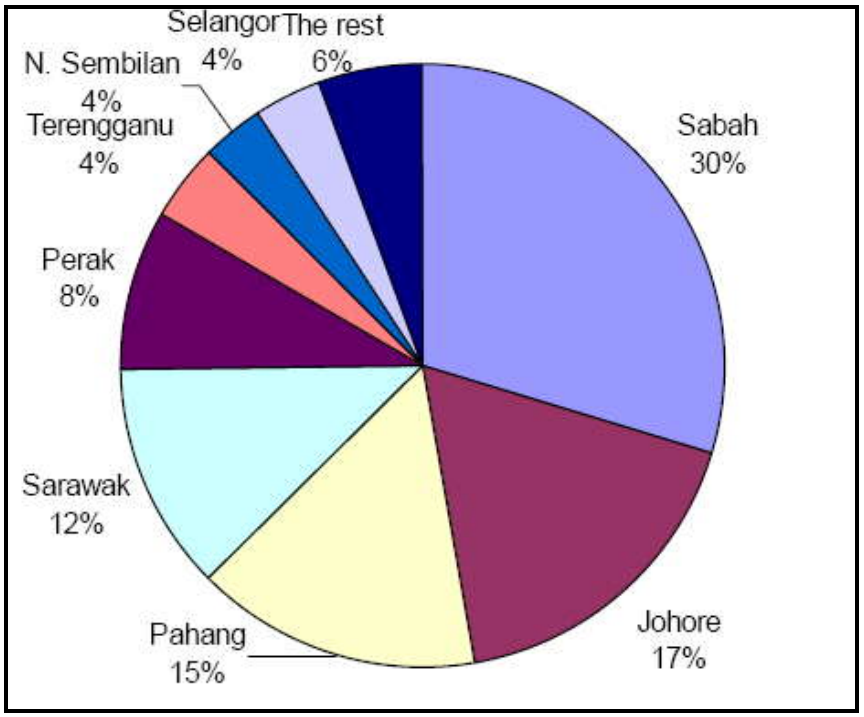

Figure 2.2: Area of palm oil plantation in the states with the highest planted area.

[MPOB, 2003]

2.4 Biomass Market Price

The following assessment intends to illustrate the relative importance of the different products from palm oil industries. Information from the table above on the energy potential in the individual products, by-products and residues is combined with price information on the products, expressed in the uniform unit RM/GJ. The purpose of the graphics is to illustrate the importance in financial terms of biomass residues as compared to the potential biomass fuels. Prices for biomass PKS and EFB are given in the individual paragraphs here. For CPO and kernels values of 1500 RM/ton and 800 RM/ton respectively is used, while the value of biogas is assumed equivalent to 85% of the cost of diesel oil, as it is assumed that the gas after some costs can substitute this fuel in the palm oil mill's diesel genset. The value of mesocarp fibers is calculated from the value of the electricity produced.

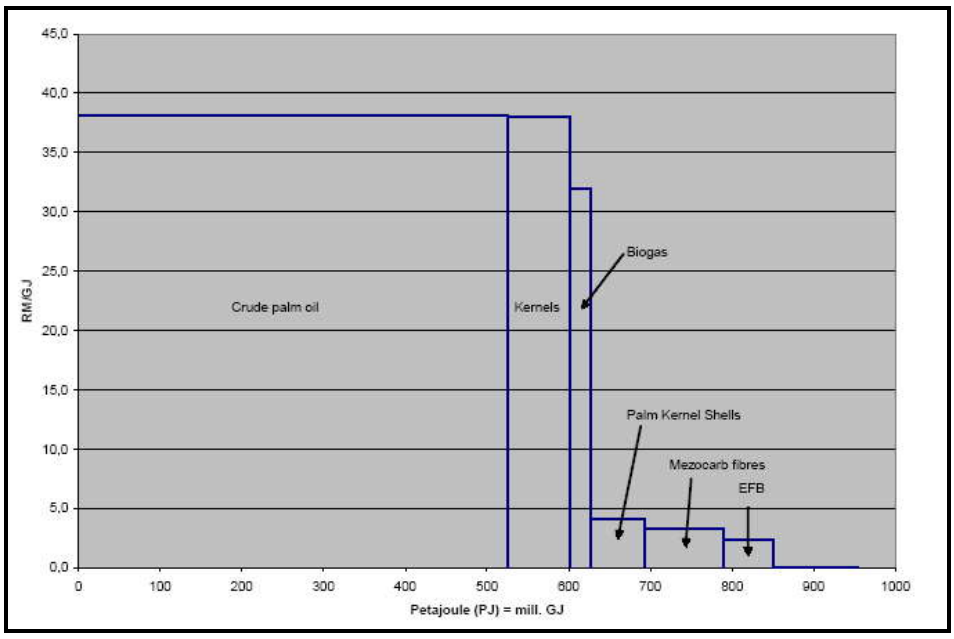

Figure 2.3: Total Biomass in Palm Oil Plantations in Malaysia [Anders, 2005]

By far the largest biomass energy source is in the main products oil and kernels, which also carries the highest value, both specific in RM/GJ and in total, as the area in