EFFECT OF SIZE PARTICLE ON PALM OIL WASTE FOR PRODUCTION OF BIO OIL THROUGH BATCH PYROLYSIS PROCESS

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APRIL 2009

DECLARATION

I declare that this thesis entitled "Effect of Size Particle on Palm Oil Waste for Production of Bio Oil through Batch Pyrolysis Process" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Dedicated, in thankful appreciation for support,
encouragement and understanding
to my beloved family and friends.

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ABSTRACT

The production of bio oil from the pyrolysis of palm oil waste (PKS and EFB) has been studied using a small lab scale pyrolysis unit. The effects of sample preparation (particle size) of the sample on the product yields and compositions were investigated .The effect of sample preparation influence the yield of the bio oil for the sample (EFB and PKS). The highest bio oil yield of PKS was obtained at 400 ^{0}C at particle size less than 5mm. For EFB, particle size (length) 5 mm -10 mm of EFB shows the higher yield of bio oil. The various characteristics of the bio oil are accomplished under these conditions and identified by the preliminary experiment conducted by using the thermo gravimetric analyzer (TGA) to determine 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 showed that the bio oil obtained from the sample (PKS and EFB) might be a potentially valuable source as a renewable fuel and for the usage of chemical feed stocks.

ABSTRAK

Penghasilan minyak bio daripada bahan buangan kelapa sawit (tandan kosong dan isirong) diuji menggunakan kaedah *pyrolysis* di dalam makmal. Untuk tujuan ini, persediaan bahan (sampel) menjadi parameter dalam kajian ini. Komposisi bahan juga dianalisis dalam kajian ini, kadar pengeluaran minyak bio yang tertinggi untuk isirong adalah pada suhu 400 ^{0}C dengan ukuran sample kurang 5 mm manakala untuk uji kaji terhadap tandan kosong, kadar pengeluaran tertinggi adalah pada ukuran sampel 5mm-10mm panjang. Karekter minyak bio yang terhasil dalam situasi ini diuji menggunakan *FTIR*, *GCMS* serta *TGA*. *FTIR* digunakan untuk mengetahui kumpulan berfungsi manakala *GCMS* digunakan untuk mengetahui komponen kimia didalam produk. TGA dalam kajian ini digunakan untuk mengetahui takat meruap sampel, baki abu dan kandungan kelembapan sampel. Dalam analisis ini, minyak bio yang diperolehi daripada sampel (Tandan kosong dan Isirong) berpotensi untuk menjadi sumber bahan api ganti dan juga untuk stok kekal bahan kimia.

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LIST OF SYMBOLS

g - gram

s - second

min - minute

^{0}C - degree celcius

Mol/g - mole per gram

Wt% - weight percentage

mm - millimeter

Mg/l - milligram per liter

Kcal - kilo calori

mL/min - milliliter per minute

in - inch

bar - pressure

µL - microlitre

LHV - low heating value

HHV - high heating value

Mj/Kg - mega joule per kilogram

Dp - diameter particle

L - length

PKS - palm kernel shell

EFB - empty fruit bunch

TGA - thermo gravimetric analyser

GC-MS - gas chromatography mass spectrometer

FTIR - fourier transform infrared spectrocopic

μm - micrometre

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Renewable energy is growing importance and it relate to the environment and security of energy supply. Ever since environmental concerns over the fossil fuels with respect to their limited reserves emerged, interest in environmental – friendly alternative energy resources that can reduce dependency on fossil fuels has been growing.

With respect to the global issues of sustainable energy and reduction in greenhouse gases, biomass is getting increased attention as a potential source of renewable energy. According to the World Energy Assessment report, 80% of the worlds primary energy consumption is contributed by fossil fuel, 14% by renewable energy (out of which biomass contributes 9.5%) and 6% by nuclear energy (Rogner *et,* 2002)

Particularly, among a number of alternative energy resources, biomass which consists mainly of cellulose, hemicelluloses, and lignin, is seen to play an important role both as chemical feedstock and as alternative to fossil fuels. Due to these facts, investigations on thermo – chemical and bio - chemical conversion technologies for biomass utilization have been conducted world wide.

Over the last two decades, a special attention has been paid to the conversion of residual biomass and renewable materials into bio fuel. (Garcia – Perez *et,* 2002) Since researches and works in relation to biomass have recently been focused on the use of biomass as a fuel.

1.2 Palm Oil Waste

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 term 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 reminder consists of huge amount of lignocellulose materials such as oil palm frond, trunk, and empty fruit bunches. The projection figure of these residues is as follows:

i. 7.0 million tonnes of oil palm trunks

ii. 26.2 million tonnes of oil palm fronds

iii. 23% of empty fruit bunch (EFB) per tonne of the fresh fruit bunch (FFB) processed in oil palm mill.

These figures depend on life span of oil palm tree that is due for replanting after about 20 -25 years old. Extracted from the paper entitle Fibre processing technology fractionation proms to produce fibrous strands from oil palm residues (Mahmudin, 2004).

Malaysia therefore has a great potential in turning its abundant supply of oil palm industry by –product into value added product. Under the present scenario, Malaysia can no longer remain idle and complacent in its positions as the top grower and supplier of palm oil. In view escalating challenge posed by other oil producing countries, Malaysia has to change its objective of being a world producer of palm oil to amongst others a leader in converting biomass waste into value added products. Oil from the palm oil fruit can produce bio diesel but not for the waste product like, empty fruit bunch, fibre, mesocarp, oil palm trunk fibre and palm kernel. All waste usually dismiss without knowing their potential for bio – oil production.

1.3 Problem Statement

For the production of bio-oil, EFB and PKS has been pyrolized in a laboratory scale electrical tubular furnace with stainless steel (316) reactor as shown in Figure 1.1. The main of pyrolysis characteristics components, hemicelluloses, cellulose and lignin of biomass were analysis using FTIR and GC. Lignin was more difficult to decompose, so high temperature needed to crack the bonding via endothermic process. The sample (EFB and PKS) shredded and sieved to get the smallest particle size range.

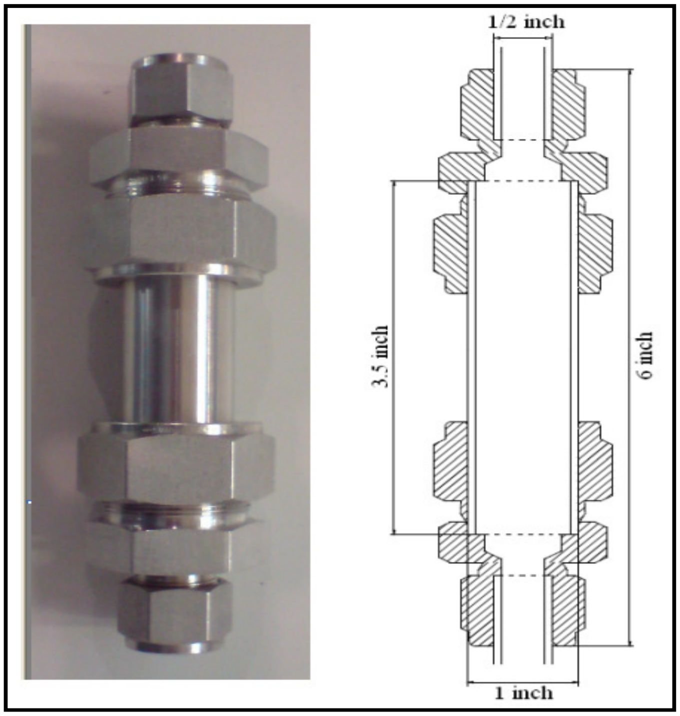


Figure 1.1: Stainless Steel Reactor

The effect of the sample preparation of the sample analyzed to study at which particle size the higher product will produce. Beside that, the retention time will also analyze when the experiment started and at the time of the production produce.

Particle size range (diameter) dp < 5 mm, which is the suitable range of the analysis for PKS while for EFB particle size range (Length) L < 1mm, 1-5 mm, 5 -10 mm and L >10 mm. At different particle size, different amount of bio oil produce; depend on their cutting size.

.

To get high yields of bio oil production, sample preparation (size of particle) is the way can be achieve. It is to ensure the sample could react at optimum process temperature and minimise their exposure to the intermediate (lower) temperatures that favour formation of charcoal.

Besides that, temperature also play important role in production of bio oil. Hence temperature 400 C ^{o} have been choose in this experiment to get high yield of bio oil instead charcoal.

1.4 Objectives Research

The objective of this research is to study:-

i) The sample preparation for empty fruit bunch (EFB) and palm kernel shell (PKS) for bio-oil production.

ii) The characteristic of bio-oil for empty fruit bunch and palm kernel shell.

1.5 Scope of Works

On this research, there are focuses on two main scopes:

- i. Palm kernel Shell
    - a. Sample preparation for temperature effect to a pyrolysis process of palm kernel shell with constant overall particle size of 1mm diameter.
    - b. The temperature effect study had been conducted at moderate temperature 200 ^{0}C, 300 ^{0}C, 400 ^{0}C, 500 ^{0}C and 600 ^{0}C.
- ii. Empty Fruit Bunch
    - a. Sample preparation for particle size effect to a pyrolysis of empty fruit bunch was investigated with constant temperature of 400 ^{0}C.
    - b. The study had been conducted for sample length of $L < 1$mm, 1-5 mm, 5-10mm, $L > 10$ mm.

1.6 Rationale and Significance

The rationale of this research is empty fruit bunch is the most waste in palm oil industry compared to others waste. It has a potential for the production of bio oil. The empty fruit bunch fibre (EFB) was identified as the first of the series of standard on oil palm fibres because of logistic reasons.

EFB has the highest fibre yield and is the only material commercially utilised for fibre extraction but there are good potentials for the exploitation of the other two materials (oil palm fronds and trunks). Besides that the characteristic of EFB fibres are clean, biodegradable and compatible than many other fibres from others.

PKS Kernel shell is a fibrous material which is easily handled in bulk directly from the product line in the palm oil manufacturing and to the end use. It consists of fractions of the nut shell. Large and small shell fractions are mixed with dust-like fractions and small fibres. Moisture content is low compared to the other biomass residues. Further more, the production of bio oil can generate the energy by further process. Hence in the end of the experiment, we can find the suitable particle size that can produce the highest value of bio oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Biomass

Biomass energy currently contributes 9–13% of the global energy supply accounting for 45±10 EJ per year or up to 14% (Thomas et.al., 2003). Biomass energy includes both traditional uses such as a ring for cooking and heating and modern uses such as producing electricity and steam, and liquid bio-fuels (Hisyam, 2006). Biomass, in the energy production industry, refers to living and recently dead biological material which can be used as fuel or for industrial production.

Most commonly, biomass refers to plant matter grown for use as bio-fuel, but it also includes plant or animal matter used for production of fibres, chemicals or heat (Volk et.al, 2006). Biomass may also include biodegradable wastes that can be burnt as fuel. It excludes organic material which has been transformed by geological processes into substances such as coal or petroleum.

The term "biomass" encompasses diverse fuels derived from timber, agriculture and food processing wastes or from fuel crops that are specifically grown or reserved for electricity generation. Biomass is a material that contain carbon and hydrogen compound which can be form as a fuel or for production.

2.2 Types of Biomass

Biomass can be split into two distinct categories first is waste biomass and second is energy crops. Waste biomass is forestry residue, sewage waste, animal farming waste, organic municipal solid waste (MSW), slaughterhouse and fishery. For energy crops is short rotation coppice (SRC), miscanthus, woodchips, straw, residue from fruit processing (e.g. stones, husks) and others. Furthermore, biomass is referring to recently or deadly organic material and it useful in providing renewable source of fixed carbon.

Each will give different range of product either gas, solid or liquid. Physical conversion involved densification; more easily handled such as briquettes particles, palletized fuel and fuel logs. These involve extrusion process of biomass particles with or without binder at higher pressure and later carbonized to obtain charcoal material (Ani, 2006).

2.3 Biomass in Malaysia

Today, about 80% of Malaysia's total population lives in Peninsular Malaysia, the hub of the country's economic activities. Like many other developing countries, energy has been the prime contributor towards the rapid growth of Malaysia's economy. Malaysia is looking forward in industrial and development sector that need sustainable energy resources.

The available fossil fuels sources now only can survive for another 20 to 30 years (Hisyam, 2006). Malaysia is the largest producer and exporter of palm oil in the world, accounting for 30% of the world's traded edible oils & fats supply. 3.88 million hectares of land in Malaysia is under oil palm cultivation producing 14 million tonnes of palm oil in 2004 (Jessada, 2007).

Currently, Malaysia faced this scenario; the growing demand of technology and becoming developed nation by 2020, limited fossil fuel reserves, only 30–40 years and net oil importer from 2040 and the major challenges to overcome this problem; fuel security, electricity sales price, renewable energy power purchasing agreement, financing assistance, lack of promotion, conventional vs. renewable energy power plant and subsidy for conventional energy (Mohamed et.al., 2006).

Malaysia government need fully supports re-biomass based power generation through various initiative and promotion program such as biogen since biomass resources is big potential for Biomass Power Co-Generation and beside that Malaysia can develop and expend the market profitability through new technology and lower production cost to overcome the challenges (Hamdan, 2004).

Energy has contributed significantly towards the rapid growth of the Malaysia economy. Energy supply infrastructure needs to be more continuously developed and being very capital intensive, it will impose tremendous pressure on the depleting resources. Successful implementation of this biomass utilization would provide the oil palm industry with an additional substantial income of over RM30 billion per year in addition to the current RM15 billion per year from the oil and its derivatives (speech from Minister of Primary Industries, Dato' Seri Dr. Lim Keng Yaik, launched the Biomass Technology Centre (BTC) and the Farm Mechanization Centre (FMC) of the Malaysian Palm Oil Board (MPOB) in Bangi, Selangor, 5 February 2002).

Furthermore, compare to the cost of fossil fuels that increasing by year in Malaysia, there is a strong reason to produce gases using cheaper raw material. As biomass is created by plants absorbing CO_2 from the air, releasing this CO_2 when oxidizing biomass does not lead to a net increase in greenhouse gas (GHG) emissions if biomass is produced in a sustainable manner. Carbon dioxide has been targeted as the greenhouse gas.

Other gases, such as CFC's and nitrous oxide offer far larger positive feedbacks to global warming than carbon dioxide. The concern, however, is over the extreme levels of carbon dioxide concentration in the atmosphere, which adds immensely to the problem of global warming. Considering this factor, offsets such as this would help to significantly reduce atmospheric concentrations of carbon dioxide. This burning biomass can be used a conventional power plant (that is, one with a conventional boiler to produce steam that runs through a turbine) built solely for the biomass is another option.

For the past decade Malaysia is dealing with serious environmental problem. The serious pollutions that occur in Malaysia are air pollution that which mainly causes by transportation and factories. Disadvantages of fossil fuel derived transportation fuels beside others problem such as greenhouse gas emissions, pollution, resource depletion, unbalanced supply demand relations, are strongly reduced or even absent with bio transportation fuels.

2.4 Biomass Technologies

There are some technologies that can convert biomass into energy and higher product value. This can be classified as show in Figure 2.1. The biochemical process leads to anaerobic digestion to produce gases and alcohol fermentation to produce ethanol. For non-biological process, it refer to thermal conversion which the main of it is converting solid waste into energy and by-product; gasification, combustion, pyrolysis and liquefaction.

Each will give different range of product either gas, solid or liquid. Physical conversion involved densification; more easily handled such as briquettes particles, palletized fuel and fuel logs. These involve extrusion process of biomass particles with or without binder at higher pressure and later carbonized to obtain charcoal material (Ani, 2006).

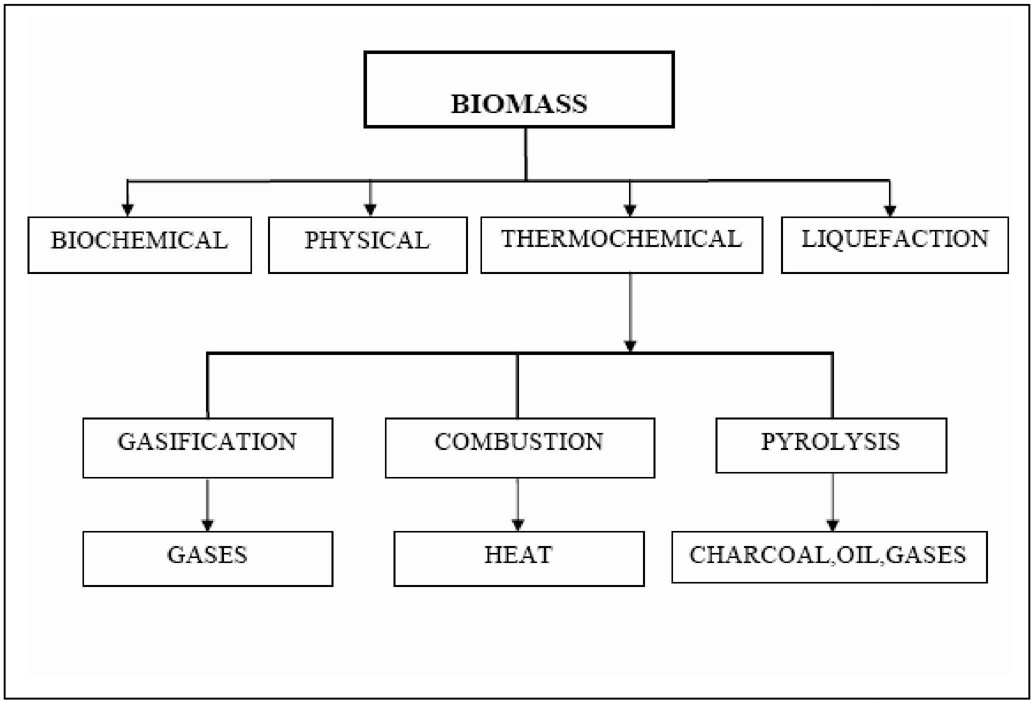


Figure 2.1: The Main Type and Process of Biomass (Ani 2006)

2.4.1 Gasification Process

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, biofuel, or biomass, into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam. The resulting gas mixture is called synthesis gas or syngas and is itself a fuel. Gasification is a method for extracting energy from many different types of organic materials.

There are four types of gasifier are currently available for commercial use now days counter-current fixed bed, co-current fixed bed, fluidized bed and entrained flow. The advantage of gasification is that the synthesis gas is a better fuel than original solid biomass, and can stored and transport more easily. The syngas is potentially more efficient than direct combustion of the original fuel because it can be combusted at higher temperatures or even in fuel cells, so that the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher or not applicable.

Syngas may be burned directly in internal combustion engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic fuel. Gasification can also begin with materials that are not otherwise useful fuels, such as biomass or organic waste. In addition, the high-temperature combustion refines out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels.

Gasification offers a combination of flexibility, efficiency, and environmental acceptability that is essential in meeting future energy requirements. Gasification of fossil fuels is currently widely used on industrial scales to generate electricity. However, almost any type of organic material can be used as the raw material for gasification, such as wood, biomass, or even plastic waste.

The future of biomass electricity generation lies in biomass integrated gasification/gas turbine technology, which offers high-energy conversion efficiencies (Ayhan, 2006). From environmental and economic viewpoints, new ways of hydrogen production, using a renewable and non-polluting source is the processes of biomass gasification. Since plants fix the CO_2 from the atmosphere during their growth, the concentration of carbon dioxide in the atmosphere would remain constant if biomass is used (Jale et.al. 2007). In addition, biomass based technologies reduce the dependence of foreign petroleum.

2.4.2 Combustion Process

Combustion or burning is a complex sequence of exothermic chemical reactions between a fuel (usually a hydrocarbon) and an oxidant accompanied by the production of heat or both heat and light in the form of either a glow or flames, appearance of light flickering.

Biomass combustion such burning fuel wood provides heat, power, or combine heat and power (CHP). More than 90% of world primary energy is converted by means of combustion to provide energy service for human (Ralph, 2003). The basic stoichoimetric equation for the combustion of wood, represented by the empirical formula of cellulose, ($C_6H_5O_5$) is illustrated by Equation 2.1.

$$(C_6H_{10}O_5)\ n + 6nO_2 \longrightarrow 6nCO_2 + 5nH_2O \qquad (2.1)$$

Carbon dioxide (CO2) and water are the final products along with energy (Donald, 1998). During combustion, the chemically bound carbon and hydrogen in the various organic components of biomass are oxidized. Incomplete combustion can result in excessive emissions of particulate matter and partially oxidized derivatives, some of which are toxic.

Chemically bound nitrogen and sulphur that may be present in the biomass are oxidized to nitrogen and sulphur oxide, mostly sulphur dioxide, but some sulphur trioxide and mostly nitric oxide, but some nitrogen dioxide (Mann et.al., 1997). Air is the usual source of the oxidant, oxygen, for biomass combustion. Small amounts of nitrogen in the air are also converted to nitrogen oxides at combustion temperatures.

2.4.3 Pyrolysis Process

Pyrolysis is thermo-chemical process whereby dry and comminuted biomass is heated in the relative absence of air and oxygen. Depending on the process condition the major product could be bio-oil, a liquid fuel, or substantial quantities char, a solid fuel or a non- condensable gaseous product which can also be burnt as fuel through its calorific value (Lim *et.al,* 2004).

From the process, three main products are formed is char (solid), pyrolitic oil (liquid) and gaseous fuel. Thus, the pyrolysis of common materials like wood, plastic and clothing is extremely important for fire safety and fire fighting (Fang *et.al,* 2006).

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It also always the first step in combustion and gasification .It also can be divided by three, first is fast pyrolysis, intermediate pyrolysis and slow pyrolysis .Pyrolysis process usually produce char, bio-oil, and gas. The production of this product is depending on the manipulated parameter that is residence time and temperature. The crude pyrolysis fuel approximates to biomass in elemental composition (Bridgwater, 2003).

2.5 Processes for Biomass Pyrolysis

Since pyrolysis is slightly endothermic (Fang He, 2006) various methods have been proposed to provide heat to the reacting biomass particles:

i. Partial combustion of the biomass products through air injection. This results in poor-quality products.

ii. Direct heat transfer with a hot gas, ideally product gas that is reheated and recycled. The problem is to provide enough heat with reasonable gas flow-rates.

iii. Indirect heat transfer with exchange surfaces (wall, tubes). It is difficult to achieve good heat transfer on both sides of the heat exchange surface.

iv. Direct heat transfer with circulating solids: Solids transfer heat between a burner and a pyrolysis reactor. This is an effective but complex technology.

For flash pyrolysis the biomass must be ground into fine particles and that the insulating char layer that forms at the surface of the reacting particles must be continuously removed. The following technologies have been proposed for biomass pyrolysis:

i. Fixed beds were used for the traditional production of charcoal. Poor, slow heat transfer resulted in very low liquid yields.

ii. Augers: This technology is adapted from a Lurgi process for coal gasification. Hot sand and biomass particles are fed at one end of a screw. The screw mixes the sand and biomass and conveys them along. It provides a good control of the biomass residence time. It does not dilute the pyrolysis products with a carrier or fluidizing gas. However, sand must be reheated in a separate vessel, and mechanical reliability is a concern. There is no large-scale commercial implementation.

iii. Ablative processes: Biomass particles are moved at high speed against a hot metal surface. Ablation of any char forming at the particles surface maintains a high rate of heat transfer. This can be achieved by using a metal surface spinning at high speed within a bed of biomass particles, which may present mechanical reliability problems but prevents any dilution of the products. As an alternative, the particles may be suspended in a carrier gas and introduced at high speed through a cyclone whose wall is heated; the products are diluted with the carrier gas. A problem shared with all ablative processes is that scale-up is made difficult since the ratio of the wall surface to the reactor volume decreases as the reactor size is increased. There is no large-scale commercial implementation.

    i. Rotating cone: Pre-heated hot sand and biomass particles are introduced into a rotating cone. Due to the rotation of the cone, the mixture of sand and biomass is transported across the cone surface by centrifugal force. Like other shallow transported-bed reactors relatively fine particles are required to obtain a good liquid yield. There is no large scale commercial implementation.

ii. Fluidized beds: Biomass particles are introduced into a bed of hot sand fluidized by a gas, which is usually a recirculated product gas. High heat transfer rates from fluidized sand result in rapid heating of biomass particles. There is some ablation by attrition with the sand particles, but it is not as effective as in the ablative processes. Heat is usually provided by heat exchanger tubes through which hot combustion gas flows. There is some dilution of the products, which makes it more difficult to condense and then remove the bio-oil mist from the gas exiting the condensers. This process has been scaled up by companies such as Dynamotive and Agri-Therm. The main challenges are in improving the quality and consistency of the bio-oil.

iii. Circulating fluidized beds: Biomass particles are introduced into a circulating fluidized bed of hot sand. Gas, sand and biomass particles move together, with the transport gas usually being a recirculated product gas, although it may also be a combustion gas. High heat transfer rates from sand ensure rapid heating of biomass particles and ablation is stronger than with regular fluidized beds. A fast separator separates the product gases and vapours from the sand and char particles. The sand particles are reheated in fluidized burner vessel and recycled to the reactor. Although this process can be easily scaled up, it is rather complex and the products are much diluted, which greatly complicates the recovery of the liquid products.

2.6 Types of Pyrolysis Technologies

Pyrolysis has been practiced for centuries for production of charcoal. This requires relatively slow reaction at very low temperature to maximize the yield. Recently, studies into the mechanisms of pyrolysis have suggested ways of substantially changing the proportion of pyrolysis product. Table 2.1 shows main pyrolysis variants.

Technology	Resident time	Heating rate	Temperature °C	Product
Carbonation	Days	Very low	400	charcoal
Conventional	5 -30 min	low	600	Oil , gas , char
Fast	0.5 - 5s	Very high	650	Bio oil
Flash liquid	< 1s	High	< 650	Bio oil
Flash gas	< 1s	High	< 650	Chemical , gas
Ultra	< 0.5	Very high	1000	Chemical , gas
Vacuum	2 – 30 s	Medium	400	Bio oil
Hydro pyro	< 10 s	High	< 500	Bio oil
Methano pyro	< 10 s	High	>700	Chemical

Table 2.1: Pyrolysis Technology Variant (Environment Department)

2.7 Pyrolysis Liquid Bio Oil

Crude pyrolysis liquid or bio oil is dark brown and approximates to biomass in elemental composition. It is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product.

Solid char may also present. Bio oil has higher heating value (HHV) of about 16 – 17 Mj/Kg as produced with about 25% wt water that cannot readily be separated. The liquid has a distinctive odour – an acrid smoky smell due to the low molecular weight aldehydes and acid – which can irritate the eyes on prolonged exposure. It is composed of a complex mixture of oxygenated compounds that provide both the potential and challenge for utilisation.

There are some important characteristic of this liquid. The most significant is that it will not mix with any conventional hydrocarbon - based fuels. Typically it is dark brown, free flowing liquid.

The colour can be almost black, through dark red – brown to dark green, being influence by the presence of micron – carbon in the liquid and chemical composition. Hot vapour filtration gives a more translucent red brown appearance owing to the absence of char. High nitrogen content can impact a dark green tinge to the liquid.

Pyrolysis liquids cannot be completely vaporised once they have been recovered from the vapour phase. If the liquid is heated to 100°C or more to try to remove water or distil off lighter fractions, it reacts firstly by polymerisation followed by thermal cracking and eventually produces a solid residue of around 50 wt % of the original liquid and some distillate containing volatile organic compounds and water.

The bio oil has been successfully stored for several years in normal storage conditions in steel and plastic drums without any deterioration that would prevent its use in any of applications tested to date. Bio oil has the advantages of easy storage and transport as well as a higher power generation efficiency than fossil fuelled systems at the smaller scales of operation that are likely to be realized from bio energy systems (Roger *et*, 2002). Hence, bio oil is one

2.8 Application of Bio Oil

Bio oil can be substitute for fuel or diesel in many static applications including boilers, furnaces, engines and turbines for electricity generation (Czernik 2004). Not only for substitute as fuel but also it could be a chemical feedstock for chemical industries. Figure 2.2 summaries the possibilities of the application bio oil.

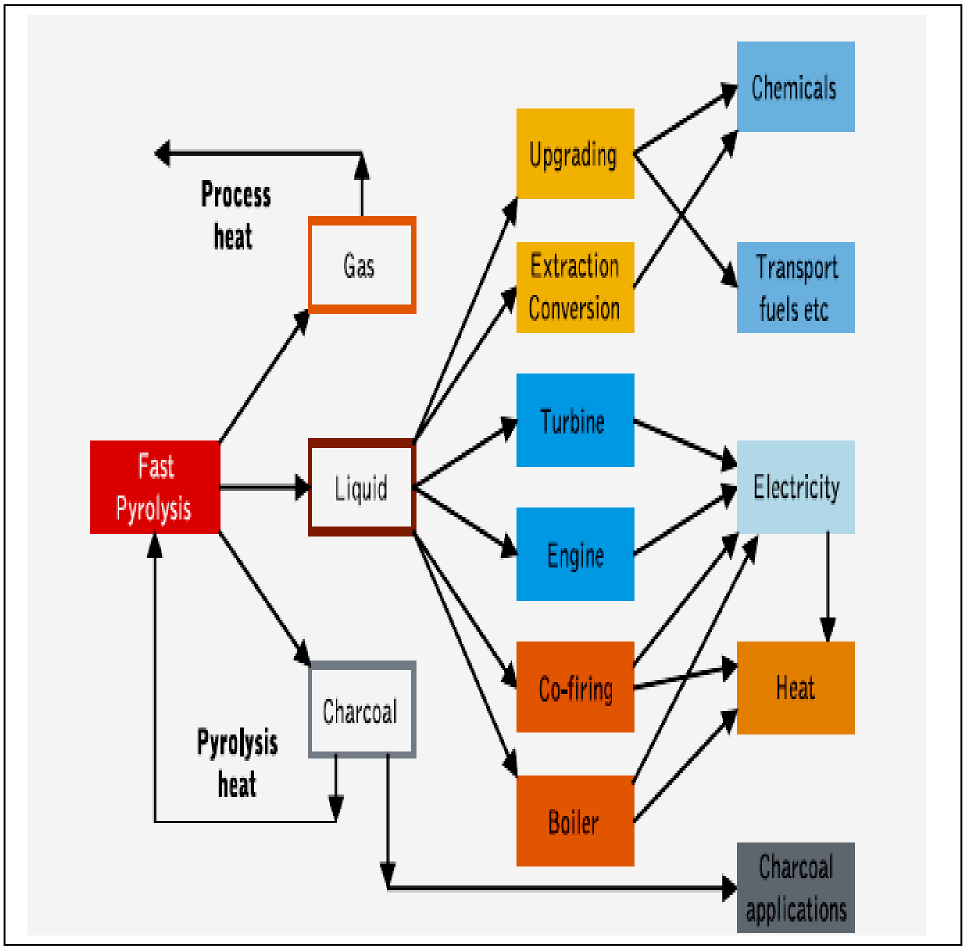


Figure 2.2: Applications Products of Fast Pyrolysis (Tony Bridgwater 2003)

2.9 Empty Fruit Bunch

Material recovery from conversion of agricultural solid wastes into potential construction products has not only benefited the environment but also helps preserve natural resources. EFB (empty fruit bunch) is one of such solid waste generated in oil palm planted throughout Malaysia over 4 million hectares land, which remains unutilised commercially.

Hence, it has been verified in engineering properties and construction products made from EFB satisfy the requirement of consumers' trend using products made from eco-friendly and natural waste. The major contributor of biomass in Malaysia that has potential to generate energy is in palm oil industry where most of the waste is empty fruit bunches (EFB), palm oil mill effluent (POME), mesocarp fiber , palm kernel shells, palm kernel cake (residue).

Oil palm production is a major agricultural industry in Malaysia. It contributes about US$ 7.3 billion in export earnings each year, mostly from the export of palm oil. About 90 million mt of renewable biomass (trunks, fronds, shells, palm press fibre and the empty fruit bunches) are produced each year. The empty fruit bunches (EFB) represent about 9% (Lim 2000) of this total. They are the residue left after the fruit bunches are pressed at oil mills, and the oil extracted.

EFB is a suitable raw material for recycling because it is produced in large quantities in localized areas. In the past, it was often used as fuel to generate steam at the mills (Ma *et al.* 1993). The ash, with a potassium content of about 30%, (Lim 2000) was used as fertilizer. Burning is now prohibited by regulations to prevent air pollution.

The EFB is now used mainly as mulch (Hamdan *et al.* 1998). Besides that, we can place around young palms which EFB helps to control weeds, prevent erosion and maintain soil moisture. Although oil from the palm tree is an excellent product for the country, residues from oil palm have not been used sufficiently.

One of the abundant lignocelluloses residues consists of empty fruit bunches (EFB), which are left behind after removal of oil palm fruits for the oil refining process at palm oil refineries.

Figure 2.3: Empty Fruit Bunch (Lepar Hilir Oil Mill)

The major contributor of biomass in Malaysia that has potential to generate energy is in palm oil industry where most of the waste is:

i. Empty fruit bunches (EFB)

ii. Palm oil mill effluent (POME)

iii. Mesocarp fibre

iv. Palm kernel shells

v. Palm kernel cake (residue)

2.9.1 Composition of EFB

Mulching growing crops with plant residue is an age-old agricultural practice. The most popular mulch is empty fruit brunch (EFB) where the material does its fibrous nature (Singh et.al, 1999). EFB rich in potash and also contain reasonable level of nutrient. The composition shows as in Table 2.2.

Parameter (%)	Dry Matter Basis		Fresh wt. Basis * (mean)
	Range	Mean	
Ash	4.8 – 8.7	6.3	2.52
Oil	8.1 - 9.4	8.9	3.56
C	42.0 – 43.0	42.8	17.12
N	0.65 – 0.94	0.80	0.32
P_2O_5	0.18 – 0.27	0.22	0.09
K_2O	2.0 – 3.9	2.90	1.16
MgO	0.25 – 0.40	0.30	0.12
CaO	0.15 – 0.48	0.25	0.10
B	9 -11	10	4
Cu	22 -25	23	9
Zn	49 - 55	51	20
Fe (mg/l)	310 - 595	473	189
Mn (mg/l)	26 - 71	48	19
C/N ratio	45- 64	54	54

* Moisture content 60 – 65

Table 2.2: Composition of EFB (Gurmit *et.al.*, 1999).

The standard is unique in that it is an indigenous standard and is the first in the world that directly relates to the oil palm residues. Extensive study and research had been conducted, there are identified critical parameters affecting the quality of the end of product. The critical characteristic of oil palm fibre include the fibre length, moisture content, oil content and impurities. Details on the acceptable limits and methods of determination are given in the standard, MS1408:1997 (P)-Specification for oil palm empty fruit bunch fibre.

The standard recommends of empty fruit bunch fibre (EFB). In quantifying the percentage proportion of fibre length, the standard has established the following numerical values as shows in Table 2.3.

Fibre Length	% Proportion (Oven dry weight basis)
> 100 mm	30
>50 – 100 mm	35
< 50 mm	35

Table 2.3: Standard Percentage Proportion of Fibre Length (Asean Secretariat 2003)

2.10 Palm kernel Shell

The palm kernel Shell (PKS) is a shell that surrounds kernel of palm fruit and a residue after extraction of palm oil process. In addition, it is the one of waste matter piled up in the area of factory farm. Palm Kernel Shell which we are exporting now is generally of following specs:

i. Moisture - 15% to 20% (Maximum)

ii. Fibre -2% to 3% (Maximum)

iii. Foreign Matter - 2%(Maximum)

iv. Hard Nut Shell – 95%

v. Kcal 4000 and above.

Figure 2.4: Raw Palm Kernel Shell (Global B2B Market, 1997)

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:

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

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

iii. 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 relevant for perspective and comparison:

				Product volume		**Heating value**		**Total potential**	
	Abr.	**Moist.**	**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**

Table 2.4: Energy Potential 2003 in Main Products, By Products and Residues from Palm Oil Industry [MPOB].

CHAPTER 3

METHODOLOGY

3.1 Introduction

The empty fruit bunch (EFB) sample and palm kernel shell (PKS) investigated in this study was taken from oil palm mill (Lepar Hilir) located near Gambang, Pahang. EFB is the waste of the oil palm after removal of oil from the fruit while PKS is the shell fractions left when the nuts inside is removed after crushing process.

3.2 Material for Sample Preparation

The material empty fruit bunch (EFB) and palm kernel shell (PKS) was investigated in this study was taken from the nearby oil palm mill (Lepar Hilir) that located near Gambang, Pahang. Empty fruit bunch (EFB) is the waste of the oil palm generated after the removal of oil by pressing the fruit. Palm kernel shell (PKS) is the shell fraction left when the nut has been removed after crushing of the nuts in the nut crasher in the palm oil mill.

The empty fruit bunch (EFB) sample which in the form of whole bunches obtained were relatively moisture content around 67%, which means that without any pre-treatment, EFB cannot be considered as a fuel. For palm kernel shell, the moisture content around 13 % to 20% based on the literature. The moisture content of the sample must be reducing as much as can to achieve the recommendation value.

Here, the sample should have the less as can moisture content because the water can influence on the basic properties of biomass fuel. Furthermore proximate analysis was determined on the EFB and PKS sample by using the thermo gravimetric analyser (TGA).

Figure 3.1: Empty Fruit Bunch Fibre

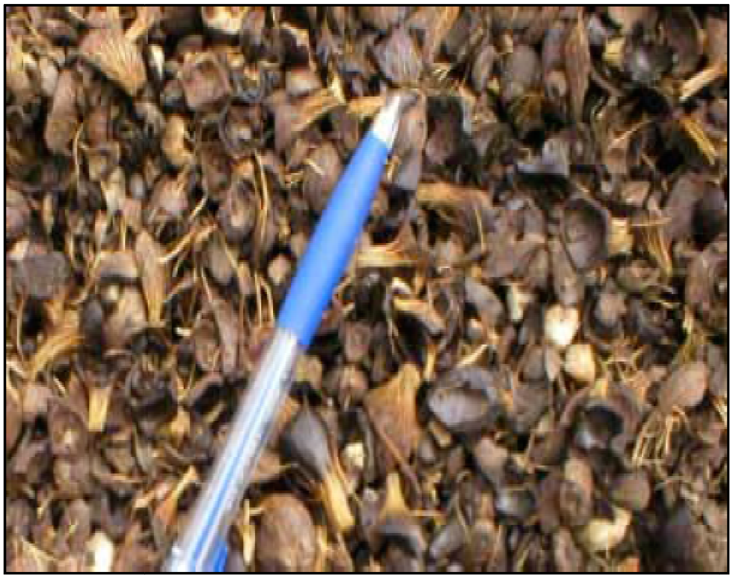


Figure 3.2: Palm Kernel Shell

3.3 Experiment Set Up and Method

Before set up this experiment, design of the reactor as shows in Figure 1.1 that made up from stainless steel tube with diameter 1 inch x 6 inch height are needed to fabricate first. This is to ensure the reactor can withstand high temperature to keep into the tubular furnace. Besides that, the glass wool was used in this experiment by putted into the reactor before place the sample. This is to avoid the sample from drop down. The design of pyrolysis system shows as in Figure 3.13.

3.4 Sample Preparation Method

In sample preparation, it can be divided by two categories which are for the effect of temperature and effect on particle size. The sample preparation plays major role in bio oil production hence it influences the yields of bio oil in term of their moisture content, cutting size, and method use in order to gain the bio oil.

3.4.1 Sample Preparation for PKS

Palm kernel shell (PKS) is the shell fraction left when the nut has been removed after crushing of the nuts was used in this experiment. It consists of fractions of the nut shell, roughly 5 – 8 mm diameter, up to about half a shell. PKS usually contains moisture content more than 12% which results in high water content in bio oil.

To ensure the content feeding and to obtain optimized yield, the feed stock was rinsed in tap water to remove soil and gravel particles. After that the sample then were dried directly under sun for 6 days to obtain the moisture below 12%. The moisture content was determined by using thermo gravimetric (TGA) as shows in Figure 3.3.

After drying process, the sample was crushed by using grinder machine (SAMA Grinder model FG 400 x 200) as shows in Figure 3.4 to about less than 5 mm in size (diameter) as shows in Figure 3.5. After the entire sample has grinded, put the samples inside the seal bag and label. The seal bag is store at ambient condition. For experiment purpose, 20 g of grinded sample are needed to use for the analysis at different temperature.

3.4.2 Sample Preparation for EFB

Chopping method is used for EFB because EFB that obtained were in bunches form. EFB manually chopped into smaller pieces that could be feed into a grinder by using a cleaver as shows in Figure 3.6. The purpose of chopping is to ensure the sample can easily to grinding and also easily to dry. When small size of the sample, more water can evaporate, hence less moisture content we obtained. In this preparation we also use thermo gravimetric (TGA) to determine moisture content of the sample. After that, the samples (EFB) were rinsed in tap water to remove soil and gravel particles.

The EFB sample usually contains moisture around 67% which is difficult to feed into the pyrolysis reactor. In addition, the high moisture content in the biomass results in high water content in the bio oil. To ensure the consistent feeding and optimized pyrolysis products, the sample (EFB) was dried direct under sunshine for the purpose of moistures removing to below 15 % moisture content. The samples were dried under the sun until all the moisture evaporated for 6 days with 3 hours which is at 11 to 1 afternoon which is in that time, evaporation rating is high.

Next the sample was grinded using a grinding machine (SAMA Grinder model FG 400 x 200). After the entire sample has grinded, the sample is stored inside the seal bag and label according to their type. Then the samples were then passed through sieve into fractions of particle size by using standard sieves model Fristch as shows in Figure 3.7. Sample was sieved for 5 minute. Next the sample was colleted and stored at the ambient temperature inside a beaker and labelled according to their sizes. Here there are 4 range of the sample size based on their length which is L > 10mm, 5 -10 mm, 1- 5 mm and L < 1mm. In this experiment, 8 g of grinded sample according to the sizes are needed to use for different particle size.

Figure 3.3: TGA Q500 V6.4 Instrument

Figure 3.4: Grinder (SAMA Grinder model FG 400 x 200)

Figure 3.5: PKS Sample (Less 5 mm)

Figure 3.6: EFB in Small Pieces

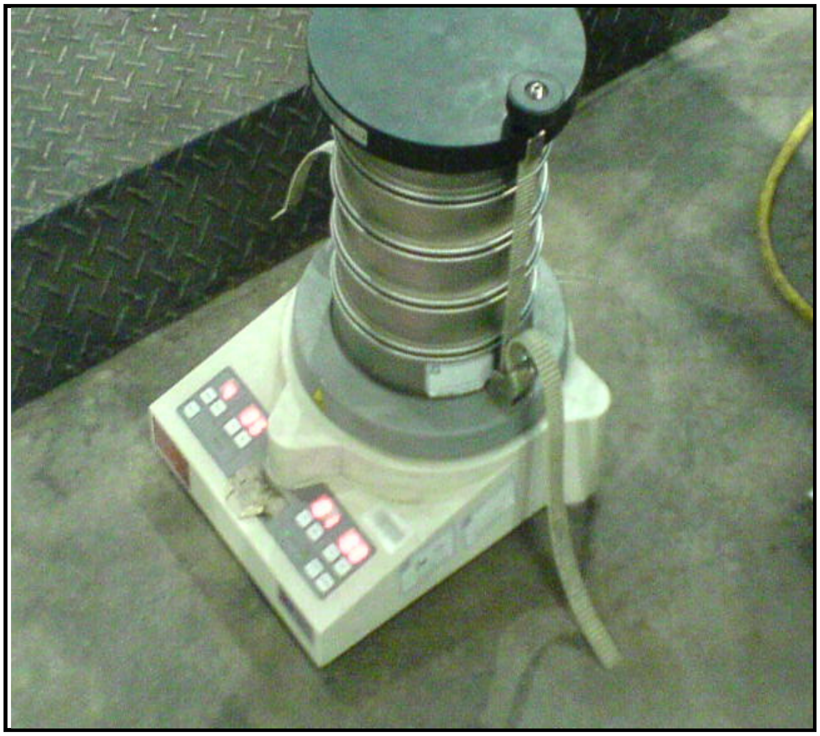


Figure 3.7: Sieve Tray (Fritch Model)

Figure 3.8: EFB Length (L> 10 mm)

Figure 3.9: EFB Length (1 - 5 mm)

Figure 3.10: EFB Length (5 - 10 mm)

Figure 3.11: EFB Length (L < 1 mm)

3.5 Pyrolysis Procedure

Pyrolysis experiments were carried out under nitrogen atmosphere at the various temperatures of 200 ^{0}C, 300 ^{0}C, 400 ^{0}C, 500 ^{0}C and 600 ^{0}C. Pyrolysis reactor used was a static batch design and made of stainless steel (316) with 1 inch diameter and 6 inch in height and was placed in an electrical tubular furnace. Pyrolysis temperature was measured with the connection of external thermocouple which was placed in the centre of pyrolysis reactor.

Before the experiments, the reactor was purged by nitrogen gas for 10 min at a flow rate of 30 ml min^{-1} to remove the air inside. In a typical pyrolysis experiment, a quantity of sample on a dry basis (20 g PKS) was loaded and then the reactor temperature was increased with a heating rate of 50 ^{0}C min^{-1} up to the desired pyrolysis temperature and hold for 8 min at the desired temperature. The nitrogen gas swept all volatile products from the reactor into the condenser. The liquid products were condensed in the condenser by cooling water. The gaseous that passed through the condenser entered the ice bath where the liquid product was collected and the remaining gases were purged out to the atmosphere.

Same to EFB sample which is the pyrolysis experiments for EFB were out under nitrogen atmosphere at four different ranges of sample length of $L < 1$mm, 1 – 5mm, 5 – 10mm, and $L > 10$mm in size. In a typical pyrolysis experiment, a quantity of 8 g of EFB (on a dry base) was loaded and then the reactor temperature was increased with a heating rate of 50 ^{0}C min^{-1} up to the desired pyrolysis temperature of 400 ^{0}C and hold for 8 min at the desired temperature. This experiment is carried out to determine the effect of the particle size on the yield of bio-oil of EFB. This study was carried out by using fabricated pyrolysis system as shows in Figure 3.12 and Figure 3.13.

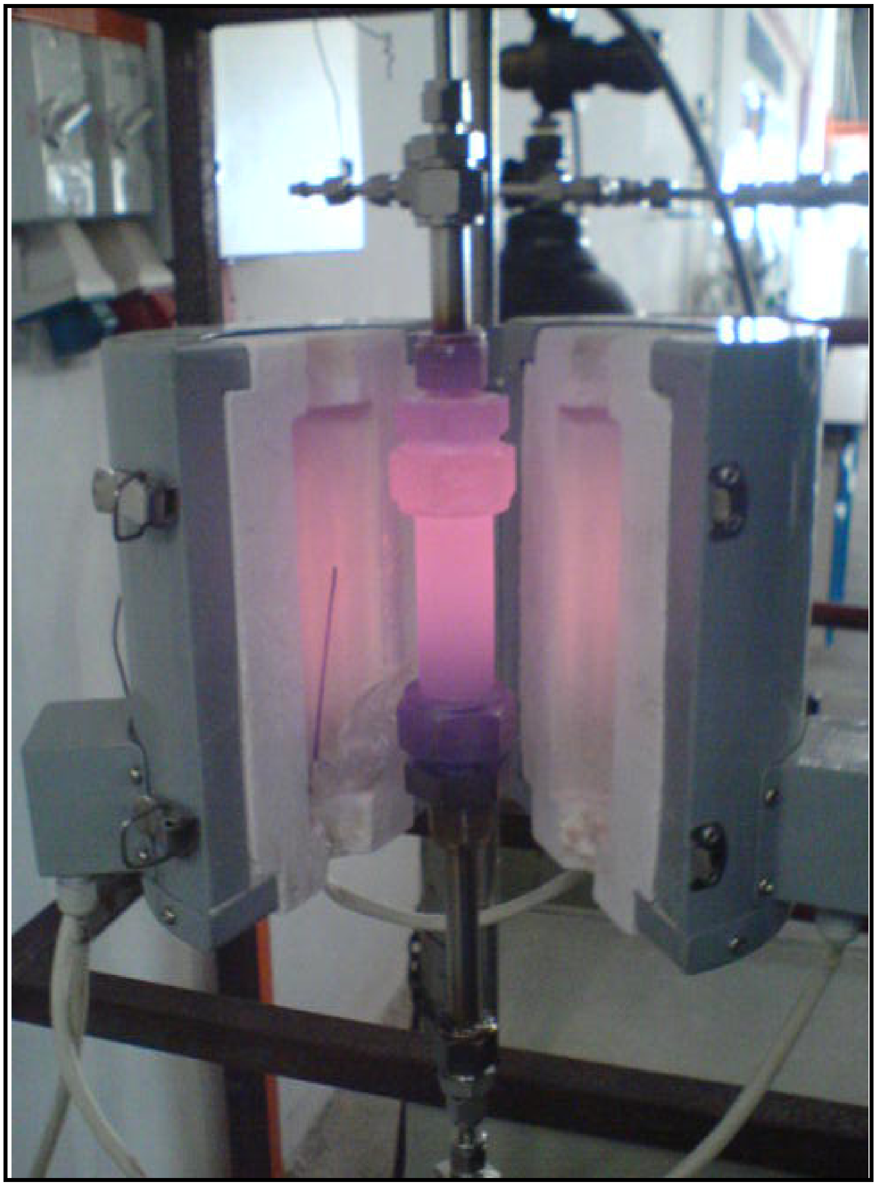


Figure 3.12: Reactor in Tubular Furnace

Figure 3.13: Pyrolysis System

3.6 Bio oil Analysis and Characterization

The conversion yield of bio-oil produced that obtained in the pyrolysis reaction will be calculated based on weight basis. Equation (3.1) will be used to calculate conversion yield for each parameters. Char yield will also be calculated from the weight basis as shown in Equation (3.2). From the weigh percent of bio-oil and char, the conversion of gas can be determined using the Equation (3.3).

$$\text{Yield of Liquid} = \frac{\text{The mount of liquid collected for certain T}}{\text{Total amount of sample in reactor}} \text{ X } 100 \tag{3.1}$$

$$\text{Yield of Solid} = \frac{\text{The amount of solid collected for certain T}}{\text{Total amount of sample in reactor}} \text{ X } 100 \tag{3.2}$$

$$\text{Yield of Gas} = 1 - \text{yield of liquid} - \text{yield of solid} \tag{3.3}$$

The bio oils selected for characterization were those obtained at the pyrolysis conditions, which gave the maximum oil yield. For this purpose, gas chromatography (GCMS) methods were used to determine the chemical composition. The summary of the GCMS analysis parameters are listed as shows in Table 3.1.

Type of Column	HP-5MS Capillary Column (30 m x 0.25 mm x 0.25 µm)
Oven (°C)	40-175-200-250
Injection (µL)	0.5
Carrier Gas	Helium
Flow rate (mL/min)	1

Table 3.1: GC-MS Analysis Parameters

Fourier transform infrared spectroscopic analysis of the bio oil was performed to determine its functional groups. The Absorption frequency spectra were recorded and plotted. In order to determine the properties of raw sample, such as moisture content, weight loss and ash content, thermo gravimetric (TGA Q500 V6.4) analysis method was used. The sample is placed on the platinum pan with starting at ambient temperature until 600 ^{0}C.

These experiments were performed under blanketed nitrogen with flow rate of 100 ml min $^{-1}$ with heating rate 20 °C. Besides that, pH, viscosity and water content of bio oil were determined by pH meter, Brookfield/LVDV-III+C/W viscometer, and moisture analyzer 787 KF Titino with Karl- Fisher reagent respectively. In determined water content, 4 ml of bio oil sample was introduced in this method.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experimental Results

Figure 4.1 shows the samples of produce EFB for and Figure 4.2 shows the samples of produce PKS after the experiment. The physical and chemical compositions of feed stock play a major role in the yield and properties of the bio-oil.

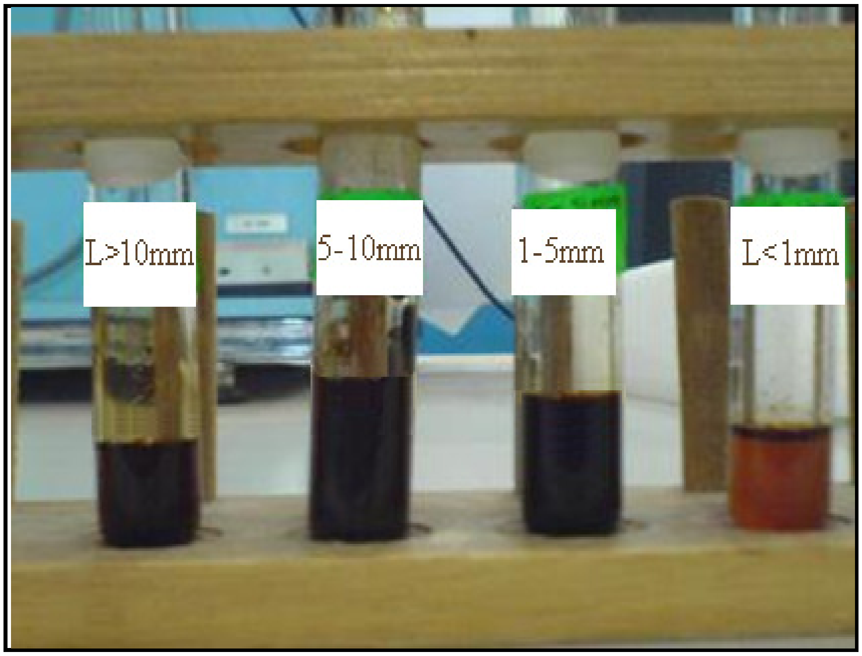


Figure 4.1: EFB Bio-oil Product from Pyrolysis

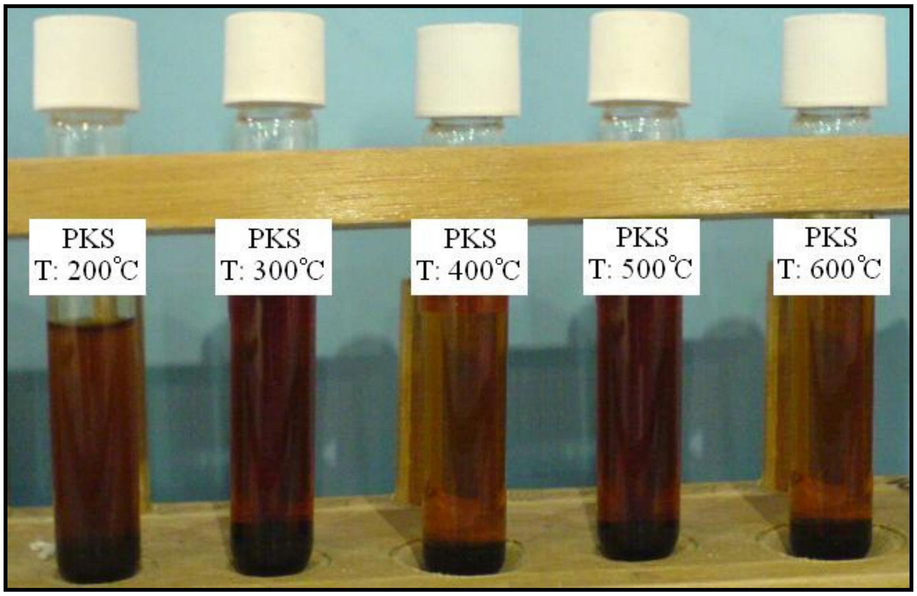


Figure 4.2: PKS Bio-oil Product from Pyrolysis

4.2 Effect of Temperature on PKS Production

The temperature range of 200 ^{0}C to 600 ^{0}C was selected as the region of interest in this study due to the result obtained from TGA, which showed as the active pyrolysis occurrence for PKS. In this study we assigned 200 ^{0}C as the minimum temperature followed by 300 ^{0}C, 400 ^{0}C, 500 ^{0}C and 600 ^{0}C as the maximum temperature for pyrolysis respectively.

Table 4.1 shows the yield of bio oil and char of PKS. In this experiment the highest yield of bio oil for PKS is 37.18 at pyrolysis temperature 400 ^{0}C with diameter particle less than 5 mm. As the temperature was increased, there was increased in the yield of bio-oil and gas but inversely decreased in the yield of char.

Hence the temperature of 400 ^{0}C gave the highest percentages of bio-oil yield as shows in Figure 4.3 compared to other temperature. Sample preparation also influence the production of bio oil for PKS which the sample size is reduce to less than 5 mm to feed in the reactor.

Temperature (^{0}C)	Yield of Bio Oil (wt %)	Yield of Char (wt %)
200	23.68	43.14
300	30.25	40.75
400	37.18	28.68
500	30.18	26.62
600	29.33	25.23

Table 4.1: Yield of Bio Oil and Char for PKS

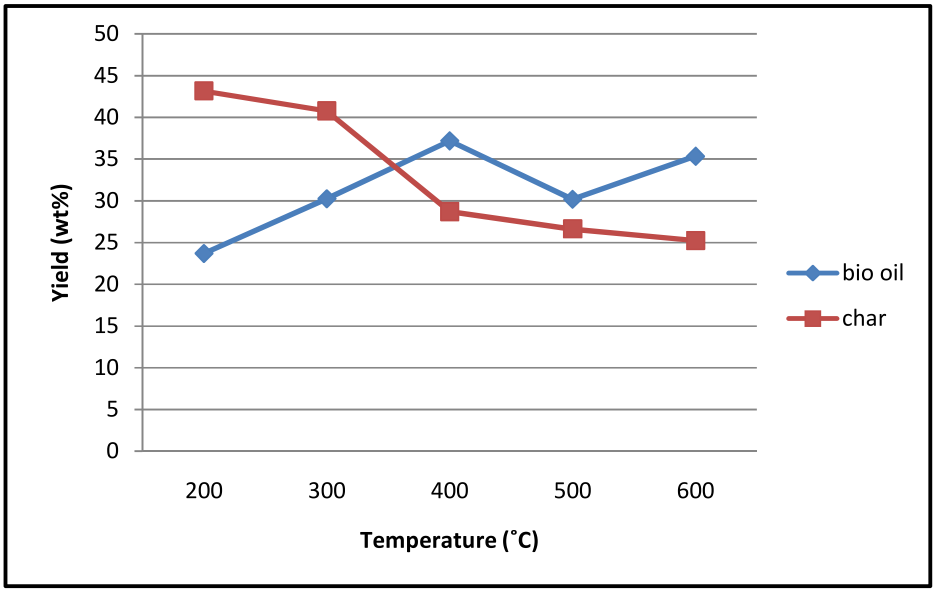


Figure 4.3: Temperature Effect the Production of Bio Oil and Char of PKS

The graph shows the trend of bio oil and char production. As the temperature was increased, there was increased in the yield of bio-oil and gas but inversely decreased in the yield of char. The experiment showed that the temperature of 400 ^{0}C gave the highest percentages of bio-oil yield which is 37.18 %. The decreased of char yield in PKS at 400 °C shows that at T = 400 °C the volatile decrease and more bio-oil is produced. Generally, the organics with low molecular weight are comparatively higher in volatility and harder to be condensed. The sample size which is less than 5 mm give influence to the production of bio oil. Hence, it preserves large surface area to react and more bio oil will produced. It influences the production yield in term of volume of bio oil that produce.

4.3 Effect of Particle Size on EFB Production

Table 4.2 shows the data on the bio oil at 400 °C pyrolysis temperature for particle sizes. The effect of particle sizes has a major effect on the process rate. Generally the increase in particle sizes cause the greater temperature gradients inside the particle , so that at a given time , the core temperature is lower than that of the surface, and this possibly gives rise to the char (solid) yields with a concomitant decrease in liquid and gases (Enginar et al.,2000). However, the experimental results show that the intermediate length of the particle sizes shows the highest yield of bio oil as shows in Figure 4.4.

Length Size (mm)	Yield of Bio Oil (wt %)	Yield of Char (wt %)
L > 10 mm	22.638	31.225
5 - 10 mm	39.525	19.612
1 - 5 mm	33.137	21.475
L < 1 mm	28.087	24.000

Table 4.2: Particle Size (Length) Effect on Product for EFB.

Figure 4.4 shows that bio oil and char yield of EFB according to the particle size. Based on our experimental result the bio – oil yield is at maximum (39.525 wt %) for particle size (length) of 5mm -10mm. The used of the smallest and largest length of particle size give 22.638 wt% and 28.638 wt% yield of bio oil respectively compared to the intermediate size. All the experiment done under the same conditions, constant temperature 400 °C, amount of sample is 8 gram at 1 bar of nitrogen gas flow and the retention time of each sample is 15 minute.

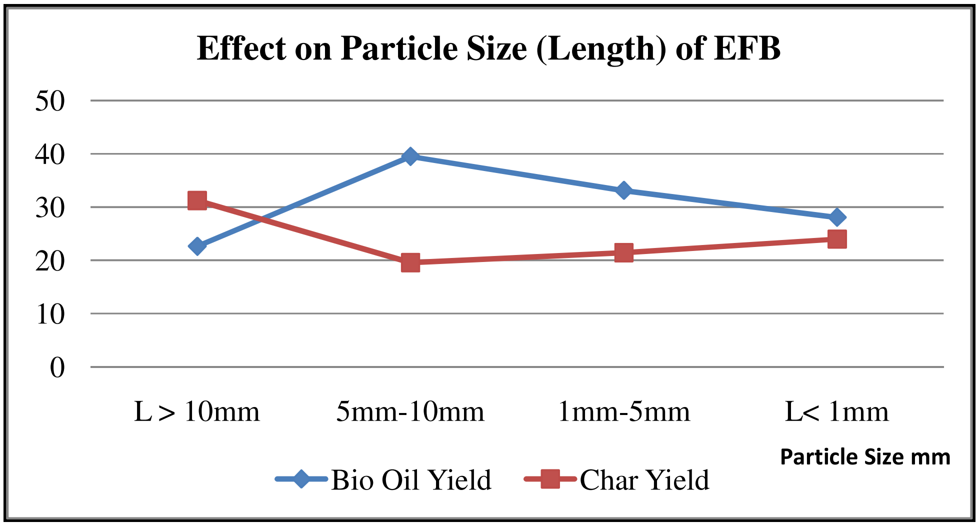


Figure 4.4: Particle Sizes Effect the Production of Bio Oil and Char of EFB

4.4 Bio oil Analysis of PKS and EFB

Table 4.3 shows the summary of the analysis of bio oil for PKS and EFB at pyrolysis condition for water content, viscosity and pH for both samples. Moisture content in EFB is 12.53 % while for PKS the value is 7.46% lower than EFB. The original moisture is derived from the feedstock and dehydration reaction during fast pyrolysis process. Water content usually varies in the range up to 30 wt% depending on the initial moisture in feedstock and the condition of the experiment (pyrolysis).

Viscosity of the product (bio oil) was determined in order to characterize the bio oil. EFB shows the high viscosity compared to PKS which is 42.53 % and 28.46 % respectively. As been stated in ‘Overview of Fuel Properties of Biomass Fast Pyrolysis Oils, Qiang Lu, Wen-Zhi Li and Xi-Feng Zhu’, bio-oils viscosity is with in 10-100cP.

The standard of the pH value for bio oil is in range of 2-4 which is the bio-oils contain for about 7-12 wt% acids. The pH reading for the sample shows that PKS and EFB product is acidic with 2.46 and 2.53 respectively.

Analysis	EFB	PKS
Water Content	12.53%	7.46%
Viscosity	42.53 cp	28.46cp
PH	2.53	2.46

Table 4.3: Summary Bio Oil Analysis

4.5 Thermo gravimetric Analysis (TGA)

Figure 4.5, the initial moisture content in the EFB is 12.18%. The value of 88.59% from initial weight will loss at temperature of 600 °C and 11.41 % solid will remain as ash residue.

Figure 4.6 shown the initial moisture content in the PKS is 11.69%. The value of 70.91% from initial weight will loss at temperature of 600 °C and 29.13 % solid will remain as ash residue. This moisture content can give impact to water content for the product as water content in bio-oil is resulted from the initial moister content in sample.

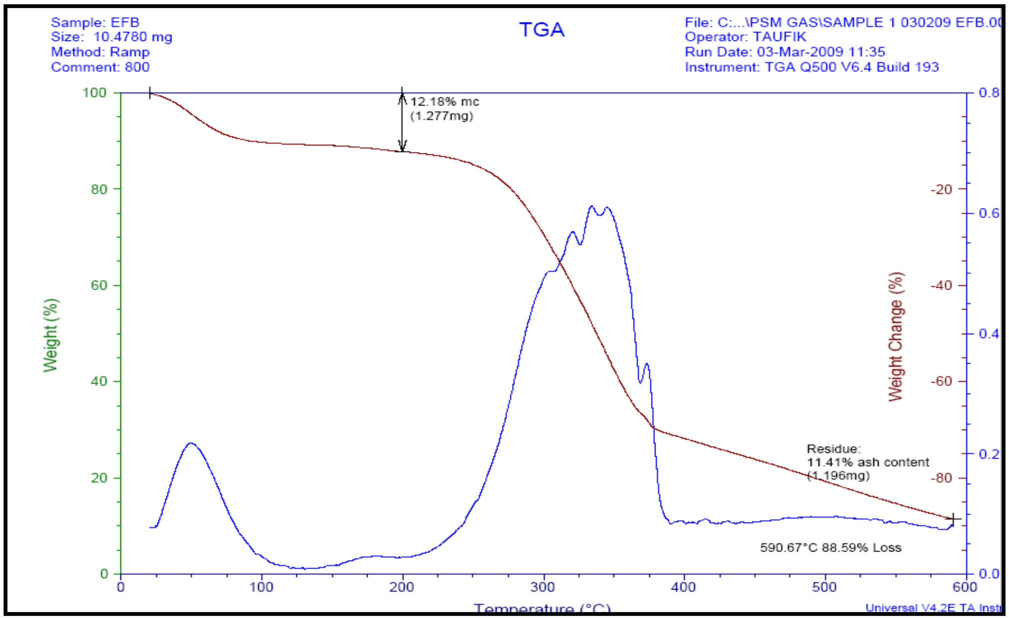


Figure 4.5: TGA Result of EFB

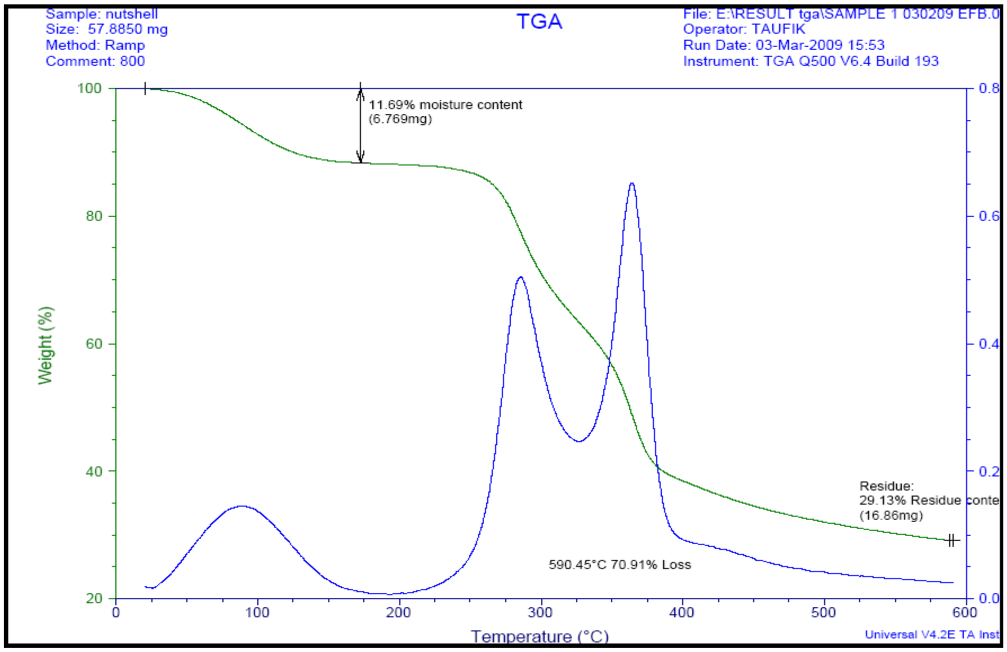
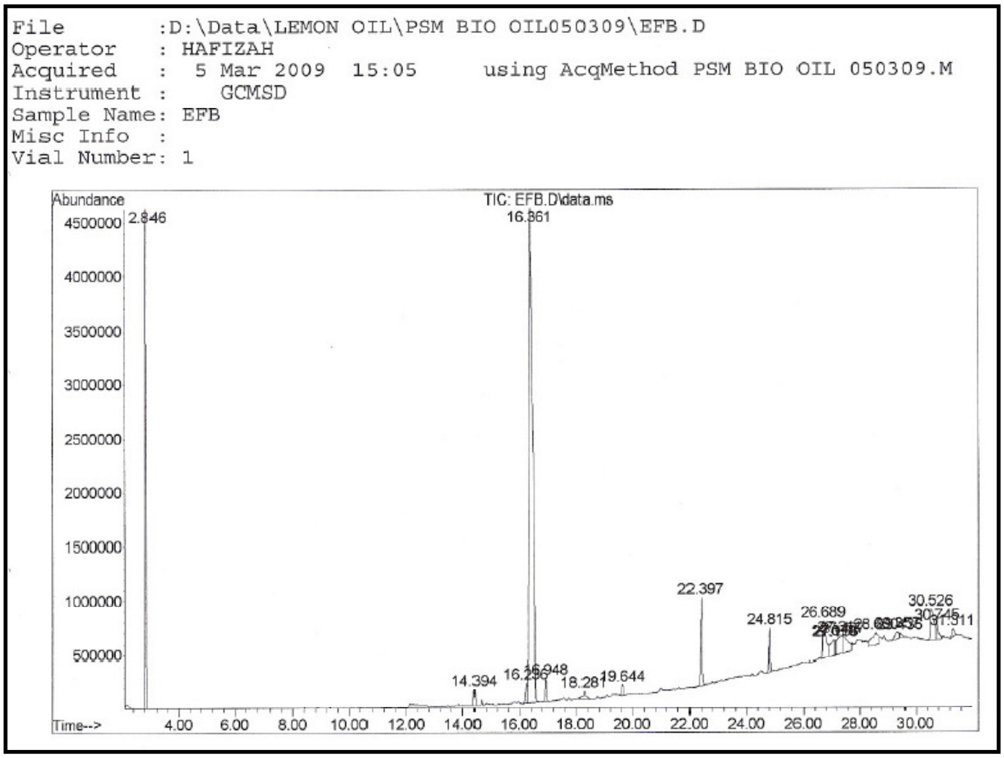


Figure 4.6: TGA Result of PKS

4.6 Gas Chromatography-Mass Spectrometer (GC-MS)

The components that can be found in EFB as in the database as Diethyl Phthalate, 1, 2-Benzenedicarboxylic acid, 1, 2- Methylpropyl ester, Dibytyl Phthalate, Hexanedioic acid, Diisooctyl adipate and Cyclohexyl as shows in Figure 4.7.

.



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Acquired    :  5 Mar 2009  15:05     using AcqMethod PSM BIO OIL 050309.M
Instrument  :    GCMSD
Sample Name: EFB
Misc Info   :
Vial Number: 1
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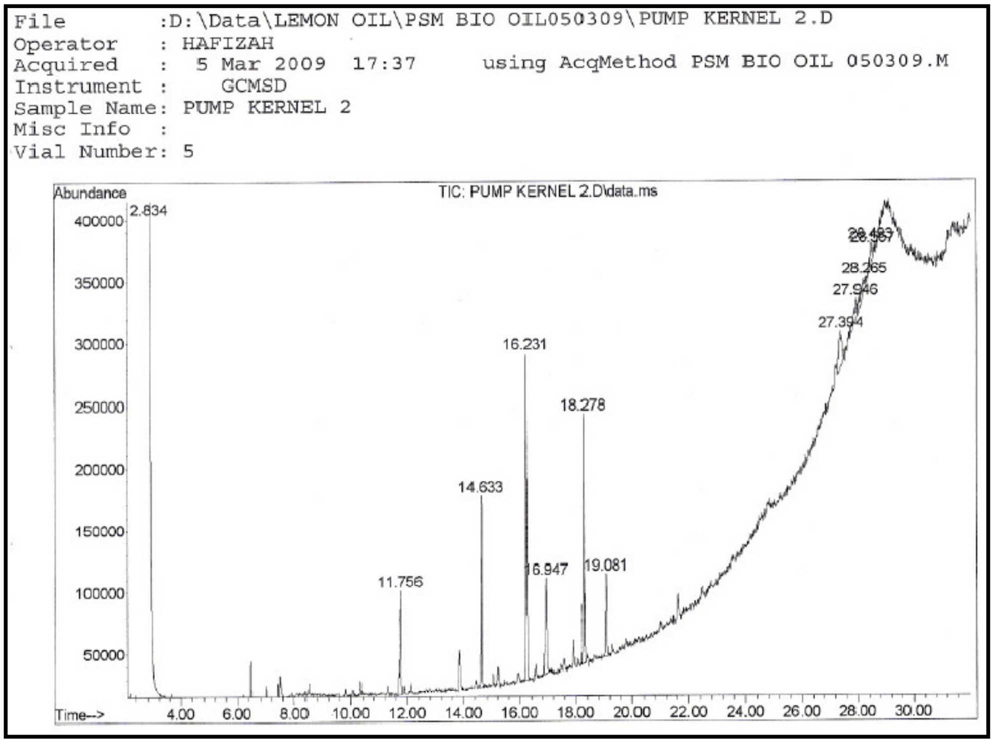
Figure 4.7: GC-MS Analysis of EFB

The components that can be found in PKS as in the database as methyl ester, hexadecanoic acid, heptadecanoic acid, and octaethylene glycol as shows in Figure 4.8.



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Operator    : HAFIZAH
Acquired    :  5 Mar 2009  17:37     using AcqMethod PSM BIO OIL 050309.M
Instrument  :    GCMSD
Sample Name: PUMP KERNEL 2
Misc Info   :
Vial Number: 5
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Figure 4.8: GC-MS Analysis of PKS

4.7 Fourier Transform Infrared (FTIR)

Fourier transform infrared (FTIR) was used in this analysis in order to determine the functional of the product. The functional groups of PKS and EFB will be determined based on the peak value from the graph shown in Figure 4.9 and Figure 4.10 respectively. The wave number of the functional group represents the functional group in the product. Table 4.4 shows the summary for the functional groups based on their peak. The functional group of the product was analysed by determined the wavelength in the graph and compared to the references. Each of the group has their own wave length.

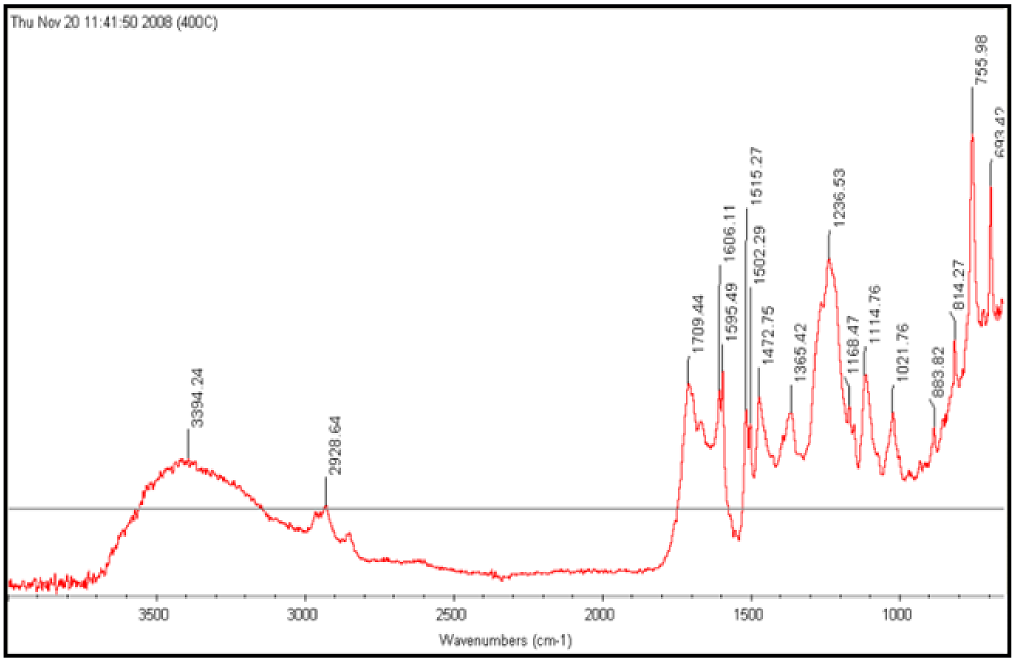

Figure 4.9: FTIR of PKS Bio-Oil

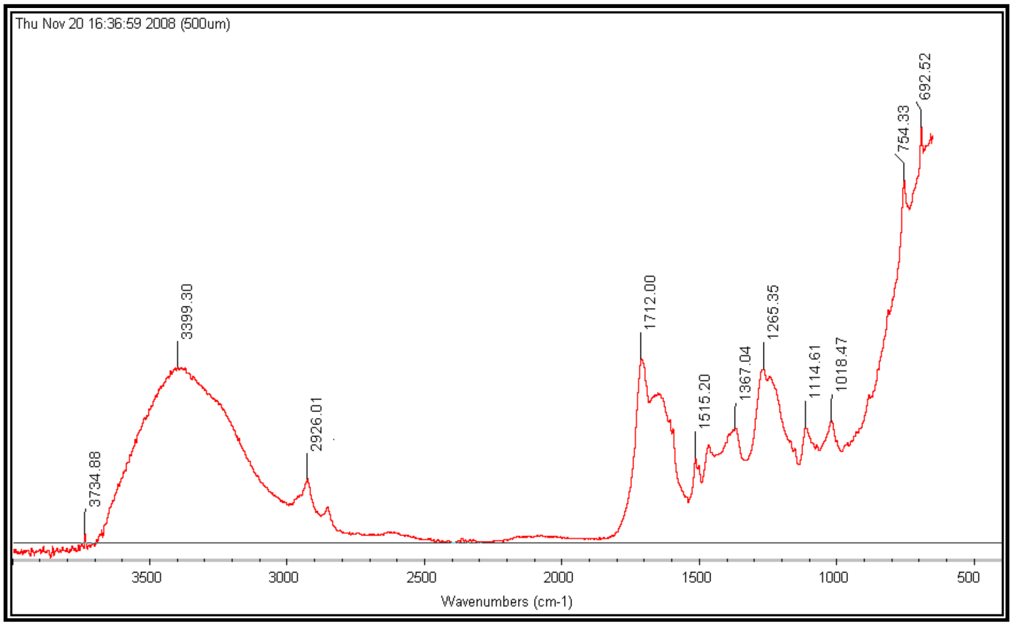

Figure 4.10: FTIR of EFB Bio-Oil

Type of Functional Group	**Wave number (cm^{-1})**	**Class of Component**	**PKS Wave number (cm^{-1})**	**EFB Wave number (cm^{-1})**
O–H stretching	3600–3300	Phenols, alcohols	3394.24	3399.30
C–H stretching	3000–2800	Alkanes	2928.64	2926.01
C _ O stretching	1750–1650	Ketones, aldehydes, carboxylic acids, esters	1709.44	1712.00
C _ C stretching	1675–1575	Alkenes	1595.49, 1606.11	-
C–H stretching	1460–1350	Alkanes	1356.42, 1472.75	1367.04,
C-O stretching	1300–950	Primary, secondary and tertiary alcohols, phenols, esters	1021.76, 1114.76, 1168.47, 1236.53	1265.35, 1114.61, 1018.47
C–H bending	900–650	Aromatic compounds	693.42, 755.98, 814.27, 883.82	754.33, 692.52

Table 4.4: Summary of EFB and PKS Bio-Oil Functional Group

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

Sample preparation of pyrolysis is one of the factors that influence the production of bio oil. Sample preparation involve in how the sample is prepared and the suitable condition for the experiment. In sample preparation, particle size, moisture content, physical and chemical properties of the sample were considered to ensure the optimum production of bio oil. Sample preparation is depend on the characteristic and properties of the biomass itself. Different sample will have different method. Hence to optimize the production of bio oil, sample preparation is the best way to increase high yield of bio oil production.

A series of slow pyrolysis experiments on empty fruit bunch (EFB) has been successfully performed using the fixed bed reactor operating at atmospheric pressure. In this study, the maximum bio oil yield of 39.5 wt % was obtained at 400 ^{o}C pyrolysis temperatures with the retention time of 15 minute and the particle size (length) in the range of 5 mm – 10 mm. In order to get high production of bio oil, preparation of the sample play important role such as particle size, moisture content and others in contribute the yield of bio oil produce. For pyrolysis on palm kernel shell (PKS) , the optimum production of bio oil yield 37.18% was obtained at temperature 400 ^{o}C with particle less than 5 mm in diameter.

The objective of this research which was to determine effect of sample preparation for temperature and particle size experiment for bio-oil production and the characteristic of bio-oil for empty fruit bunch and palm kernel shell has been successfully achieved. The result has shown that sample preparation is important in order to obtain optimum yield of bio oil.

Generally, bio-oils are considered as low-grade liquid fuels when compared with petroleum fuels. The poor fuel properties such as the complex multiphase structures, high contents water that can cause low heating values, poor ignition and combustion properties. Furthermore, bio-oils are also chemical and thermal instability with low pH values. In spite of these poor fuel properties, bio-oils also have some promising properties because they have many valuable chemical compounds and the usage for chemical feedstock. At present, many bio-oils are less to meet the fuel specifications, and therefore, they are not accepted commercially. Further work is required to be done in the future to improve the properties of bio-oils.

5.2 Recommendation

Based on the result and discussion, these recommendations can be taken into consideration to upgrade future studies of pyrolysis process in biomass:

i. Use fast pyrolysis system to get more production of bio oil.
ii. Use different types of sample such as palm frond, mesocarp fibre, and etc.
iii. Add more range size of the sample.
iv. Use different heating temperature.

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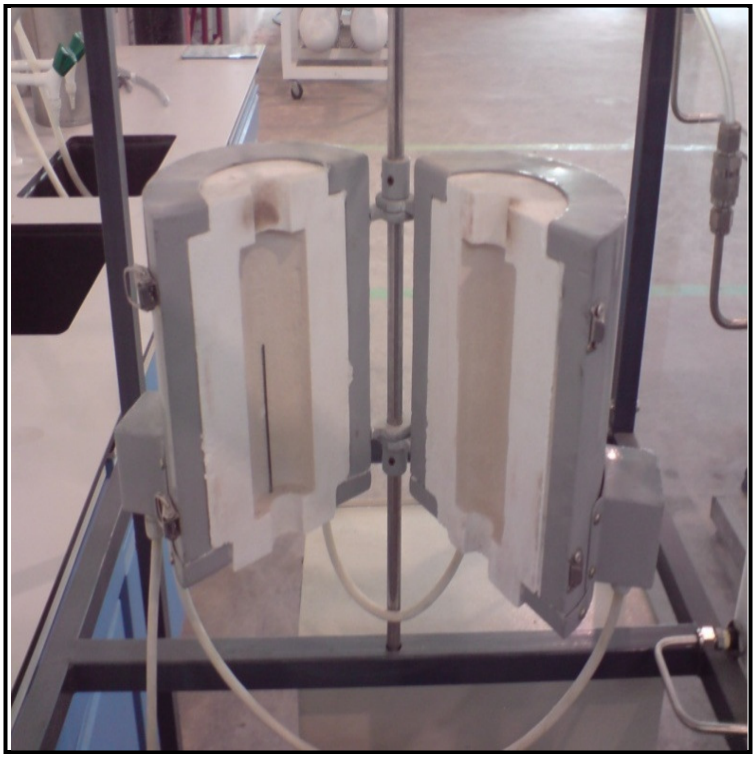
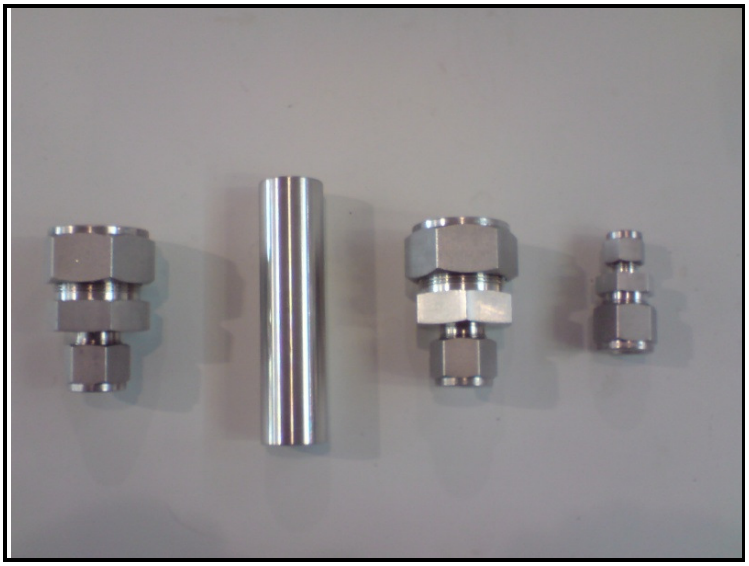
APPENDIX A

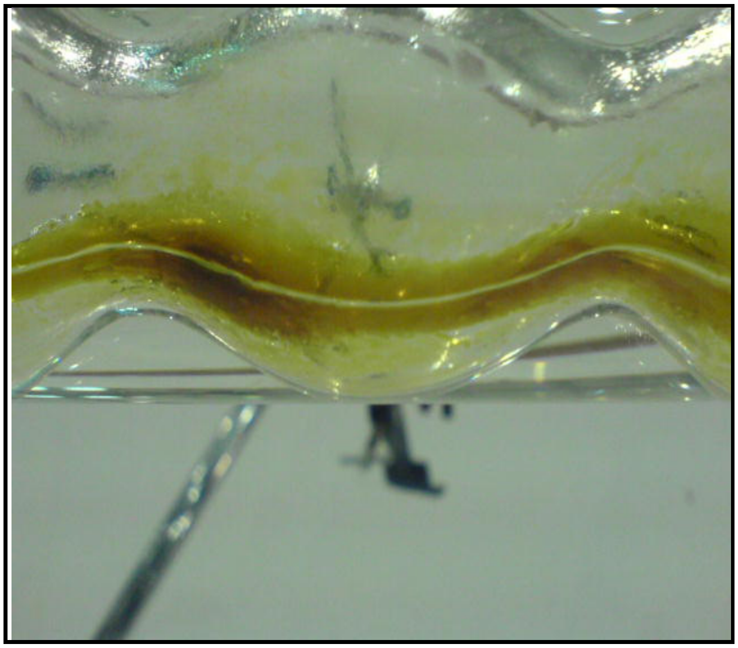
Pyrolysis Picture



Picture 1: Electric Tubular Furnace



Picture 2: Part of Core Holder

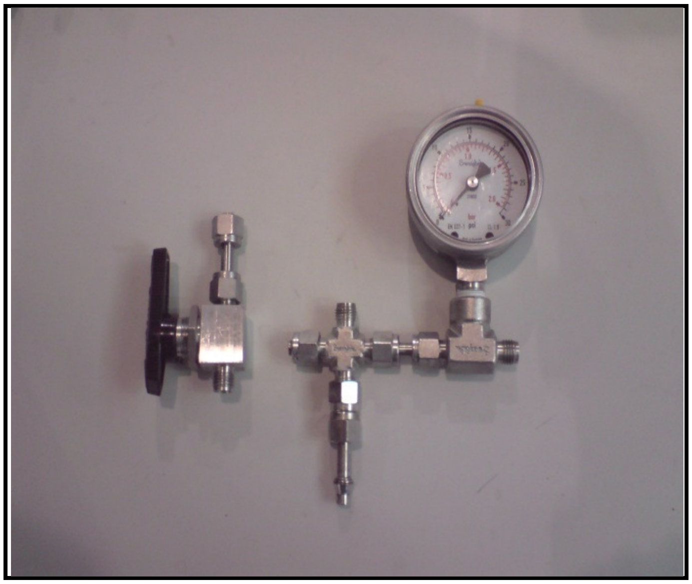


Picture 3: Part of Condensation of Biogas

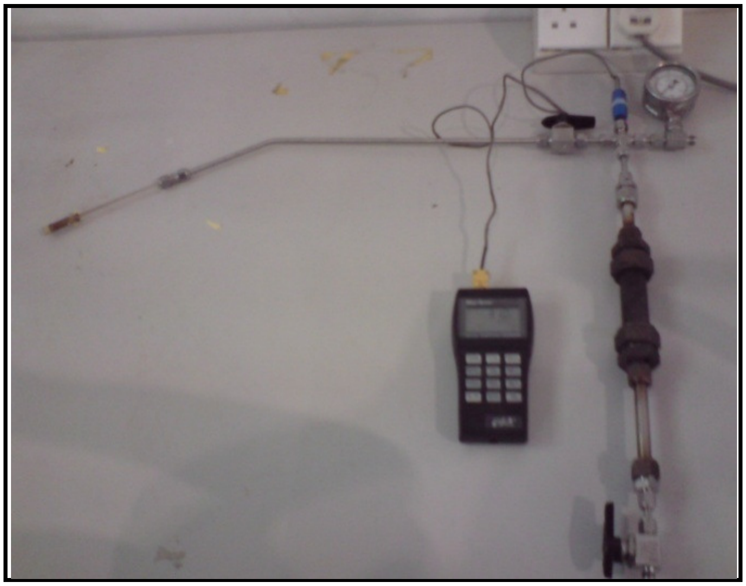
Picture 4: Charcoal Product

Picture 5: Temperature Controller

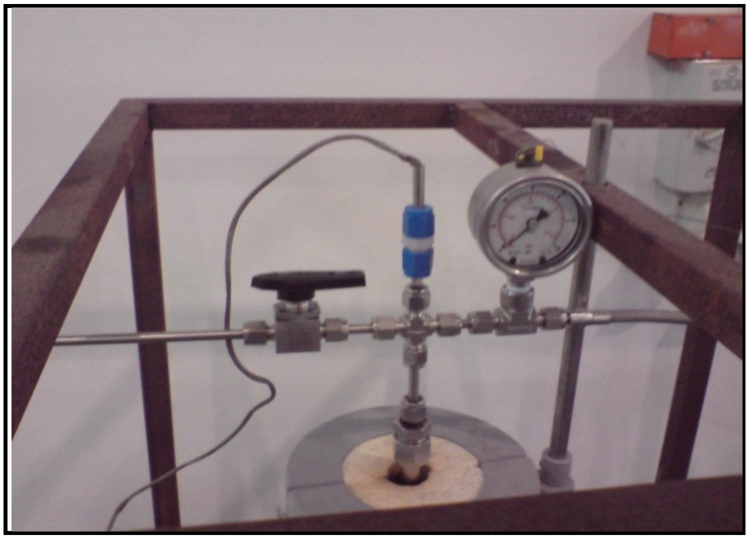
Picture 6: Nitrogen Tank



Picture 7: Valve and Pressure Gauge



Picture 8: System Cooling Process



Picture 9:- Jointing and Fitting

Picture 10: Bio oil Collector

APPENDIX B

Empty Fruit Bunch (EFB) Palm Kernel Shell GC-MS Result

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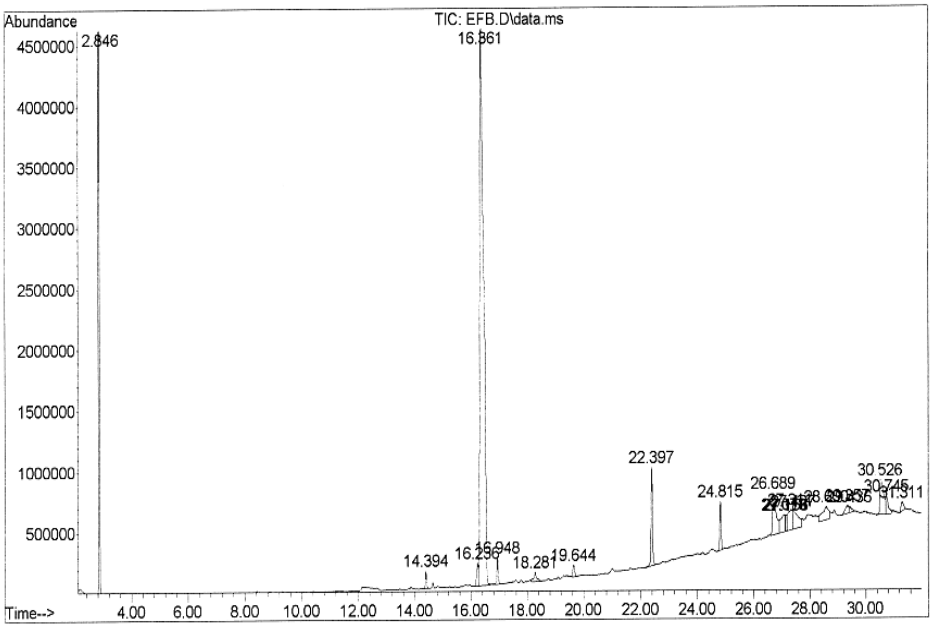

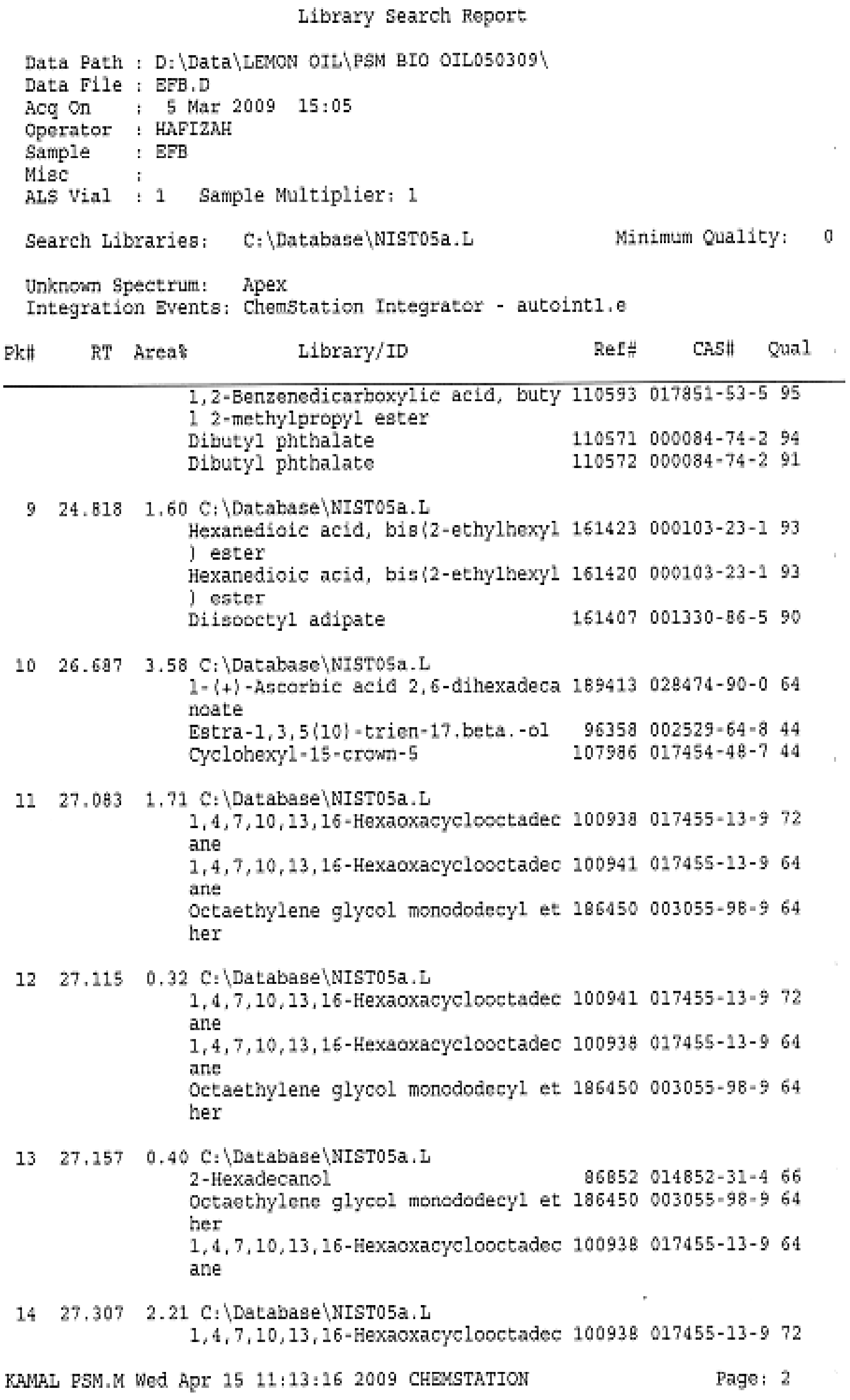

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 Sample    : EFB
 Misc      :
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                l 2-methylpropyl ester
                Dibutyl phthalate                  110571 000084-74-2 94
                Dibutyl phthalate                  110572 000084-74-2 91

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                ) ester
                Hexanedioic acid, bis(2-ethylhexyl 161420 000103-23-1 93
                ) ester
                Diisooctyl adipate                 161407 001330-86-5 90

 10  26.687  3.58 C:\Database\NIST05a.L
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                noate
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                Cyclohexyl-15-crown-5              107986 017454-48-7 44

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                ane
                1,4,7,10,13,16-Hexaoxacyclooctadec 100941 017455-13-9 64
                ane
                Octaethylene glycol monododecyl et 186450 003055-98-9 64
                her

 12  27.115  0.32 C:\Database\NIST05a.L
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                ane
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                her

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                ane

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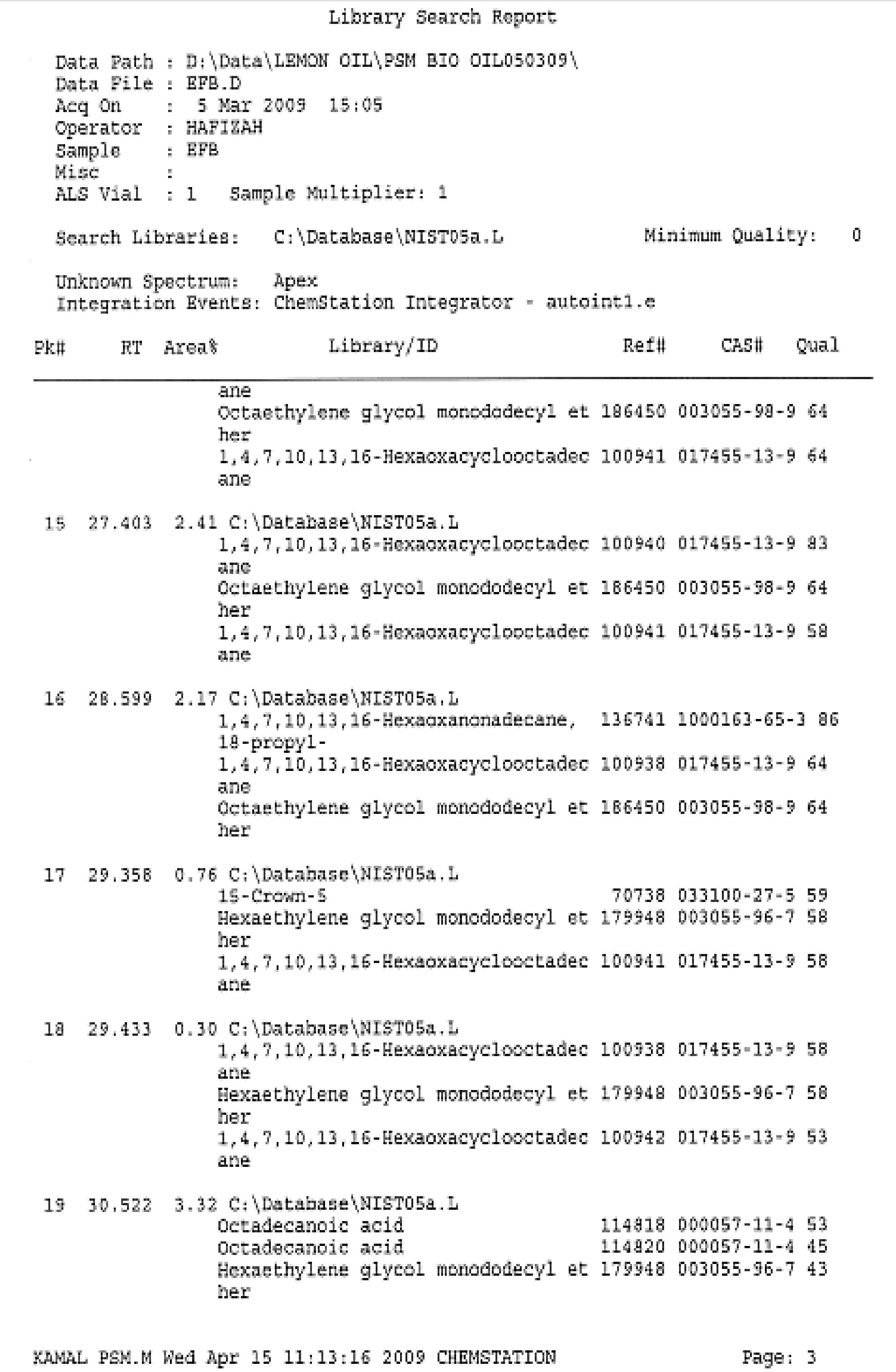

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 Sample    : EFB
 Misc      :
 ALS Vial  : 1   Sample Multiplier: 1

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                 18-propyl-
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                 her

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                 her
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                 ane

 18  29.433  0.30 C:\Database\NIST05a.L
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 58
                 ane
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                 her
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100942 017455-13-9 53
                 ane

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                 Hexaethylene glycol monododecyl et 179948 003055-96-7 43
                 her

KAMAL PSM.M Wed Apr 15 11:13:16 2009 CHEMSTATION               Page: 3
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                         Library Search Report

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  Sample    : EFB
  Misc      :
  ALS Vial  : 1   Sample Multiplier: 1

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                 ane

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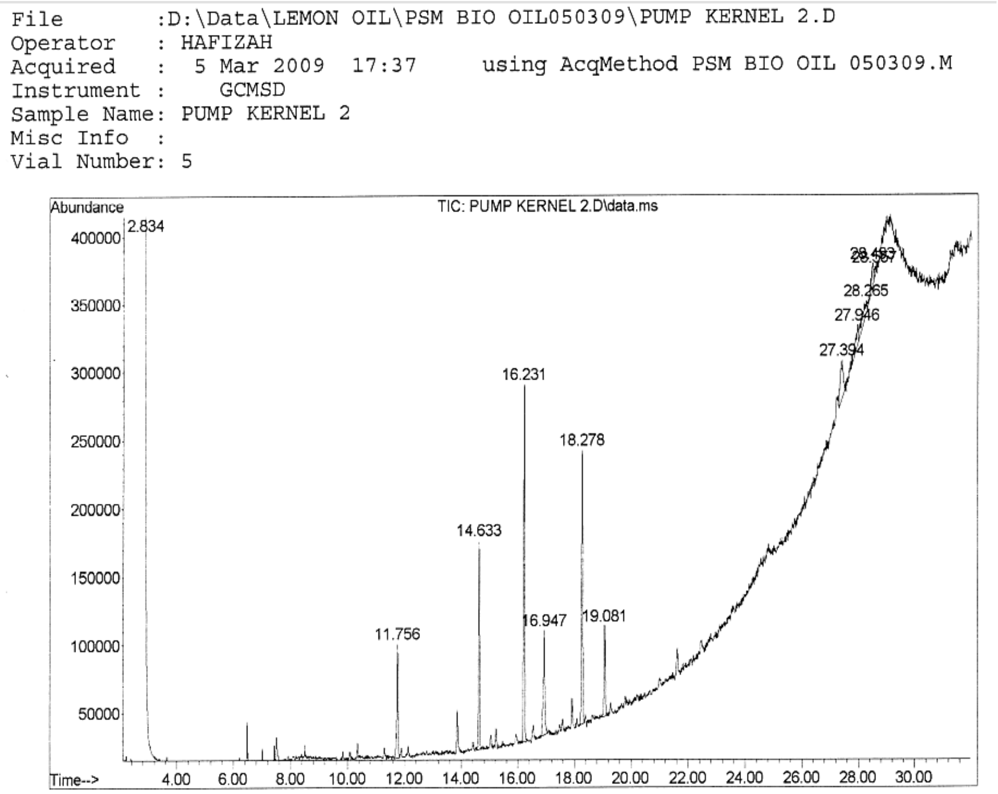
Pump Kernel Shell (PKS)



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Misc Info  :
Vial Number: 5
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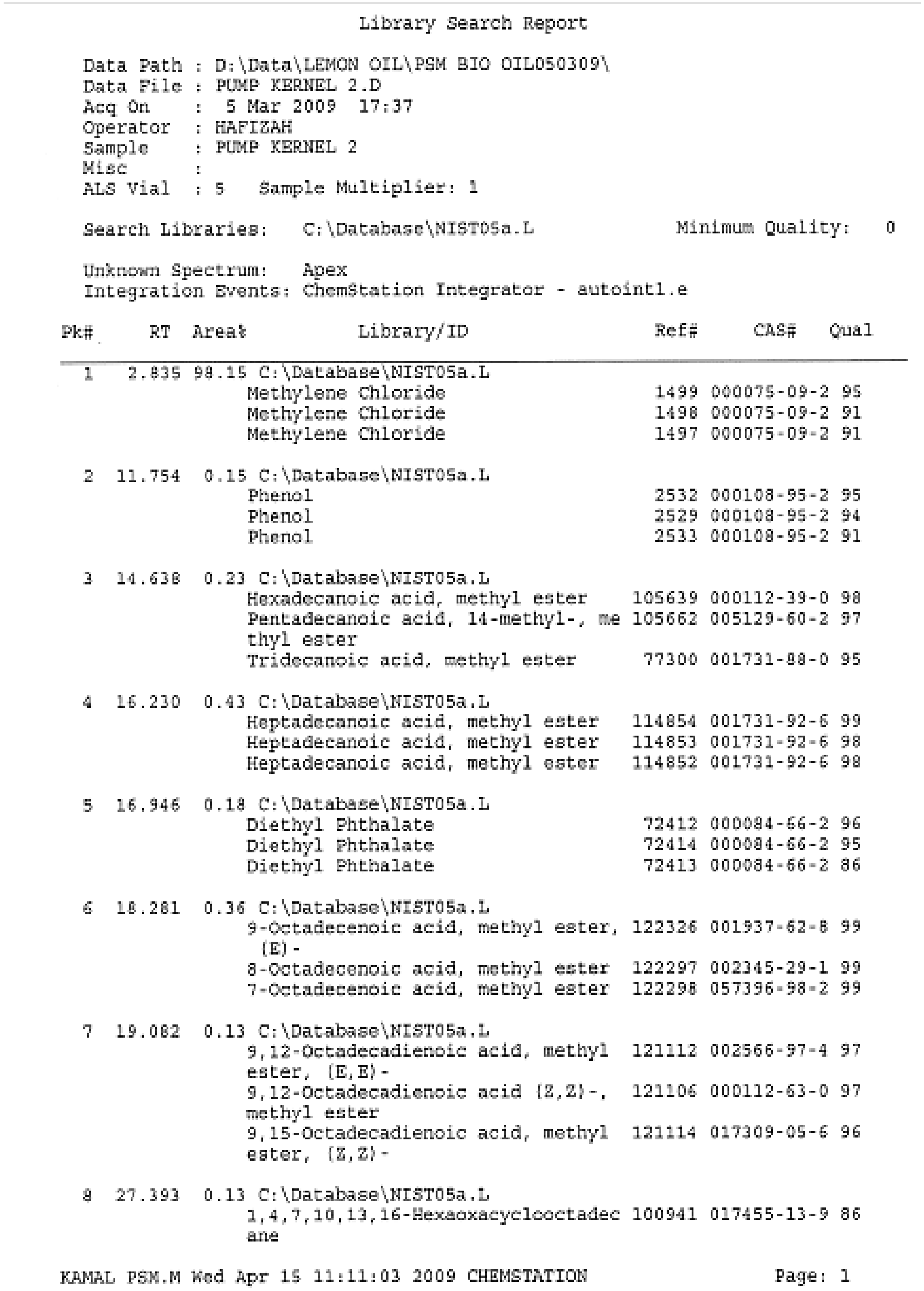

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                         Library Search Report

   Data Path : D:\Data\LEMON OIL\PSM BIO OIL050309\
   Data File : PUMP KERNEL 2.D
   Acq On    :  5 Mar 2009  17:37
   Operator  : HAFIZAH
   Sample    : PUMP KERNEL 2
   Misc      :
   ALS Vial  : 5   Sample Multiplier: 1

   Search Libraries:   C:\Database\NIST05a.L           Minimum Quality:   0

   Unknown Spectrum:   Apex
   Integration Events: ChemStation Integrator - autoint1.e

 Pk#      RT  Area%          Library/ID                  Ref#     CAS#   Qual
_______________________________________________________________________________
  1   2.835 98.15 C:\Database\NIST05a.L
                 Methylene Chloride                       1499 000075-09-2 95
                 Methylene Chloride                       1498 000075-09-2 91
                 Methylene Chloride                       1497 000075-09-2 91

  2  11.754  0.15 C:\Database\NIST05a.L
                 Phenol                                   2532 000108-95-2 95
                 Phenol                                   2529 000108-95-2 94
                 Phenol                                   2533 000108-95-2 91

  3  14.638  0.23 C:\Database\NIST05a.L
                 Hexadecanoic acid, methyl ester        105639 000112-39-0 98
                 Pentadecanoic acid, 14-methyl-, me     105662 005129-60-2 97
                 thyl ester
                 Tridecanoic acid, methyl ester          77300 001731-88-0 95

  4  16.230  0.43 C:\Database\NIST05a.L
                 Heptadecanoic acid, methyl ester       114854 001731-92-6 99
                 Heptadecanoic acid, methyl ester       114853 001731-92-6 98
                 Heptadecanoic acid, methyl ester       114852 001731-92-6 98

  5  16.946  0.18 C:\Database\NIST05a.L
                 Diethyl Phthalate                       72412 000084-66-2 96
                 Diethyl Phthalate                       72414 000084-66-2 95
                 Diethyl Phthalate                       72413 000084-66-2 86

  6  18.281  0.36 C:\Database\NIST05a.L
                 9-Octadecenoic acid, methyl ester,     122326 001937-62-8 99
                  (E)-
                 8-Octadecenoic acid, methyl ester      122297 002345-29-1 99
                 7-Octadecenoic acid, methyl ester      122298 057396-98-2 99

  7  19.082  0.13 C:\Database\NIST05a.L
                 9,12-Octadecadienoic acid, methyl      121112 002566-97-4 97
                 ester, (E,E)-
                 9,12-Octadecadienoic acid (Z,Z)-,      121106 000112-63-0 97
                 methyl ester
                 9,15-Octadecadienoic acid, methyl      121114 017309-05-6 96
                 ester, (Z,Z)-

  8  27.393  0.13 C:\Database\NIST05a.L
                 1,4,7,10,13,16-Hexaoxacyclooctadec     100941 017455-13-9 86
                 ane

KAMAL PSM.M Wed Apr 15 11:11:03 2009 CHEMSTATION                Page: 1
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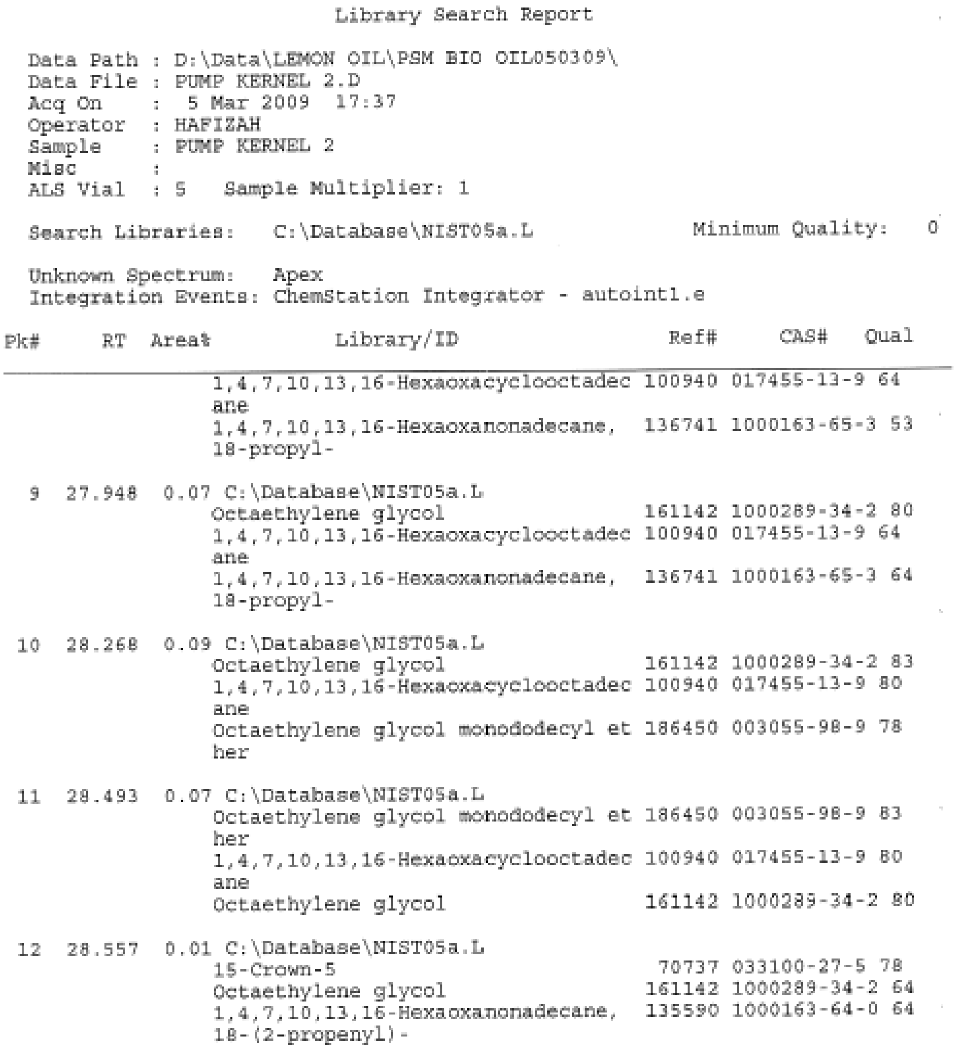

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                          Library Search Report

 Data Path : D:\Data\LEMON OIL\PSM BIO OIL050309\
 Data File : PUMP KERNEL 2.D
 Acq On    :  5 Mar 2009  17:37
 Operator  : HAFIZAH
 Sample    : PUMP KERNEL 2
 Misc      :
 ALS Vial  : 5   Sample Multiplier: 1

 Search Libraries:    C:\Database\NIST05a.L          Minimum Quality:   0

 Unknown Spectrum:    Apex
 Integration Events: ChemStation Integrator - autoint1.e

Pk#     RT  Area%             Library/ID                   Ref#      CAS#   Qual
_________________________________________________________________________________
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100940 017455-13-9 64
                  ane
                  1,4,7,10,13,16-Hexaoxanonadecane,  136741 1000163-65-3 53
                  18-propyl-

  9  27.948   0.07 C:\Database\NIST05a.L
                  Octaethylene glycol                161142 1000289-34-2 80
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100940 017455-13-9 64
                  ane
                  1,4,7,10,13,16-Hexaoxanonadecane,  136741 1000163-65-3 64
                  18-propyl-

 10  28.268   0.09 C:\Database\NIST05a.L
                  Octaethylene glycol                161142 1000289-34-2 83
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100940 017455-13-9 80
                  ane
                  Octaethylene glycol monododecyl et 186450 003055-98-9 78
                  her

 11  28.493   0.07 C:\Database\NIST05a.L
                  Octaethylene glycol monododecyl et 186450 003055-98-9 83
                  her
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100940 017455-13-9 80
                  ane
                  Octaethylene glycol                161142 1000289-34-2 80

 12  28.557   0.01 C:\Database\NIST05a.L
                  15-Crown-5                          70737 033100-27-5 78
                  Octaethylene glycol                161142 1000289-34-2 64
                  1,4,7,10,13,16-Hexaoxanonadecane,  135590 1000163-64-0 64
                  18-(2-propenyl)-
```