ANALYSIS OF BIO-OIL FROM PALM OIL WASTES THROUGH BATCH PYROLYSIS PROCESS

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APRIL 2009

I declare that this thesis entitled "Analysis of Bio-oil from Palm Oil Wastes 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.

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

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ABSTRACT

Malaysia is well known as the top largest producer of palm oil in the world. The abundance of biomass from palm oils agriculture industry would make a great benefit is they were used as a new source in fulfilling energy demand which increased year by years. The biomass can be converted into valuable product via pyrolysis process. Pyrolysis is thermal degradation either in the complete absence of oxidizing agent which is air or oxygen. The products of pyrolysis are bio-oil, char and gas. In this research, the pyrolysis of palm oil wastes (Pump Kernel Shell (PKS), Empty Fruit Bunch (EFB) and Mesocarp Fiber) was performed using a static batch reactor which being heated by a tubular furnace. Preliminary analysis was conducted using thermogravimetric analyzer (TGA) to determine the volatility, ash residue, moisture content and weight loss. 3 different physical properties were investigated on these bio-oils which are water content, pH, and viscosity. The functional groups of the product which is bio oil are identified by using Fourier Transform Infrared spectrometer (FTIR). Gas Chromatography-Mass Selectivity (GC-MS) was used to identify the component exists in the bio-oils. From the result, the pHs for all products were very acidic with pH value are 2.46, 2.53 and 2.56 respectively for Pump Kernel Shell (PKS), Empty Fruit Bunch (EFB) and Mesocarp Fiber. The viscosity values range was 33-43 cP and the water content in the bio-oils were 7-13 % weight. The result of FTIR and GC-Ms shows that, there are many complex compounds which would be a ideal for chemical feedstock and with undergoing upgrading process, can be used as fuel.

ABSTRAK

Malaysia amat terkenal sebagai pengeluar terbesar buah kelapa sawit di dunia. Biomass yang banyak dari industri penanaman kelapa sawit boleh memberi manfaat besar jika ianya digunakan sebagai sumber tenaga baru bagi memenuhi permintaan terhadap sumber tenaga yang kian meningkat dari tahun ke tahun. ‘Biomass’ ini boleh ditukar kepada produk yang bernilai melalui proses yang dipanggil ‘Pyrolysis’. ‘Pyrolysis’ ialah penguraian termal tanpa kehadiran agen pengoksidaan iaitu udara atau lebih tepat oksigen. 3 produk yang terhasil melalui ‘Pyrolysis’ ialah ‘Bio-oil’, arang dan gas. Di dalam kajian ini, proses ‘Pyrolysis’ dilakukan terhadap hasil buangan kelapa swit (tandan sawit kosong dan sirat Mesocarp) dengan mengunakan static reaktor ‘batch’ yang dipanaskan oleh ‘Tubular Furnace’. Analisis saringan dilakukan dengan mengunakan ‘Thermogravimetric Analyzer’ (TGA) untuk menentukan mudahruapan, arang, kandungan air dan juga berat yang hilang pada setiap sampel. 3 sifat fizikal yang berlainan bagi setiap ‘bio-oil’ dikaji iaitu kandungan air, pH dan juga kelikatan. Kumpulan berfungsi yang terdapat di dalam produk iaitu ‘bio-oil’ dikenal pasti melalui ‘Fourier Transform Infrared Spectrometer’ (FTIR).‘Gas Chromatography-Mass Selectivity’ (GC-MS) pula digunakan untuk mengenalpasti komponen-komponen yang wujud di dalam ‘bio-oil’. Daripada keputusan yang diperolehi, pH untuk semua bio-oil menunjukkan bahawa bio-oil adalah sangat berasid dengan nilai pH adalah 2.46, 2.53 and 2.56 bagi Pump Kernel Shell (PKS), Tandan Sawit Kosong (EFB) and Sirat Mesocarp. Nilai kelikatan untuk ketiga-tiga produk ‘bio-oil’ berada dalam linkungan nilai 33-43 cP dan kandungan air di dalam ‘bio-oil’ adalan 7 hingga 13 % berat.

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cm - Centimeter

°C - Celsius

Wt% - Weight Percentage

kg - Kilogram

kJ - Kilo Joule

s - Second

CH_4 - Methane

CO_2 - Carbon Dioxide

min - Minutes

T - Temperature

M^3 - Meter cubic

GJ - Giga Joule

Tn - Tonnes

h - Hour

mm - Millimeter

kPa - Kilo Pascal

g - Gram

%	-	Percent
psi	-	Pressure unit
cP	-	Centi Poise
µm	-	Micrometer
mL	-	milliliter
He	-	Helium

CHAPTER 1

INTRODUCTION

1.1 Research Background

Biomass refers to living and recently dead biological material that can be used as fuel. Biomass is the fourth largest source of energy in the world and particularly become an attractive energy source more many countries because of it availability and sustainability. Biomass is mainly derived from the agriculture or forestry sector. Today, various forms of biomass are consumed all over the world for energy generation. Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security. The use of these materials will depend on safe state of the art, economic and technologies that are used to transform them into manageable products. One of the indigenous biomass resources in Southeast Asia is derived from the oil palm. The oil palm empty fruit bunches, fiber and shell which are generally considered as 'waste' are generated every year in Malaysia, with an annual increment of 5% (S. Mohamad Asri et al., 2009).

There are 3 methods in biomass conversion via thermochemical which are combustion, gasification and pyrolysis. Pyrolysis is considered to be an emerging technology for liquid oil production among these three methods in thermochemical. Pyrolysis is a thermal degradation of biomass under moderate temperature in the absence of oxygen. Pyrolysis products consist of bio-oil (condensable gas), synthetic gas (non-condensable gas), and char (Boateng et al., 2006).

Bio-oil has some advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. (Rahman, 2007). Bio-oils also referred to as biomass pyrolysis liquids, pyrolysis oils, or bio-crude oils, are dark brown, free flowing liquids with an acrid or smoky odor (Anja Oasmaa et al., 2009). They are complex mixtures of compounds that are derived from the depolymerization of cellulose, hemicellulose and lignin. Chemically, they comprise quite a lot of water, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds (Qiang Lu et al.,2009). Bio-oils have been regarded as promising candidates to replace petroleum fuels to be used in various thermal devices. However, bio-oils are totally different from petroleum fuels. Therefore, the successful utilization of bio-oils in terms of liquid fuels requires adequate understanding of their fuel properties. Analysis on the bio-oil physically and chemically is required in order to get better understanding about the characteristic and properties of the bio -oil.

1.2 Problem Statement

Projects and research in pyrolysis had been developing since 2 decade ago. Pyrolysis process produced bio-oils as its primary product and said to be a well suitable candidate to replace crude oil. In order for bio-oils to become a fuel replacement, an investigation on bio-oils properties and chemical compound in bio-oil had to be determined to find the effectiveness and suitability as a new energy source.

Devices such as diesel engines, boilers, furnaces, and gas turbines rely on spray combustion for energy conversion (T. Tzanekatis, 2008). To understand bio-oil spray behavior, a thorough knowledge of liquid properties is required. The fuel properties that most affect atomization quality and spray combustion behavior are density and viscosity. Other relevant properties of bio-oil that can affect in combustion, fueling and storage are water content and pH or acidity.

It is important to determine the physical and chemical characteristic of palm oil wastes (Pump Kernel, Empty Fruit Bunch (EFB) and Mesocarp Fiber) bio-oils from batch pyrolysis process as a potential fuel substitute. Through Fourier Transform Infrared (FTIR) and Gas Chromatography-Mass Selectivity (GC-MS), the functional group and composition in bio-oils can be analyzed. Physical properties of these bio-oil were also been investigated. 3 different physical properties were investigated on these bio-oils which are water content, pH, and viscosity.

1.3 Objective

1.3.1. To determine the physical properties of bio-oils which are bio-oils water content, viscosity and also acidity or pH.

1.3.2. To investigate the functional groups exist in the bio-oil via Fourier Transform Infrared and the component of bio-oils through Gas Chromatography-Mass Selectivity (GC-MS).

1.4 Scope of Works

1.1.1. The scope of this project is to use Palm oil wastes as the biomass sources which are Empty Fruit Bunch (EFB), Mesocarp Fibers and Pump Kernel Shell (PKS). The most abandon biomass in Malaysia come from the palm oil plantation. With production of billion tonnes per annum, palm oil wastes can be a great source for pyrolysis process in producing bio-oils.

1.1.2. The pyrolysis process is conducted in a batch process. The samples will first be filed into the reactor and then heating it until the desired temperature. A tubular reactor is use as a heating source.

1.1.3. Only bio-oils and char as a by-product will be collected. The gas by-product will be vent.

1.1.4. 3 physical properties of bio-oil which are the water content in the bio-oil, the pH and viscosity will be investigated. In determining the functional group, Fourier Transform Infrared will be used and Gas Chromatography- Mass Selectivity is use in determining chemical compound in the bio-oils.

1.2 Rationale and Significance

Biomass Pyrolysis is not a new technology but the importance of this technologies nowadays has become more crucial since crude oil became depleted and the environmental concern of global warming. Many researches had been conduction about the usefulness of pyrolysis and proven that this technology is worthy to be developed. Previous researches mainly focus on getting the highest production yield of bio-oils with little understanding about the fuel properties.

The focus of this project is on analysis of the bio-oil from palm oil wastes. The importance in analyzing the bio-oils is to discover studying yet understanding the physical properties and chemical components in the bio-oil in order to gain knowledge about the characteristic and benefit as a new energy source replacing the fossil fuel that is widely used in current world.

CHAPTER 2

LITERATURE STUDY

2.0 Renewable Energy

With the increasing evidence of global warming, unstable crude oil's prices in world market, depletion in current reservation with only few effort in finding new crude oil's reservoir source and idea of being carbon neutral becoming more prominent, the increase in interest in renewable energy is growing rapidly. Renewable energy takes on many forms, and usually describes using natural resources that won't run out.

There are several main renewable energy technologies in use, most of which are directly or indirectly due to the sun such as wind turbine, solar power and power generation from sea wave. But these kinds of renewable energy is not commercially used and based on geography of certain places for example, in sunny climates, it makes more sense to create renewable energy from solar panels, whereas in coastal areas, it may be more efficient and effective to use wave or tidal power.

To overcome these, biomass seems be more promising as a source of renewable energy as it is more reliable and sustainable source. Biomass can be found anywhere and can be replaced. As the need for alternative forms of energy become more important, biomass can play a bigger part for the production of fuel and electricity generations.

2.1 Biomass

Biomass refers to living and recently dead biological material that can be used as fuel or for industrial production. Most commonly, biomass refers to plant matter grown to generate electricity or produce biofuel, but it also includes plant or animal matter used for production of fibers, chemicals or heat. Biomass may also include biodegradable wastes that can be burnt as fuel. Fossil fuels such as coal and oil are not considered to be biomass as they are not recently dead, nor were they produced especially to become biomass.

Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth and heavy metals. These metals are often found in functional molecules such as the porphyrins which include chlorophyll which contains magnesium.

The carbon used to construct biomass is absorbed from the atmosphere as carbon dioxide (CO_2) by plant life, using energy from the sun.

Plants may subsequently be eaten by animals and thus converted into animal biomass. However the primary absorption is performed by plants.

If plant material is not eaten it is generally either broken down by microrganisms or burned:

- If broken down it releases the carbon back to the atmosphere, mainly as either carbon dioxide (CO_2) or methane (CH_4), depending upon the conditions and processes involved.
- If burned the carbon is returned to the atmosphere as CO_2.

These processes have happened for as long as there have been plants on Earth and is part of what is known as the carbon cycle.

2.1.1 Biomass Major Component

Biomass consists of three major components: cellulose, hemicellulose and lignin. Cellulose is a straight and stiff molecule with a polymerization degree of approximately 10.000 glucose unite (C6 sugar) Hemicellulose are polymers built C5, C6 sugars with a polymerisation degree of about 200 sugar units. Both cellulose and hemicellulose can be vapored with negligible char formation at temperatures above 500 "C. Lignin is a three dimensional branched polymer composed phenolic units. Due to the aromatic content of lignin, it degrades slowly on heating and contributes to a major fraction of the char formation. In addition to the major cell wall composition like cellulose, hemicellulose and lignin, biomass often contains varying amounts of species called "extractives". These extractives, which are soluble in polar or no polar solvents, consists of terpenes, fatty acids, aromatic compounds and volatile oil.

2.1.2 Difference between Biomass and Fossil Fuels

Fossil fuel such as coal, oil and gas are also derived from biological materials, however material that absorbed CO_2 from the atmosphere many millions of year ago. As fuel, they offer high energy density, but making use of that energy involves burning the fuel, with the oxidation of the carbon to carbon dioxide and the hydrogen to water (vapor). Unless they are captured and stored, these combustion products are usually released to the atmosphere, returning carbon sequestered millions years ago and thus contributing to increase CO_2 atmospheric concentrations.

Biomass takes carbon out of the atmosphere while it is growing and returns it as it is burned. If it is managed on a sustainable basis, biomass is harvested as part of a constantly replenished crop. This is either during woodland or arboricultural management or coppicing or as part of a continuous program of replanting with new growth taking up CO_2 from the atmosphere at the same time as it is released by combustion of the previous harvest. This maintains a closed carbon cycle with no net increase in atmospheric CO_2 level.

2.1.3 Categories of Biomass Material

Within the Biomass definitions, biomass for energy can include a wide range of materials. Biomass had been categorized for easy description. There are 5 basic categories of biomass materials as listed in table 2.1.

Table 2.1: Categories of Biomass

Biomass Categories	
Virgin Wood	Forestry, Arboricultural, Wood processing plant
Energy Crops	High yield crops grown specifically for energy applications
Agricultural Residues	Residues from Agriculture, Harvesting or Processing
Food Waste	Food and drink manufacture, Preparation and processing and Post customers waste
Industrial Waste and Co-Products	Manufacturing and Industrial Processes

2.1.4 Biomass In Malaysia

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. Based on the researched from the World Wildlife Fund

(WWF), Malaysia is currently the world's largest producer of palm oil, contributing of 50.9% of total global production.

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 and empty fruit bunches. The projection figures of these residues are as follows:

- 7.0 million tonnes of oil palm trunks
- 26.2 million tonnes of oil palm fronds
- 23% of Empty Fruit Bunch (EFB) per tonne of Fresh Fruit Bunch (EFB) processed in oil palm mill

Based on the above, Malaysia therefore has a great potential in turning its abundance supply of palm oil industry by products into value added products.

Figure 2.1: Empty Fruit Bunch Wastes (MPOA, 2003)

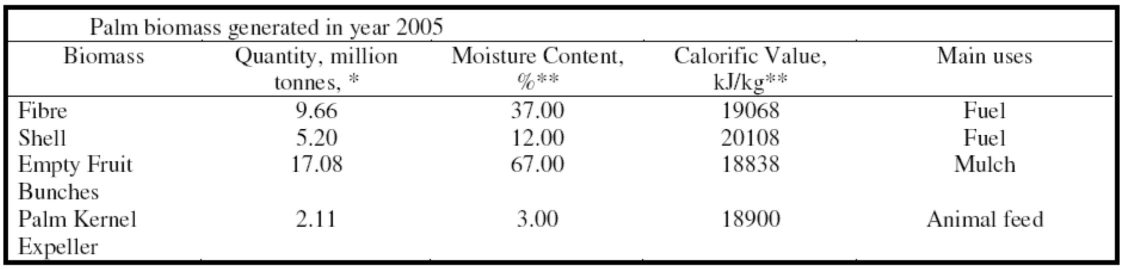
Under the present scenario, Malaysia can no longer remain idle and complacent in its position as the top grower and supplier of palm oil. In view of the escalating challenge posed by the other oil producing countries, Malaysia has to change its objective of being a world producer of palm oil to amongst others a leader in converting biomass waste into value-added products. Malaysia has therefore to seriously resort in aggressive R&D to support its ambition.

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)

As been stated above, the types and amounts of these biomass generated in 2005 are tabulated in table below.

Table 2.2: Biomass Generated in 2005 (A.B. Nasrin, 2008)



Palm biomass generated in year 2005

Biomass	Quantity, million tonnes, *	Moisture Content, %**	Calorific Value, kJ/kg**	Main uses
Fibre	9.66	37.00	19068	Fuel
Shell	5.20	12.00	20108	Fuel
Empty Fruit Bunches	17.08	67.00	18838	Mulch
Palm Kernel Expeller	2.11	3.00	18900	Animal feed

2.1.5 Biomass Conversion

There are 2 method for biomass conversion with are the Biological Method and Thermochemical Method. Biomass such as forest residue, agricultural residue and organic food processing waste can be converted to chemical and energy product via either biological (Lin and Tanaka, 2006) or thermochemical processes (Caputo et al., 2005). Biological conversion of low valued lignocellulosic tp commercial chemical and energy products, particularly ethanol, still face challenges in low economy and efficiencies (Lin and Tanaka, 2006). Thermochemical conversion provides a competitive ways to produce chemicals and energy products from low value and highly distributed biomass resources with large variation of properties. Combustion, Pyrolysis and Gasification are 3 main thermochemical conversion methods (Knoef et al., 2005)

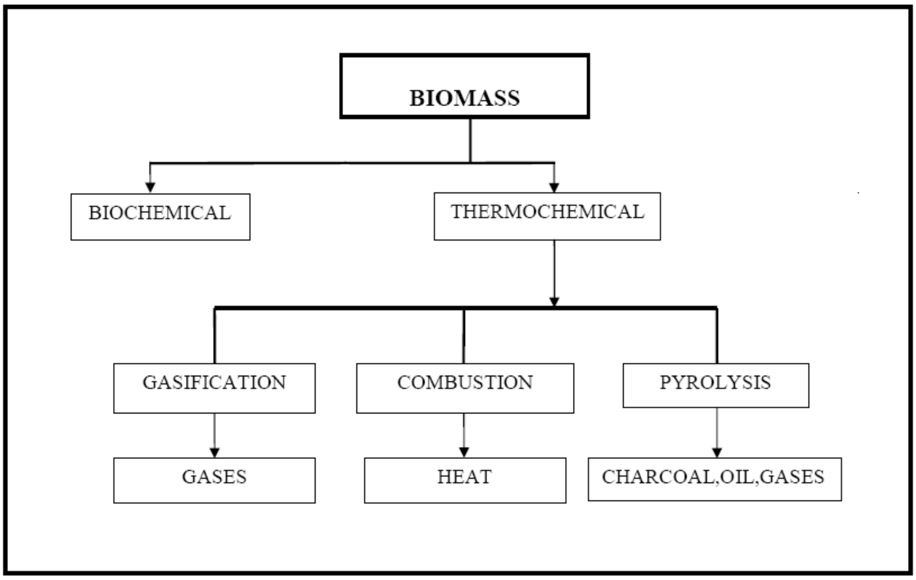


Figure 2.2: Main Processes of Biomass Conversion

Figure 2.2 summarized the thermochemical method and the products from the process. Combustion is the conventional of chemical energy stored in an organic matter into heat, generating carbon dioxide and water as the final products. Combustion usually produces hot gas at temperature around 800°C to 1000°C. Pyrolysis is the conversion of biomass into liquid, solid and gaseous fraction by heating the biomass in the absent of air or oxygen at relatively low temperature around 300°C to 800°C. Gasification is the partial oxidation of organic matter at a high temperature to convert the organic matter into a combustible gas mixture called syngas, which mainly consist of carbon monoxide, hydrogen, methane and carbon dioxide. Gasifiers are operate at approximately 800°C to

1000°C although a non-catalytic entrained flow gasifier could be operated at a temperature as high as 1300°C. Among 3 processes in Thermochemical method, Pyrolysis is said to be the most suitable method in providing substituted energy source as it can produce bio-oils.

2.2 Pyrolysis

Pyrolysis is thermal degradation either in the complete absence of oxidizing agent, or with such a limited supply that gasification does not occur to an appreciable extent or may be described as partial gasification. Relatively low temperatures are employed of 500 to 800 °C, compared to 800 to 1000 °C in gasification. Three products are usually produced: gas, pyrolysis oil and charcoal, the relative proportions of which depend very much on the pyrolysis method, the characteristics of the biomass and the reaction parameters.

2.2.1 History of Pyrolysis

Direct Combustion is the old way of using biomass. The biomass is completely transformed into heat, but the efficiency is just about 10 percent. The gasification pushes to the maximum level the cracking of biomass by completely transforming it into a combustible gas before burning it. The charcoal production, the slow pyrolysis of wood at temperature 500 °C is a process that charcoal makers have exploited for thousands years. Charcoal is a smokeless fuel which is still used for heating purposes. It first technological use can be dated back to the Iron Age when charcoal was used in ore melting to produce iron.

2.2.2 Classification of Pyrolysis

Pyrolysis has been practiced for centuries for production of charcoal. This requires relatively slow reaction at very low temperatures to maximize solid yield. More recently, studies into the mechanisms of pyrolysis have suggested ways of substantially changing the proportions of the gas, liquid and solid products by changing the rate of heating, temperature and residence time.

High heating rates, of up to a claimed 1000 °C/s or even 10000 °C/s, at temperature below about 650 °C and with rapid quenching, causes the liquid intermediate products of pyrolysis to condense before further reaction breaks down higher molecular weight species into gaseous products. The high reaction rates also minimize char formation, and under some condition no char is apparently formed. At high maximum temperature, the major product is gas. Pyrolysis at these high heating rates is known as fast or flash pyrolysis according to the heating rate and residence time, although the distinctions are blurred. Other work has attempted to exploit the complex degradation mechanisms by carry out pyrolysis in unusual environment. The main pyrolysis variants are listed in Table 2.2 and the characteristics of the main models of pyrolysis are summarized into Table 2.3.

Table 2.3: Pyrolysis Technology Variant (FOA, 2009)

Tech.	**Residence time**	**Heating rate**	**Temperature °C**	**Products**
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	< 1 s	high	< 650	bio-oil
Flash-gas	< 1 s	high	< 650	chemicals, gas
Ultra	< 0.5	very high	1000	chemicals, gas
Vacuum	2-30s	medium	400	bio-oil
Hydro-pyro.	< 10s	high	< 500	bio-oil
Methano-pyro.	< 10s	high	> 700	chemicals

Table 2.4: Characteristics of Pyrolysis Technologies (FOA, 2009)

	Flash low T	**Flash high T**	**Slow**	**Carbonization**
Feedstocks				
Feedsize	small	small	moderate	large
Moisture	v.low	v. low	low	low
Parameters				
Temp °C	450-600	650-900	500-600	450-600
Pressure, bar	1	0.1- 1	1	1
Max. input, t/h	0.05	0.02	5	10
Product				
Gas, % wt dry	< 30	< 70	< 40	< 40
MJ/Nm3	10-20	10-20	5-10	2-4
Liquid %	< 80	< 20	< 30	< 20
MJ/Kg	23	23	23	10-20
Solid %	< 15	< 20	< 30	< 35
MJ/Kg	30	30	30	30

2.2.3 Advantages of Pyrolysis

The biomass pyrolysis is attractive because solid biomass and wastes which are very difficult and costly to manage and can be readily converted into liquid products. These liquids, as crude bio-oil or slurry of charcoal of water or oil, have advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. The energy densities are summarized in Table 2.5.

The crude pyrolysis oil is a blank fluid which often named as bio-oil, pyrolysis oil, or just oil. The other main product is slurry which can be made from waste and charcoal with chemical added to stabilize the suspension. Stable and mobile concentration of up to 60% wt has been reported. Slurries can also be made from the oil and charcoal.

In pilot plant, the gas is usually flared but in a commercial process it would be used to drive the process or use it as a fuel drying or power generation.

In transport, the bulk density is important, and some estimated values are given in Table 2.5. Oil and slurry mixture have a clear advantage over wood chips and straw in transport bulk density and notable in energy density. For longer distance collection of biomass, this difference may be a decisive factor.

Storage and handling may be important because of seasonal variations in production and demand of some storage will always be required. Apart from the bulk density and the energy consideration, it is important that raw biomass will deteriorate during storage due to biological degradation process. Char, however, is very stable and will not biologically degrade. Another important factor is handling, in which liquids have significant advantages over solids.

Generally liquid products are easier to control in the combustion process and this is important in retrofitting existing equipment. Current oil fired burners can not be fully directly with solid biomass without any modification of the unit, which may not be interested in uncertain fuel markets. However, Bio-oil, char-oil slurry and char-water slurries are likely to be required only relatively minor conversion of the equipment or even none in some case. Powered coal burners can relatively easily accept charcoal as a partial fuel replacement, as long as the volatile content is compatible with the burner design.

In power station, the gas turbines can readily fired with bio-oil and slurry fuels although there is needed with the alkali ash in the char content of the slurry. Some modified engines can be used to use the upgraded oil. In some countries, there is a market for charcoal lumps and briquettes for leisure and industrial application.

Table 2.5: Energy and Density Characteristic (FOA, 2009)

Feed	Bulk density (Kg/M^3)	Heating value dry basis (GJ/Tn)	Energy density (GJ/M^3)
straw	100	20	2
woodchips	400	20	8
pyro-oil	1200	25	30
charcoal	300	30	9
char-water slurry (50/50)	1000	15	15
char-oil slurry (20/80)	1150	23	26

2.2.4 Pyrolysis Product

There are 3 products in biomass pyrolysis. The primary product is the bio-oil. 2 other products are the by-products from pyrolysis process which are the char or biochar and also syngas (incondensable gas).

2.2.4.1 Bio-oils

Bio-oils also referred to as biomass pyrolysis liquids, pyrolysis oils, or bio-crude oils, are dark brown, free flowing liquids with an acrid or smoky odor. They are complex mixtures of compounds that are derived from the depolymerization of cellulose, hemicellulose and lignin. Chemically, they comprise quite a lot of water, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds. The molecular weights of these compounds vary significantly, from as low as 18 (water) to as high as 5000 or more (pyrolytic lignins). The average molecular weight varies in the range of 370–1000 g/mol. Till now, over 300 organic compounds have been identified in different bio-oils. Most of the compounds are in low concentrations. Fractionation is widely used to separate bio-oils into groups of compounds to facilitate analysis and quantification of compounds and. However, complete chemical characterization of bio-oils is almost impossible mainly due to the presence of pyrolytic lignins. The pyrolytic lignins are derived from the partial cracking of lignin molecules. They cannot be determined by gas chromatography or high performance liquid chromatography. Analysis of the pyrolytic lignins shows that they are constituted by oligomers (mainly tetramers), and their basic units are very similar to milled wood lignins. As can be seen, bio-oils are totally different from petroleum fuels in chemical compositions, which will result in the vast difference in the fuel properties between them.

The chemical compositions of bio-oils are determined by many factors, such as biomass type, feedstock pretreatment (particle size and shape, moisture and ash contents), pyrolysis conditions (temperature, heating rate, residence time, pressure, gaseous environment) as well as vapor filtration and condensation (filter type, condensing method and medium, cooling rate). Therefore, bio-oils produced from different materials and by different pyrolysis reactors may differ greatly from one another. As a result, the fuel properties of different bio-oils usually vary in wide ranges

2.2.4.2 Char

Char is the by-product from pyrolysis. In this process, biomass is heated to the point where volatile gases and liquids are driven off and condensed into a product call bio-oil. What remains is almost pure carbon, called char, pyrolysis char or biochar with a varying ash content that depends on the type of biomass used. Interest in the char has grown as more companies explore processing technology and new uses for biomass.

The yield of char products from pyrolysis varies heavily with temperature. The lower the temperature, the more char is created per unit biomass. Fast pyrolysis yields 60% bio-oil, 20% biochar, and 20% syngas, and can be done in seconds, whereas slow pyrolysis can be optimized to produce substantially more char approximately around 50%, but takes on the order of hours to complete. Alternatively, microwave technology has recently been used to efficiently convert organic matter to biochar on an industrial scale, producing more than 50% char.

Biochar is a fine-grained charcoal high in organic carbon and largely resistant to decomposition. As a soil amendment, biochar creates a recalcitrant soil carbon pool that is carbon-negative, serving as a net withdrawal of atmospheric carbon dioxide stored in highly recalcitrant soil carbon stocks. The enhanced nutrient retention capacity of biochar-amended soil not only reduces the total fertilizer requirements but also the climate and environmental impact of croplands. Char-amended soils have shown 50 - 80 percent reductions in nitrous oxide emissions and reduced runoff of phosphorus into surface waters and leaching of nitrogen into groundwater. As a soil amendment, biochar significantly increases the efficiency of and reduces the need for traditional chemical fertilizers, while greatly enhancing crop yields. Renewable oils and gases co-produced in the pyrolysis process can be used as fuel or fuel feedstocks. Biochar thus offers promise for its soil productivity and climate benefits.

2.3 Current Status of Technology

In European, a demonstration plant of 500 kg/h is currently operating in Italy for liquid production. There are plans for small commercial units to be derived from this technology in Italy, Spain and Greece as LEBEN projects. A 250 kg/h pilot plant based on the Waterloo processes has been constructed in Spain. Several plants are in operation at a demonstration level for sewage sludge and refuse/WSW in West Germany at capacities up to 2 t/h, based on slow temperature pyrolysis.

Elsewhere, a number of demonstration plants for flash pyrolysis are operation in North America at a scale of up to 25 kg/h with plans for several commercial developments ranging up to 40 kg/h, including a commercial installation planned for California based on the SERI ablative pyrolysis and sewage sludge pyrolysis in Canada and Australia. Examples of current research and development activities are listed in Table 2.7. Some properties that have been reported are summarized and compared in Table 2.6.

2.3.1 Fixed Bed Reactor

Charcoal can be produced with a fixed bed reactor in which the biomass feedstock is partially gasified by air. The company Bio-Alternative SA operated a downdraft fixed bed gassier of 1 m diameter and 3 m height (Bridgwater, 1991). With a biomass throughput of 2000kg/h. Products of this process are gas, viscous tars and charcoal of which the yield is maximized. For fir and beech wood, charcoal yields of 300 weight percent on fed wood basis have been achieved. All products are used as energy carriers.

Table 2.6: Characteristic of Various Pyrolysis Technology for Bio-oil (FOA, 2009)

Technology	GIT	Ensyn	laval	SERI	Twente
Temperature [°C]	500	550	480	510	600
Pressure [bar a]	1.0	1.0	0.01	1.0	1.0
Flow rate [kg/h]	50	50	30	30	12
dp [mm]	0.5	0.2	10	5	0.5
t gas [s]	1.0	0.4	3	1	0.5
t solid [s]	1.0	0.4	100		0.5
gas yield [wt%]	30	25	14	35	20
tar yield [wt%]	60	65	65	55	70
Char yield [wt%]	10	10	21	10	10

Table 2.7: Comparison of Pyrolysis Process Technologies: ranking according to the desired products (FOA, 2009)

Technology	**Organization**	**Capacity (kg/h)**	**Desired Gas/Tar/char**		**T (°C)**
			product	**(Wt%)**	
Fixed bed	Bio-Alternative	2000	Char	55/15/30	500-800
Fluid bed	THEE	500	Gas	80/10/10	650-1000
Radiation Furnace	Univ. Zaragoza	100	Gas	90/8/2	1000-2000
Conventional	Alten (KTI+ Itaenergy)	500	Tar		
Circulation fluid bed	Ensyn Engineering	30	Tar	25/65/10	450-800
Fast entrained flow	Georgia Tech Research Ins.	50	Tar	30/60/10	400-550
Vacuum	Laval University	30	Tar	15/65/20	250-450
Vortex reactor	Solar Energy research Ins.	30	Tar	35/55/10	475-725
low temperature	Tubingen University	10			
Flash fluid bed	Waterloo University	3	Tar	20/70/10	425-625
Rotation cone reactor	Univ. Twente	10	Tar	20/70/10	500-700

2.3.2 Fluidized Bed Reactor

The well known fluid bed reactor technology has been applied by Kosstrin (1980), Gourtay et al (1987) and Scott et al (1988). Tar yields, produced by a medium scale (100kg/h) fluid bed reactor, are quite low due to cracking of the vapors in the large volumes of bed and freeboard. Fluid bed reactor technology offers good possibilities in gasifying biomass feedstocks with minimum tar formation. In that case, bed material should be selected on basis of optimum catalytic tar cracking behavior. If, however, tar is the product aimed at, a non-catalytic shallow fluid bed should be applied followed by immediate quenching of the gaseous products.

2.3.2 Specific Technologies for Bio-oils Production

Bio-oil production is maximal at medium process temperatures (450-650) and short vapor residence times in the reactor. Useful criteria for selecting pyrolysis technologies for bio-oil production are: i) the bio-oil yield per unit of mass of wood which should be as high as possible, ii) the reactor capacity of the process should be as large enough to limit the number of scale-up steps to full plant capacity. Pyrolysis technologies include in the following survey are selected on the basis of these criteria. Accordingly, it was decided to consider only processes with bio-oil yield larger than 50 weigh percent on dry wood basis and a plant capacity of more than 10 kg/h.

a) Entrained Flow Reactor

Biomass pyrolysis in an entrained flow reactor has been studied by Gorton et al (1990) at the Georgia Institute of Technology, Atlanta, GA, U.S.A. The vertical reactor tube has a length of 6.4m and an internal diameter of 0.15m. Air and propane are introduced stoichiometrically and combustion in the bottom section of their reactor. The produced hot flue gas flows upwards through the tube while passing the biomass fees point. In this way the thermal energy of the combustion gas is used to heat the biomass particles and, if necessary, provide the heat of the pyrolysis reaction. Typical operation condition are ratio of carrier-gas mass flow over the pyrolysis mass flow of about 4, a reactor inlet temperature of 900 °C, an atmospheric reactor pressure and a reactor throughput of 500 kg.h. The disadvantage is that it needs large amount of carrier gas (Nitrogen).

b) Circulating fluid bed reactor

An up flow circulating fluid reactor has been operated by Ensyn in Ottawa, Canada (Graham, 1988). Unfortunately there is no literature available reporting the dimension and the flow rates of the preheated carrier gas and sand for this process. Typical operation of this reactor is a temperature 600 ° C and a biomass throughput of 100 kg/h. It is claimed 60% bio-oil can be achieved with poplar wood as the feed stocks. The use of the sand as a heat carrier offers the advantage of a compact construction because of the high heat transfer rate from the sand to biomass particles. Another advantage is the short residence time of gas, by which secondary tar cracking is suppressed. When this reactor becomes scales-up, special attention should be pay to the rapid mixing of biomass particles with solid heat carrier. Again the requirement of carrier gas is a disadvantage.

c) Vacuum Furnace Reactor

The vacuum pyrolysis of aspen polar in a multiple hearth reactor has been studied by Roy et al (1992, 1993) at the University of Laval, Quebec, Canada. Six heated hearths with a diameter of 0.7 m are staked on top of a total height of 2 m as part of the reactor. Wood is fed into the top compartment of reactor and transported downwards by gravity and by the action of scrapers which at present in each compartment. If the biomedicine is converted completely, the bottom compartment contains only charcoal which can be easily removed from the reactor. The temperature of top hearth is about 200 °C and increases towards the bottom the reactor where it reaches 400 ° *C* to achieve maximum bio-oil products. A vacuum pump is used to keep the reactor pressure at a value of 1 KPa. A difficulty in scaling -up the reactor is necessary installing a large capacity vacuum pump which is sensitive to fouling and also it is very expensive.

d) Vortex reactor

A vortex reactor has been constructed by Diebold and Power (1988) at solar Energy Research Institute, Golden, Co. U.S.A. This reactor has a tube diameter of 0.13 m and a length of 0.7 m For proper operation the reactor, biomass particles should be entrained in a nitrogen flow with velocity of 400 m/s and enter the reactor tube tangentially. For such condition the biomass particles experience high centrifugal forces which induce high particle ablation rates on the heated reactor wall (625 °C). The ablating particles leave a liquid film of bio-oil on the wall which evaporates rapidly. If the wood particles are not converted completely they may be recycled with a special solids recycle loop. In their paper, Dieblod and Power (1988) estimate the number of cycles required to achieve completely conversion of the biomass particles to be about 15, which is considered to be quit high. However, 80 weight percent on dry wood basis has been archived up to now.

2.4 Application of Bio-Oils

In addition to use as a fuel for power and heat, bio-oil can serve as the base for the manufacture of a wide range of organic chemicals. These uses are introduced here as the bio-oils have been applied by certain parties.

2.4.1 Power and Heat Generation

The nearest term commercial use of bio-oil is in generation of power and heat. With modest equipment modifications, bio-oil can be substituted for fuel oil or diesel in a number of static applications including stationary diesel engines, gas turbines, boilers and furnaces. Bio-oil has been successfully test co-fired with coal, providing 5% of the BTU value to a 20 MW boiler. Bio-oil has a successful record of utilization in commercial boilers to provide industrial process heat and drying, and is approved for use in district heating utility boilers in Sweden. ORENDA Aerospace Corporation has tested bio-oil in its 2.5 MW combustion turbine-powered generator.

2.4.2 Chemicals Feedstock

A wide range of chemicals can be extracted from bio-oil, and are an attractive possibility to producers of bio-oil because they generally offer much higher value added compared to fuels and energy products. Chemicals can be isolated, extracted and processed to meet customer specifications, and it is likely that the remaining bio-oil will still retain some value as a fuel. In order to recover specific chemicals for value-added use, it is necessary that these chemicals be present in the bio-oil in large enough quantity to make recovery economic. For wood-based bio-oil, such chemicals include hydroxyacetaldehyde, acetic acid, formic acid, levoglucosan and levoglucosenone (H.Colin, 2005)

These chemical compounds have the potential to serve as the basis for a wide variety of chemicals. Food flavorings are extracted from bio-oil in a number of countries, including the United States. Researchers are also working on developing natural resins and polymers for use in engineered wood products; these have already undergone mill trials. Additional tested uses of bio-oil include: as a base for organic wood preservatives, as an ingredient in slow-release fertilizer used in commercial agriculture, as an octane enhancer and as a hydrogen source. A product has been developed using bio-oil that serves as an emissions control agent for SOx and NOx in coal combustors.

2.4.3 Bio-Refinery

Some advocates of bio-oil see it as the core product of a “bio-refinery” or “bioplex”, where an economically optimum combination of energy, chemicals and materials are manufactured. This is an integrated approach where the forest industry, agricultural sector and municipalities provides the feedstock and are the users of energy and chemicals from the facility. The energy and utility industries provide investment, and serve as customers and distributors of energy and fuels.

2.5 Bio-Oils Upgrading

Considerable effort have been devoted to pyrolysis derived bio-oil upgrading and involved large variety of techniques. The primary objective for bio-oil upgrading is to obtain energies-carrier with improved products quality. Integrated fuels and chemical strategies are an attractive option to increase the economic attractiveness of bio-oils. A large number of processes have been reported to upgrade fast pyrolysis oil to improve its product properties and to extent the range of applications in the field of energy generation and chemical production. Upgrading technology may be classified as follows:

- physical upgrading
- chemical upgrading

2.5.1 Physical Upgrading of Bio-Oils

Examples of physical upgrading are blending with petroleum diesel using surfactants and with additives or solvents, all with the objective to improve the product properties. Furthermore, typical separation processes like extraction and distillation are used to recover valuable chemicals.

One example of bio-oils upgrading to liquid energy carrier by physical processing is by blending the bio-oils with alcohols. Bio-oils blends with alcohols have been investigated to improve the product properties and to make the product suitable for use in stationary and in-stationary internal combustion engines. Methanol was found to be the most effective alcohol among others alcohols (F.Husein et.,al). It has higher homogeneity, lower viscosity, lower density and lower flash points and considerably higher HHV's (high heating value). The reduction in the viscosity was ascribed to a stabilizing effect of the alcohols on the water-insoluble high molecular weight lignin-derived fraction. Alcohol addition also had a positive effect on storage stability and the rate of molecular weight built-up during aging was lowered. Low concentrations of alcohols ($\leq$5 wt %) prevented bio-oils from aging by a few months, while higher alcohol content (up to 10 wt %) retarded aging by almost a year. The most interesting features offered by this approach are its simplicity, low cost of the alcohol and the beneficial effects on the product properties. Hence, alcohol has been suggested to be the most practical approach for bio-oils upgrading. From a chemical point of view, it was found that both ester and acetal formation occurs like in Figure 2.3. This is also an indication that aldehydes and organic acids are responsible for the relatively poor storage stability of bio-oils. Although product properties were improved, there were no any indications whether the product is suitable as a transportation fuel.

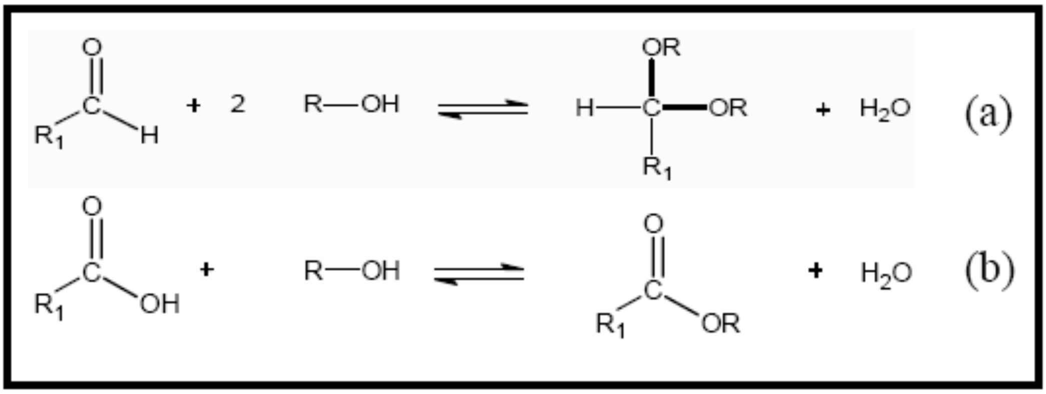


Figure 2.3: Reaction during Alcohol Addition

This is one example of bio-oils upgrading currently studied. Others methods of bio-oils upgrading by physical upgrading are summarized in Figure 2.4.

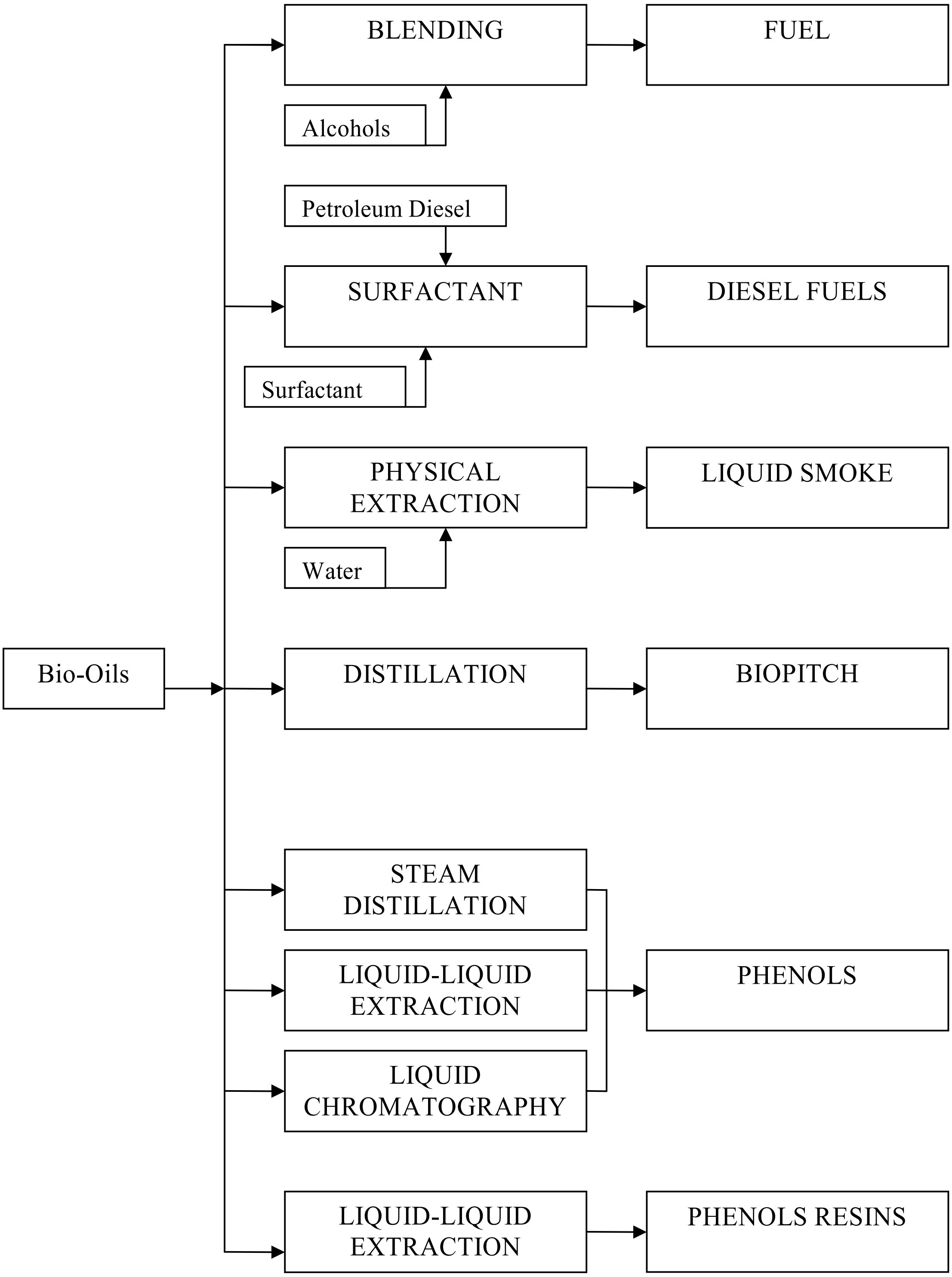


Figure 2.4: Chemicals and Fuels from Bio-oils from Physical Upgrading

2.5.2 Chemical Upgrading of Bio-Oils

The production of liquid BO derived products with improved product properties for use in power and heat generation and in stationary and in-stationary internal combustion engines has been investigated by various authors. Among them, hydrotreating of bio-oils for the production of hydrocarbon like products was given most attention. The hydro-process is performed in hydrogen providing solvents activated by the catalysts of Co–Mo, Ni–Mo and their oxides or loaded on Al_2O_3 under pressurized conditions of hydrogen or CO. Oxygen is removed as H_2O and CO_2, and then the energy density is elevated. P.V. Pindoria (1997) hydrotreated the volatiles from fast pyrolysis process in a two stage reactors. Hydro-cracking without catalysts was operated in the first stage, and catalytic hydrotreatment was operative in the second stage with lower temperature and the same pressure compared with that in the first stage. The analysis indicated that the deactivation of the catalyst did not result from carbon deposition. Instead, the embodiments of volatile components blocked the activated sites in the zeolite catalyst. This hydro-process produced much water and complicated the bio-oil with many impurities. The reaction, also known as a hydrodeoxygenation (HDO) reaction, is shown as below.

$$-(CH_2O)- + H_2 \longrightarrow -(CH_2)- + H_2O$$

The reaction has strong analogies with typical refinery hydrogenations like hydrodesulphurization (HDS) and hydrodenitrification (HDN). In general, most of the hydrodeoxygenation studies have been performed using existing hydrodesulphurization (HDS) catalysts (NiMo and CoMo on suitable carriers) (Mahfud et.,al). Such catalyst need activation using a suitable sulphur source and this is a major drawback when using nearly sulphur-free resources like BO. Table 2.8 shows the summary of bio-oils chemical upgrading for chemical and fuels productions.

No	Product Category	Process category	Application	Approach
1	Power	P^1	Gas turbine	Alcohol addition
2	Fuel	C^1	Transportation fuel	2 stages Hydro-cracking by HZSM-5, 350-450°C
3	Fuel	C	Transportation Fuel/ Gasoline blending	2 stages Hydro-treating using HDS Cat. 250-450°C, 2000 psig.
4	Power	P	Stationary Diesel Engine fuel	Emulsification using surfactants.
5	Fuel	C	Transportation Fuel	Hydro-treating-FCC dual treatment
6	Fuel Chemical	C	Transportation Fuel/Power	Alcoholysis by reactive adsorption using molecular sieve 3A
7	Chemical Fuel	C	H_2	Steam reforming for H_2 production using Ni-based catalyst or noble metal catalyst
8	Chemical	C	Levoglucosane	Recovery by extraction.
9	Chemical	P	Calcium salt (road de-icers) (Calcium formate, C. acetate, propionate)	Distillation of aqueous BO to obtained acids – pH adjustment of the distillate using alkaline followed by water evaporation.
10	Chemical	C	Resins and Adhesives Phenol Formaldehyde	Series of liquid-liquid extraction of BO using solvents like ethyl acetate followed by sequential back-extraction with water and bicarbonate solution.
11	Chemical	C	Bio-pitch, electrode manufacturing	Bio-oil-charcoal distillation in bench scale. Application as a binder in bio-electrode.
12	Chemical	P	Liquid smoke	Water separation to reduce benzyl-α-pyrene to < 1 ppb
13	Chemical	P	Syringol	Syringol (92% yield) obtained from vacuum PO by steam distillation
14	Chemical	P	Phenol & Phenolics	Tar conversion to light oil. Phenolic compounds were further separated from the oil by liquid-liquid extraction using alkali and organic solvents.
15	Chemical	C	Syngas	Bio-oil conversion to gas was 83 wt %, whereas gas production was 45 L/100 g of bio-oil at 800°C and a constant nitrogen flow rate of 30 mL/min.
16	Chemical	C	Bio-Lime^{TM}	Acidic pyrolysis oil is neutralized by basic alkaline earth metal compounds. Resulting metal carboxylates are used for flue gas treatment.

Table 2.8: Summary of Bio-Oils Chemical Upgrading for Chemical and Fuels Productions

CHAPTER 3

METHODOLOGY

3.1 Introduction

There are 3 steps in the methodology for this research. The first step can be categorized into 2 which are sample preparation, designing and fabrication. In the sample preparation, all samples were dried under the sun light and then being grinded. Designing the pyrolysis unit is involved the designing of the reactor and tubing. The fabrication is focus on fabricating the reactor, connection and sample collector.

The second step is the experimental procedures which involve the blank test, purging also experimental work and condition. The third step in about analysis of the products which are the bio-oils. The physical and chemical properties of the bio-oils were studied.

3.2 Pre-Experimental Setup

Pre-experimental setup is a procedure before beginning the experiment. This step is more focus on preparing samples, designing the reactor and Pyrolysis system.

3.2.1 Sample Preparation

The biomass samples are the palm oil wastes that generated from the palm oil plantation. The palm oil wastes are the Empty Fruit Bunch (EFB), Mesocarp Fibers and Pump Kernel Shell (PKS). These samples obtained from local palm oil factory located in Lepar Hilir 4, Kuantan. The samples were rinsed with tap water to remove soil and gavel particles. After being rinsed, these palm oil wastes were dried under the sun for 5 days in order to completely dry the samples and also to remove the initial moister content in the samples.

After being dried, the samples were taken to FKKSA laboratory for further process. The samples need to be grinded into smaller particle and the samples are being grinded using grinding machine. The purpose of this step is to appropriate with the heat transfer principle. Smaller samples has larger surface for heat to contact.

Figure 3.1: Grinding Machine

Grinded samples were put into sieve machine. Sieve machine was used to separate the grinded samples into particular size at which the particle can pass through the tray. The smallest sample will left as the bottom of the tray.

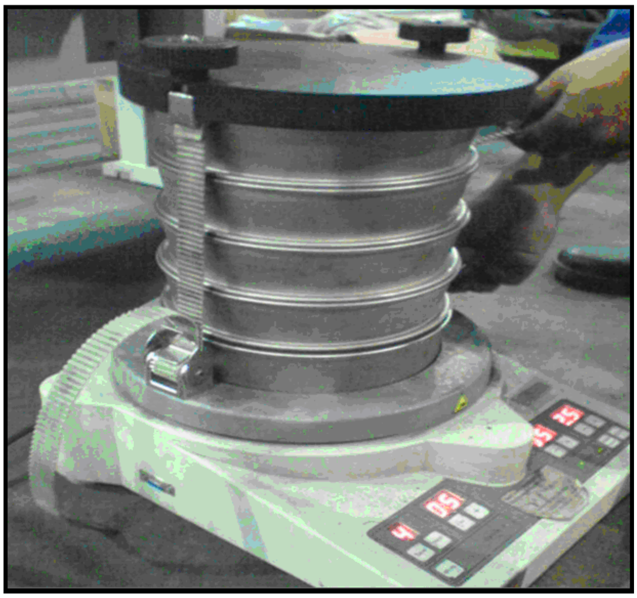


Figure 3.2: Sieve Machine

Figure 3.3: Mesocarp Fiber Sample

Figure 3.4: PKS Sample

Figure 3.5: EFB Sample

3.2.2 Designing

The tubular furnace needs to be considerate in order to design the reactor. Reactor and tubular furnace is the main part of pyrolysis process in which the cracking process occurs in the reactor as being heated supplied by tubular furnace. Pyrolysis reactor used was a static batch design and made of stainless steel (316) for it material selection. The reactor is 6 inch in length. The main core of the reactor is at the center with length of 3.5 inch and cross sectional of 1 inch. It been connected with 2 connecting pipe with 1/2 inch diameter.

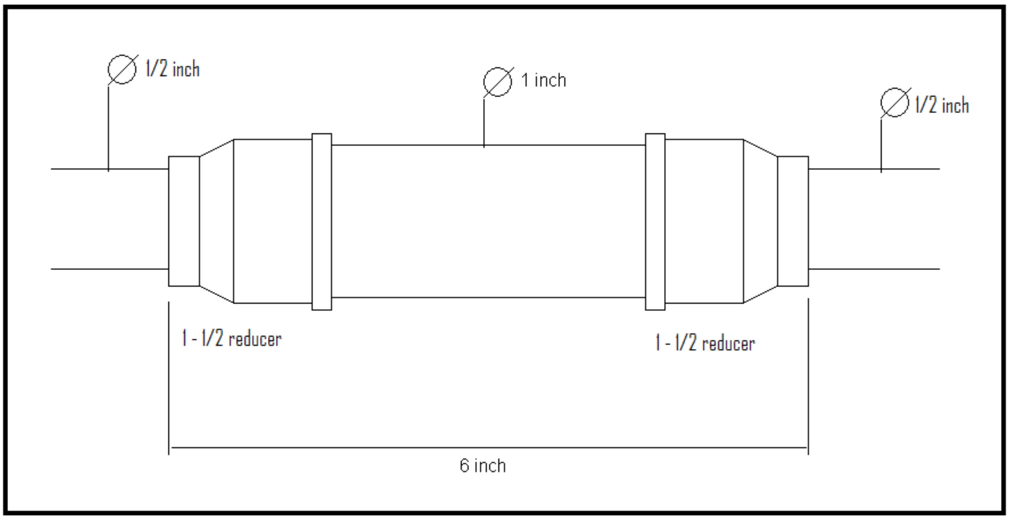


Figure 3.6: Reactor Design

3.2.3 Pyrolysis Unit

The tubular furnace is the most important part in pyrolysis unit. It provides the heat using electric energy to heat the samples. The tubular furnace in controlled by the controller. The controller can set desired temperature, ramping time and heating rate of the tubular furnace. Sample is filled in the reactor and was placed into the tubular furnace for heating purpose. It is important to determine the temperature inside the reactor because the set heating temperature is different with the temperature inside the reactor. In order to determine the temperature inside the reactor, thermocouple was placed inside the reactor and connected to the temperature reader. Nitrogen was used for purging and leakage test purpose. Condenser was used as a first stage of cooling process to condense the pyrolysis gas into liquid product. The cooling medium is tap water. Sample collector is placed inside the ice bath. Ice bath was filled with dried ices and act as second cooling process because not all condensable gas will be condensed at the condenser. The summary of pyrolysis unit is list in table 3.1 below:

Table 3.1: Pyrolysis unit and Function

Component	**Function**
Tubular Furnace	Heating Supply
Reactor	Sample being placed and heated
Controller	Setting temperature, ramping time and heating rate of the tubular furnace
Temperature reader with thermocouple	Temperature reading inside the reactor
Nitrogen Tank	Supply nitrogen for purging
Pressure Gauge	Pressure reading during purging
Condenser	Condensing the gas product
Ice Bath	Second cooling process to condense the gas
Bio-oil collector	A bottle to collect the liquid product

Figure 3.7: Pyrolysis Unit

Figure 3.8: Tubular Furnace with Reactor

3.3 Experimental Setup

After finish with design and fabrication of Pyrolysis system, the experimental setup is a procedure or works that need to be done during the experimental process. In experimental process, there are 2 important procedures before proceeding to experiment.

3.3.1 Blank Test

The purpose of blank test is to determine the temperature inside the reactor. This is an important procedure because the temperature inside the reactor is different with the set temperature. In blank test, no samples were added.

3.3.2 Purging

After fabrication, it is important to check if there any leakage in the system. Nitrogen was used as purging medium. In this test, all valves were closed and nitrogen was set to flow through the system for about 30 minutes at 5 psi. If the pressure gauge at the pyrolysis system has same reading with the pressure gauge at the regulator, meaning there is no leakage.

Purging is also the first procedure before starting the pyrolysis experiment. The basic principle of pyrolysis process is that heating was done without the presence of oxygen. Nitrogen is very suitable because of it inert property. The purging process is done for about 10 minutes with at 3psi. The flow of Nitrogen replaces the air from the reactor and permits the pyrolysis reaction under anaerobic condition which mean without air condition.

3.3.3 Experimental Procedures

The experiments were conducted without the presence of oxygen in the pyrolusis system. For EFB and Mesocarp Fiber, 10 g for each sample and 20 g of PKS were loaded into the reactor. The desired temperature is at 500C for all samples in pyrolysis experiment. The temperature was increased with a heating rate of 50C min-1 up to the desired temperature and then holds for 8 min at the desired temperature.

Bio-oils product will be collected in the product collector while char can be collected in the reactor. Incondensable gas will be vented away into the atmosphere.

3.4 Analysis

Analysis procedure consists of two stages; the samples analysis and liquid product analyses. The first analysis was performed on palm oil waste samples using TGA. The liquid products were analyzes using FTIR, and GC-MS. The water content, viscosity and pH were also been tested.

3.4.1 Termogravimetric Analyzer (TGA)

This analysis was performed to determine the volatility, ash content, moisture content of the sample. Thermogravimetric (TG) analysis of PKS was carried out by using TGA Q500 V6.4 instrument. The sample of PKS about 58 mg, EFB with 10.48g and 12g of Mesocarp Fiber was placed in the standard platinum pans. The TG experiments were performed under the flow of nitrogen with the flow rate of 100 ml min^{-1}. The temperature was increased from the ambient temperature to 600 ^{0}C with a heating rate of 20 ^{0}C min^{-1}.

3.4.2 Viscosity

Viscosity is a measure of a resistance of the liquid to flow. The viscosity of the fuel is important among others because of its effect on pumping and injecting of fuel. Bio-oils from each sample were tested using Brookfield/LVDV-III+C/W viscometer at room temperature of 22°C.

3.4.3 pH

The pH was tested using pH meter. The electrode was immersed within the bio-oil samples for about 5 minutes at point which the reading of pH meter became stable. The measurements were performed at room temperature which is at 22°C.

Figure 3.9: pH Meter

3.4.4 Water Content

In determining water content of bio-oil, Karl-Fischer titration method was introduced as this is the most recommended method because some water in bio-oils is in the form of aldehyde hydrates, while much of it is probably hydrogen bonded to polar organic compounds and any distillation method would also distilled other water soluble compounds.

Bio-oil's water content was determined by using Moister Analyzer 787 KF Titrino with Karl-Fischer Reagent. 4mL of bio-oil sample was introduced into the Moister Analyzer container and the titration was take place without any contact with air as it will affect the reading because of the moister in air.

Figure 3.10: Moisture Analyzer

3.4.5 Fourier Transform Infrared (FTIR)

The functional groups of bio-oils were analyzed by using Fourier Transform Infrared (FTIR) spectrophotometer. The absorption spectrum was generated when light passes through the sample to a depth of few micrometers. In this analysis mode, a crystal prism with a high refractive index physical contacts the surface layer of the specimens. Absorption bands were detected from the corresponding vibration modes within the surface of the materials contacting the prism. Basically, FTIR measure vibrational excitation of atom around the bonds that connect them (K. Unapumnuk). Each molecule shows a characteristic infrared spectral pattern in the absorption region due to bonding strength and motion. Characteristic peaks were absorbed for specific functional group, a result of stringing bending, other modes of vibration or a combination of both.

Figure 3.11: Fourier Transform Infrared (FTIR)

In this study, a small droplet of the bio-oil was deposited on Potassium Bromide (KBr) pressed disk and the spectrum was acquired via transmission infrared (IR) spectrometry. Pure spectrum of bio-oils was obtained since KBr contains no absorption bands in the IR region. IR vibration frequencies characterized the presence or absence of functional group of hydrocarbon. The result of FTIR is in graph were the functional groups will be determined based on the peak value from the graph.

3.4.6 Gas Chromatography-Mass Selectivity (GC-MS)

Before being introduced to GC-MS, a good clean up and the necessary concentration of the analyte was required for the analysis. 2µL portion of each bio-oil samples was diluted in 10ml of DiChlroMetane (DCM) HPLC Grade. The diluted bio-oils were filtered using 2µm filtered syringe. The final elution was 10mL for each samples and then being introduced into GC-MS vials.

The chemical compositions of the bio-oil were analyzed by using a Gas Chromatography (GC), and the compounds were determined by using a Mass Selectivity (MS) detector equipped with a 30.0 m × 250 µm × 0.25 µm nominal columns HP-5MS. Helium gas was employed as the carrier gas at a constant flow rate of 1 ml/min. The heating of the column started at 40 ^{o}C for 10 minutes, and programmed to 175 °C by a rate of 2 °C/min and held for 20 min. After that, the temperature was increased to 200 °C with the rate of 1 °C /min and finally, the temperature was ramped to 250 °C at the rate of 4°C/min and kept isothermal for 20 min. The summary of oven temperature programmed for this study is shown in table 3.2 and GC-MS analysis parameters are listed in Table 3.3 below.

Table 3.2: Oven Temperature Programmed

Temperature (°C)	Rate (°C/min)	Hold (min)
40	-	10
175	2	20
200	1	20
250	4	20

Table 3.3: GC-MS Parameter

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 (He)
Flow rate (mL/min)	1

CHAPTER 4

RESULT AND DISCUSSION

4.1 Bio-Oils

The bio-oils obtained were dark brown in color with undesirable smoky odor. The tar-containing solid of the pyrolysis liquid was sediment gradually on the bottom of the barrel forming a thick sludge especially for the PKS derived bio-oil. it is free flowing liquid which shows that it has abundance of water content.

Figure 4.1: Bio-oil products

4.2 Thermogravimetric Analyzer

The primary purpose of Thermogravimetric Analyzer for the analysis of the sample is to determine the volatility, ash content, moisture content of the sample. The volatility is important in studying the component's volatility of the sample and to determine the temperature which most of the component undergoing the cracking process took place. The result for mesocarp fiber, EFB and PKS were shown in figure 1, figure 2 and figure 3 respectively.

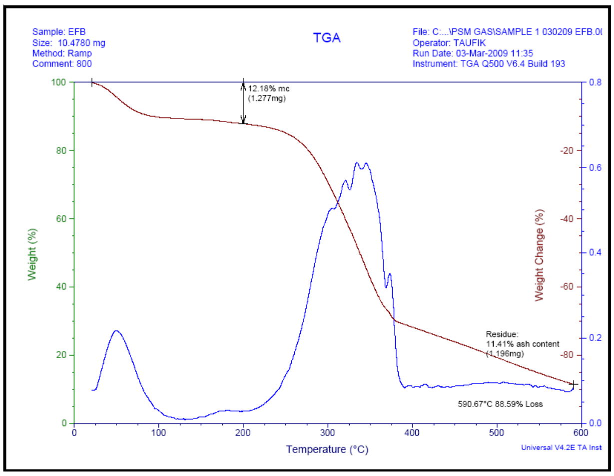


Figure 4.2: TGA Result for EFB

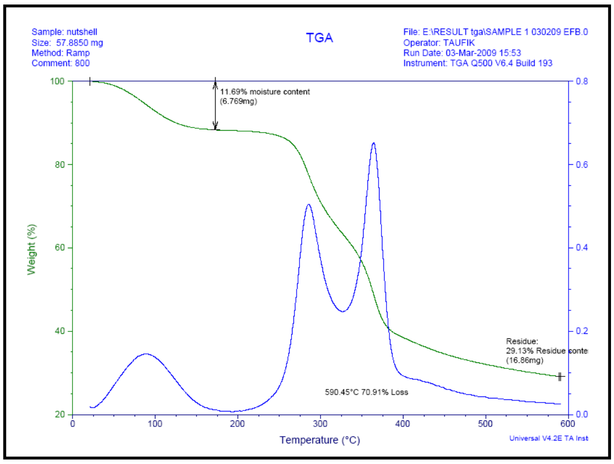


Figure 4.3: TGA Result for PKS

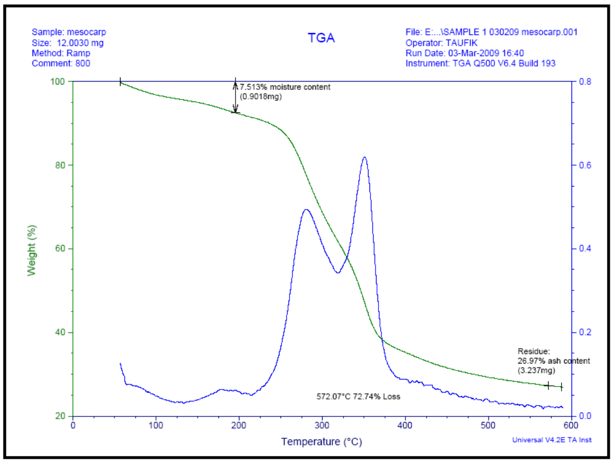


Figure 4.4: TGA Result for Mesocarp Fiber

From the result, the line decrease as temperature increase which indicates the decreasing of sample's weight as heating temperature increased. The decreasing pattern of weight was shown in 2 ways. The first pattern is where all water content will be evaporated from the sample and can be detected by the TGA unit. Determining the initial moisture content can be very important as it can give effect for the water content in the bio-oils. The second decreasing pattern shows that the decreasing of dry samples as the component became volatile and cracking process occur under high temperature. At the end of the line were the remaining of ash residue and weight loss can be determined. The value of ash residue can be a key in determining the % weight of char that will be produced in pyrolysis process. From the result, the initial moisture content in the Mesocarp Fiber, EFB and PKS are 12.18%. 88.59% from initial weight will loss at temperature of 600°C and 11.41% solid will remain as ash residue.

The second line in all 3 graphs refers to the component volatility of the palm oil wastes samples. In other word, the components become volatile and crack at an elevated temperature. This result will give first hypothesis in determining the temperature where the components in samples start to crack via pyrolysis process. Figure 1 and 3 shows a similar pattern where there are 2 peaks which indicate the more volatility component and less volatility component. The cracking process starts to occur at 250. At 350, heavier component which are less volatile start to crack. The line pattern soon decrease as the temperature increase which stated that there are not much left component that undergoing the cracking process. The TGA result of EFB is shown is figure 2. Same as the other result, the components in the sample starts to crack at 250. The highest peak is at around at 350 which indicate much of the component is undergoing the process at that temperature.

4.3 Viscosity

The viscosity for PKS, EFB and Mesocarp Fiber are 28.46 cP, 42.53 cP, and 33.56 cP. The result was in range for viscosity of bio-oil as been stated in previous research such as in Overview of Fuel Properties of Biomass Pyrolysis Oils. Generally, viscosities of bio-oils vary in a wide range (10–100 cP) (Qiang Lu, Wen-Zhi Li and Xi-Feng Zhu, 2009).

Table 4.1: Viscosity of Bio-oil from Palm oil wastes

Sample	Viscosity cP
PKS	28.46
EFB	42.53
Mesocarp Fiber	33.56

4.4 Acidity or pH

The pH value for PKS, EFB and Mesocarp Fiber are 2.46, 2.53 and 2.56. From the results, the bio-oil is very acidic. This is because, the bio-oil contain acids. Bio-oils contain for about 7-12wt% acids with pH reading range of 2-4 (Overview of Fuel Properties of Biomass Fast Pyrolysis Oils, Qiang Lu, Wen-Zhi Li and Xi-Feng Zhu, 2009). Acidity also connected to corrosion and from the acidity property that bio-oil had, bio-oils is very corrosive and would be such a problem for storage as corrosive resistance material should be used. The corrosion-resistant materials include stainless steel, cobalt materials and various polymers such as polyethylene, polypropylene and polyester resins. The corrosion rates would also be enhanced at elevated temperatures or with the increase in water contents of bio-oils.

Table 4.2: pH of Bio-oil from Palm oil wastes

Sample	pH
PKS	2.46
EFB	2.53
Mesocarp Fiber	2.56

4.5 Water Content

The moisture content for PKS, EFB and Mesocarp Fiber are 7.46%, 12.53% and 9.21%. From the result, EFB has the highest water content among the sample. This is because EFB has the highest initial water content and the initial water content in the sample can give a direct impact to the bio-oil product. The increasing of bio-oil water content that the initial water content of it sample can be cause of dehydration process during the pyrolysis. The results from the moister analyzer are shown in table 2 below.

Table 4.3: Water Content in bio-oils of palm oil wastes

Sample	Water Content %
PKS	7.46
EFB	12.53
Mesocarp Fiber	9.21

From the result, water is abundant in bio-oils compared to other oils. It results from original moisture in feedstock and dehydration reactions during pyrolysis process. The water contents of bio-oils usually vary in the range up to 30 wt%, depending on the initial moisture in feedstock and pyrolysis conditions. The presence of water has both negative and positive effects on the storage and utilization of bio-oils. On the one hand, it lowers heating values, and may cause phase separation of bio-oils. Moreover, it increases ignition delay, and reduces combustion rates and adiabatic flame temperatures during the combustion process. In addition, it will lead to premature evaporation and subsequent injection difficulties during the preheating process. On the other hand, it helps to reduce viscosity and facilitate atomization. Furthermore, it is beneficial for reducing pollutant emissions during combustion. Water lowers and evens the temperature profiles in chambers that are important for suppressing NO_x formation. It also contributes to the microexplosion of droplets, which is beneficial for sufficient combustion. In addition, OH radicals from water can inhibit the formation of soot and can also accelerate its oxidation.

4.6 Fourier Transform Infrared

Using FTIR in analyzing bio-oils from palm oil wastes is very important to determine the functional groups exist in the bio-oils. The result of FTIR is in graph where the functional groups will be determined based on the peak value from the graph as had been shown above on figure 4.5, figure 4.6 and figure 4.7.

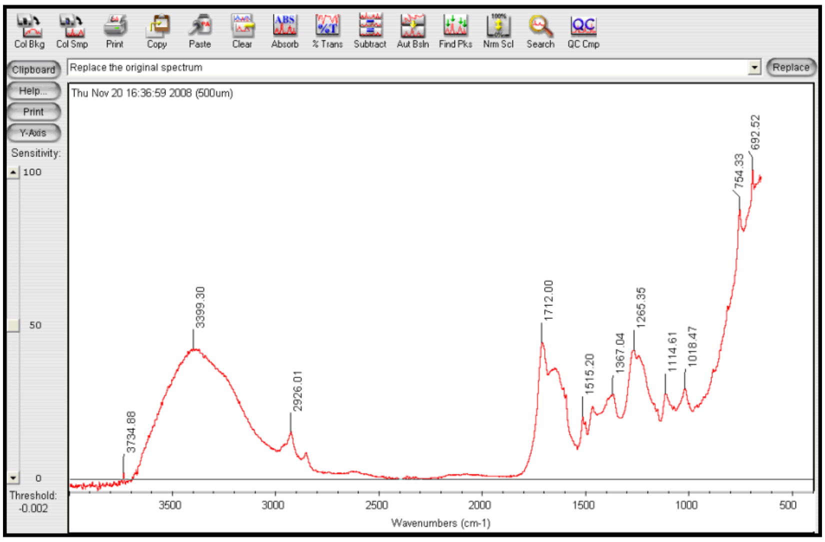


Figure 4.5: FTIR Result of EFB

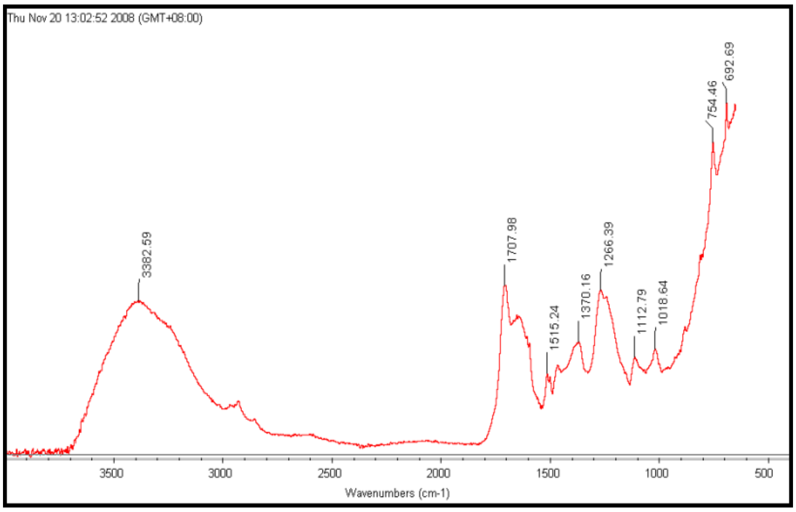


Figure 4.6: FTIR Result of Mesocarp Fiber

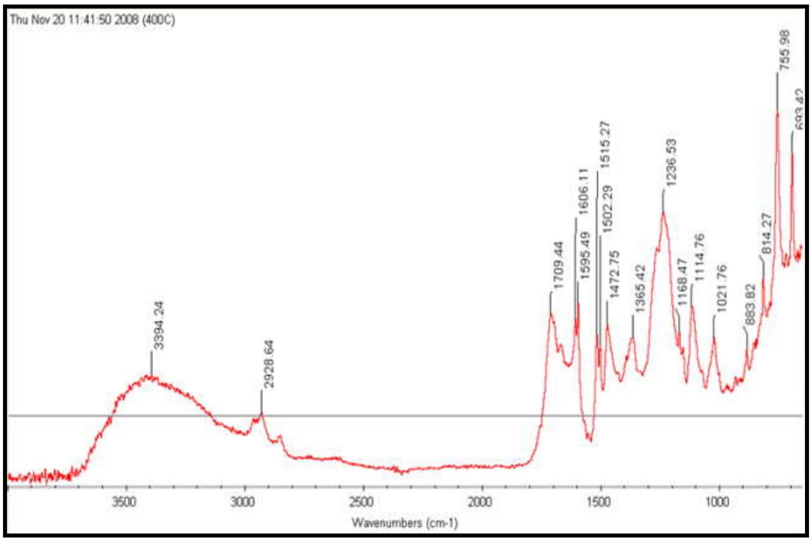
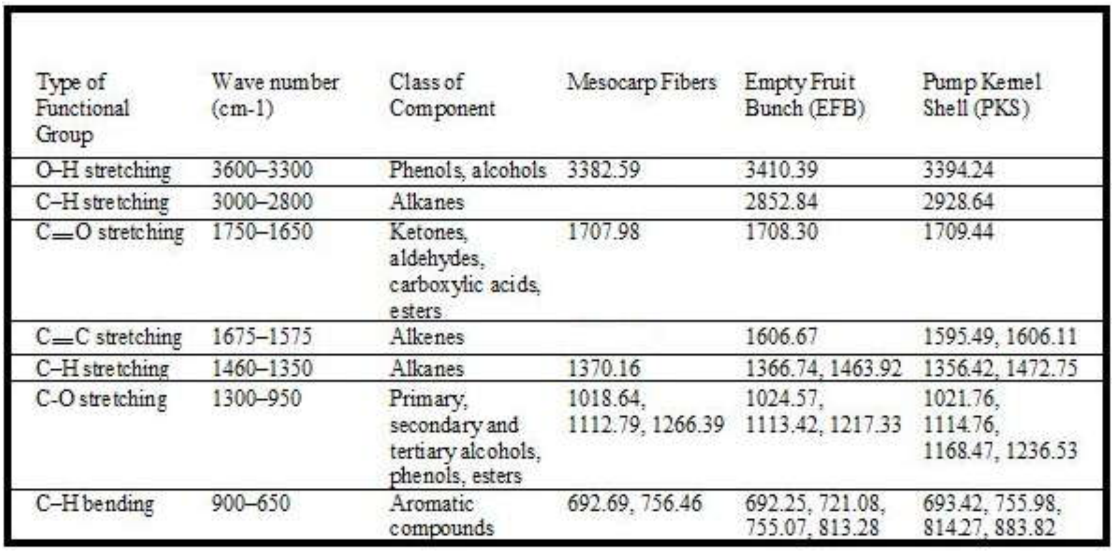


Figure 4.7: FTIR Result of PKS

The O---H stretching vibrations between 3300 and 3600 cm^{-1} of the bio-oils and the polar subfractions, namely ether and methanol, indicate the presence of phenols and alcohols. From the result, the strong and broad band at 3410, 3382 and 3394 (cm^{-1}) on those samples were the characteristic of O–H stretching vibrations. Obvious shoulder at between 1750–1650 (cm^{-1}) was characterized by C=O stretching vibration. The bands are compatible with the presence of ketone, aldehyde, carboxylic group and esters. The C=C stretching of alkenes compounds were detected at 1606 and 1595 cm^{-1} band for EFB and PKS respectively. A bending vibration between 1460 and 1350 cm^{-1}, which were assigned to C–H stretching of alkane group, were detected in those 3 bio-oils even though it was not found via GC–MS analysis. Perhaps, the compound yield was very small to be detected during the analysis. C–H stretching is extremely valuable for the detection of methyl group (Wang et al., 2007). Meanwhile, the peak between 1300 and 950 (cm^{-1}) showed the C–O stretching and O–H bending due to the presence of primary, secondary and tertiary alcohols. Other weak absorbance observed at nearly 650–900 (cm^{-1}) indicated the existence of some substituted aromatic groups. The results are summarised in Table 4.4

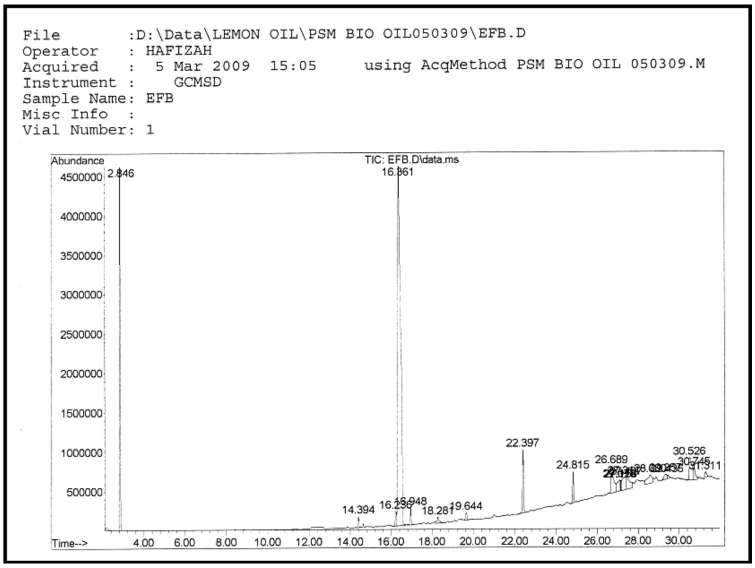
Table 4.4: Summary of Class of Compound is Bio-oil of Palm Oil Wastes



Type of Functional Group	Wave number (cm-1)	Class of Component	Mesocarp Fibers	Empty Fruit Bunch (EFB)	Pump Kernel Shell (PKS)
O–H stretching	3600–3300	Phenols, alcohols	3382.59	3410.39	3394.24
C–H stretching	3000–2800	Alkanes		2852.84	2928.64
C═O stretching	1750–1650	Ketones, aldehydes, carboxylic acids, esters	1707.98	1708.30	1709.44
C═C stretching	1675–1575	Alkenes		1606.67	1595.49, 1606.11
C–H stretching	1460–1350	Alkanes	1370.16	1366.74, 1463.92	1356.42, 1472.75
C-O stretching	1300–950	Primary, secondary and tertiary alcohols, phenols, esters	1018.64, 1112.79, 1266.39	1024.57, 1113.42, 1217.33	1021.76, 1114.76, 1168.47, 1236.53
C–H bending	900–650	Aromatic compounds	692.69, 756.46	692.25, 721.08, 755.07, 813.28	693.42, 755.98, 814.27, 883.82

4.7 Gas Chromatography-Mass Spectrometry (GC-MS)

The identification of component found in bio-oils was determined by National Institute of Standard and Technology 05a.L (NIST 05a.L). The result for EFB, Mesocarp Fiber and PKS are shown in figure 4.8, figure 4.9, 4.10. The results show that, the degrading of lignin, cellulose and hemicellulose from pyrolysis and reformation during that process forming many complex components. All of these components can be categories into Alkanes, Alkenes, Ester, Alcohols, Acids and Phenolic compounds. The details the compounds available in Appendix B which are the GS-Ms result.



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Sample Name: EFB
Misc Info  :
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Figure 4.8: GC-MS Result of EFB

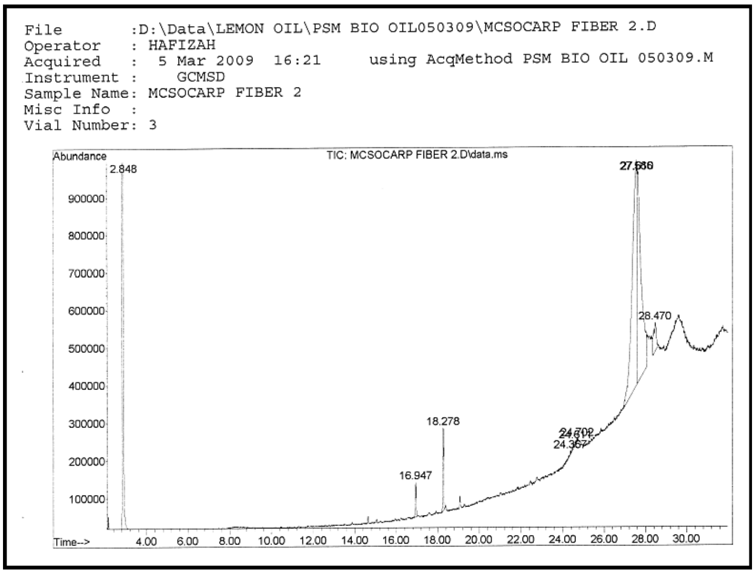

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Figure 4.9: GC-MS Result of Mesocarp Fiber

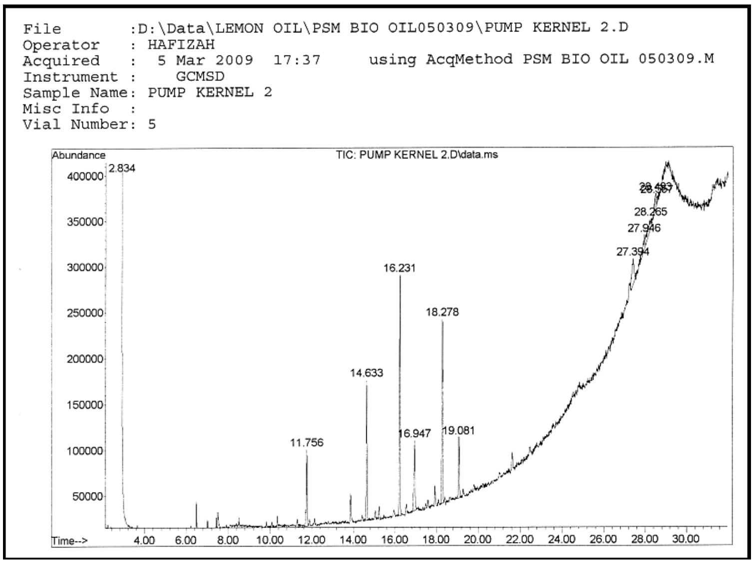

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Figure 4.10: GC-MS Result PKS

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Pyrolysis is a thermal degradation process of biomass without the present of air or oxygen. 3 products were produced which are the bio-oils as a primary product in this process. Another 2 co-products is the gas (syngas or incondensable gas) and solid residue (char). The fraction of these 3 products were influenced by the parameters or operating conditions for the experiment. Series of experiments perform using the Conventional pyrolysis with static batch reactor method on palm oil wastes had proven the process with this equipment and design was a success in producing the bio-oils.

Analysis performed on the bio-oils of palm oil wastes shows that Bio-oils are low-grade liquid fuels when compared with petroleum fuels. The poor fuel properties include the complex multiphase structures, high contents of water in the bio-oil that can cause, low heating values and poor ignition and combustion properties. Bio-oils are also chemical and thermal instability with low pH values which will result in corrosion that make hard for storage the bio-oils as corrosion resistance material should be used and will cost higher than usual oil storage. In spite of these poor fuel properties, bio-oils also have some promising properties. Because they have many chemical compounds content, they can also be chemical feedstock. Compared for direct using of biomass in producing heat and energy, bio-oils has higher heating value which is good for generation power especially for turbine.

There are several power plants in the world using the pyrolysis process to produce energy source but only limitation for the fueling of turbine. At present, many bio-oils cannot meet the fuel specifications, and therefore, they cannot be accepted commercially. Further work is required to be done in the future to improve the properties of bio-oils. For the commercialization of bio-oils as liquid fuels, fuel specifications need to be established as in the case of petroleum fuels.

5.2 Recommendation

Based on self understanding from the research and finding of pyrolysis process, and also from literature review, there are several recommendation that would be useful for future investigation.

5.2.1 Different Samples

Different samples mean using different source of biomass. Palm oil wastes are not the only wastes generated in Malaysia. Other plantation industries such as Jatropha, or rice paddy can also be source of biomass. Biomass wastes are not only limitation to wastes that come from plantation, but can come from other industries such as processing industries that generate wastes of biomass such as food processing industries. Different biomass can give large differences in bio-oils properties.

5.2.2 Different Pyrolysis Process

This research is about the Conventional Pyrolysis with static batch reactor. This type of pyrolysis gives an average yield of bio-oils production. For future investigation on pyrolysis, the fast pyrolysis with fluidize bed reactor would be a great recommendation. This is typically a hard because of better understanding, creativity in designing and fabricating, higher cost for better equipment will be needed.

5.2.3 Analysis of Product

In this research, the major focus is on the analysis of the bio-oil. Analysis of bio-oil is fairly wide because bio-oils physical and chemical properties can be vary depending on their biomass source and operating condition during pyrolysis. Other aspect of physical properties can be done for future work such as the flash point, the homogeneity, the carrion of bio-oils toward specific metal materials and many more. This will give a better understanding about the characteristic of the bio-oils. The char also can be analyzed in order to gain knowledge about it beneficial.

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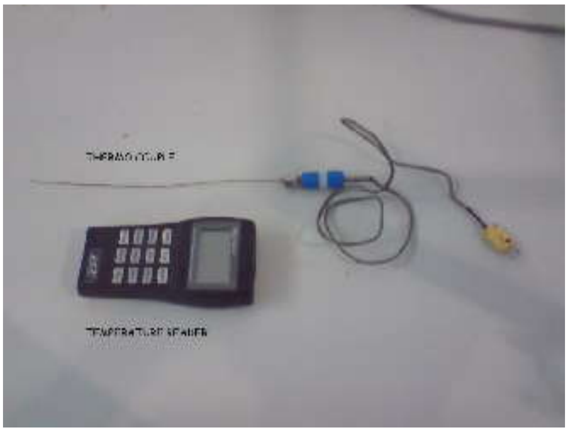
APPENDIX A

PYROLYSIS UNIT

Picture 1: Reactor



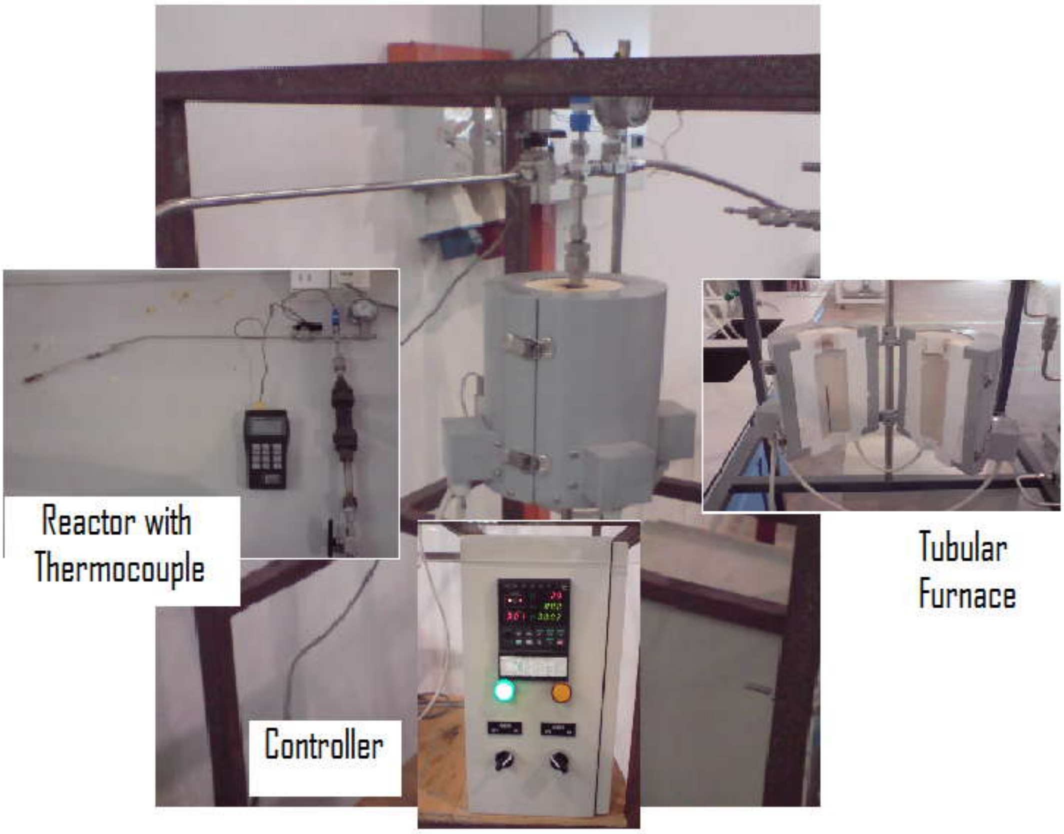
Picture 2: Thermocouple and Temperature Reader

Picture 3: Condenser

Picture 4: Bio-oil Collector

Picture 5: Nitrogen Tank

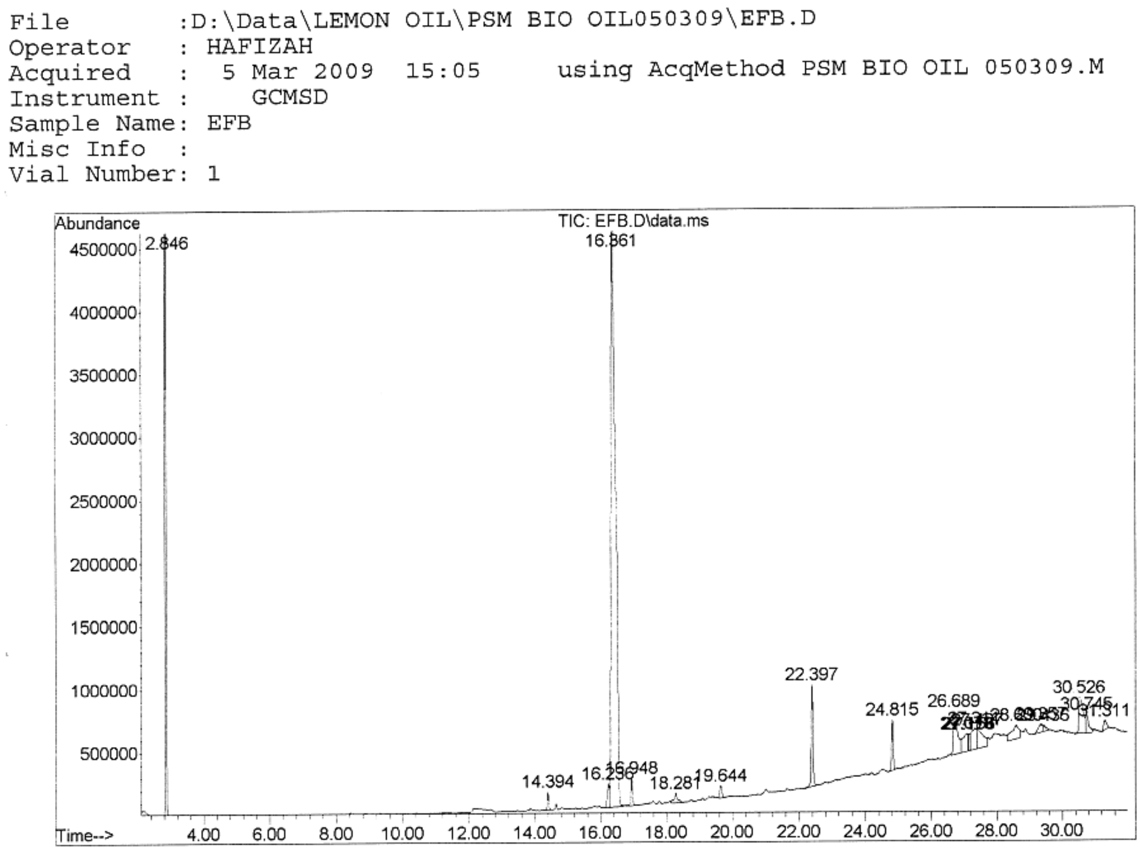
Picture 6: Pressure Gauge and Valve



Picture 7: Tubular Furnace and Controller

APPENDIX B

EMPTY FRUIT BUNCH (EFB)



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                   hyl ester

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                   9-Octadecenoic acid (Z)-, methyl e 122323 000112-62-9 72
                   ster
                   6-Octadecenoic acid, methyl ester, 122327 002777-58-4 70
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                   Phthalic acid, hexyl octadecyl est 184674 1000309-06-2 80
                   er

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Misc      :
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                  her

 12  27.115  0.32 C:\Database\NIST05a.L
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100941 017455-13-9 72
                  ane
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 64
                  ane
                  Octaethylene glycol monododecyl et 186450 003055-98-9 64
                  her

 13  27.157  0.40 C:\Database\NIST05a.L
                  2-Hexadecanol                       86852 014852-31-4 66
                  Octaethylene glycol monododecyl et 186450 003055-98-9 64
                  her
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 64
                  ane

 14  27.307  2.21 C:\Database\NIST05a.L
                  1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 72
```

```
                              Library Search Report

  Data Path : D:\Data\LEMON OIL\PSM BIO OIL050309\
  Data File : EFB.D
  Acq On    :  5 Mar 2009  15:05
  Operator  : HAFIZAH
  Sample    : EFB
  Misc      :
  ALS Vial  : 1   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
_______________________________________________________________________________
                    ane
                    Octaethylene glycol monododecyl et 186450 003055-98-9 64
                    her
                    1,4,7,10,13,16-Hexaoxacyclooctadec 100941 017455-13-9 64
                    ane

 15  27.403  2.41 C:\Database\NIST05a.L
                    1,4,7,10,13,16-Hexaoxacyclooctadec 100940 017455-13-9 83
                    ane
                    Octaethylene glycol monododecyl et 186450 003055-98-9 64
                    her
                    1,4,7,10,13,16-Hexaoxacyclooctadec 100941 017455-13-9 58
                    ane

 16  28.599  2.17 C:\Database\NIST05a.L
                    1,4,7,10,13,16-Hexaoxanonadecane,  136741 1000163-65-3 86
                    18-propyl-
                    1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 64
                    ane
                    Octaethylene glycol monododecyl et 186450 003055-98-9 64
                    her

 17  29.358  0.76 C:\Database\NIST05a.L
                    15-Crown-5                          70738 033100-27-5 59
                    Hexaethylene glycol monododecyl et 179948 003055-96-7 58
                    her
                    1,4,7,10,13,16-Hexaoxacyclooctadec 100941 017455-13-9 58
                    ane

 18  29.433  0.30 C:\Database\NIST05a.L
                    1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 58
                    ane
                    Hexaethylene glycol monododecyl et 179948 003055-96-7 58
                    her
                    1,4,7,10,13,16-Hexaoxacyclooctadec 100942 017455-13-9 53
                    ane

 19  30.522  3.32 C:\Database\NIST05a.L
                    Octadecanoic acid                  114818 000057-11-4 53
                    Octadecanoic acid                  114820 000057-11-4 45
                    Hexaethylene glycol monododecyl et 179948 003055-96-7 43
                    her
```

```
                         Library Search Report

  Data Path : D:\Data\LEMON OIL\PSM BIO OIL050309\
  Data File : EFB.D
  Acq On    :  5 Mar 2009  15:05
  Operator  : HAFIZAH
  Sample    : EFB
  Misc      :
  ALS Vial  : 1   Sample Multiplier: 1

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

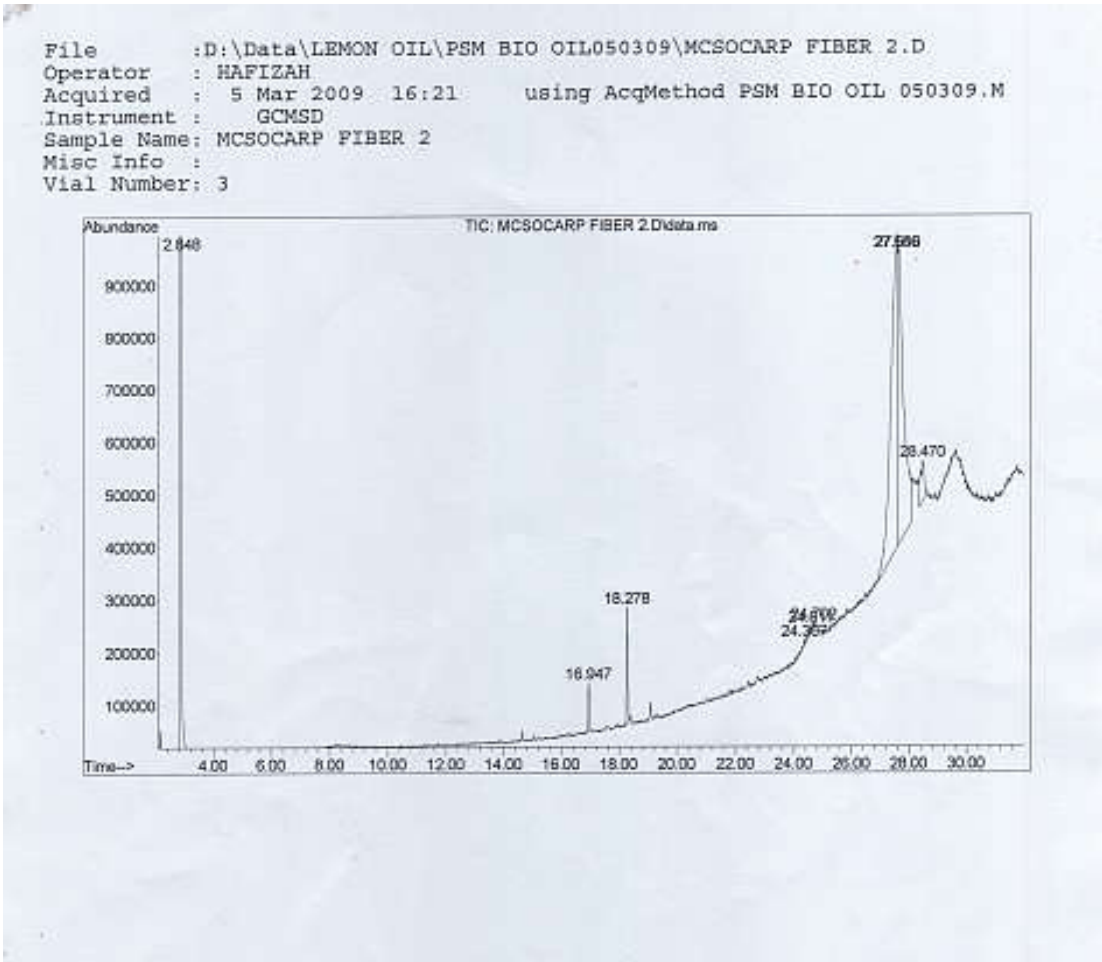
  Unknown Spectrum:   Apex
  Integration Events: ChemStation Integrator - autoint1.e

Pk#     RT  Area%            Library/ID                  Ref#      CAS#   Qual
______________________________________________________________________________

 20  30.747  1.13 C:\Database\NIST05a.L
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100942 017455-13-9 47
                 ane
                 Hexaethylene glycol monododecyl et 179948 003055-96-7 47
                 her
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 47
                 ane

 21  31.313  0.55 C:\Database\NIST05a.L
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100942 017455-13-9 52
                 ane
                 Hexaethylene glycol monododecyl et 179948 003055-96-7 52
                 her
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100941 017455-13-9 50
```

MESOCARP FIBER



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File        :D:\Data\LEMON OIL\PSM BIO OIL050309\MCSOCARP FIBER 2.D
Operator    : HAFIZAH
Acquired    :  5 Mar 2009  16:21     using AcqMethod PSM BIO OIL 050309.M
Instrument  :    GCMSD
Sample Name: MCSOCARP FIBER 2
Misc Info   :
Vial Number: 3
```
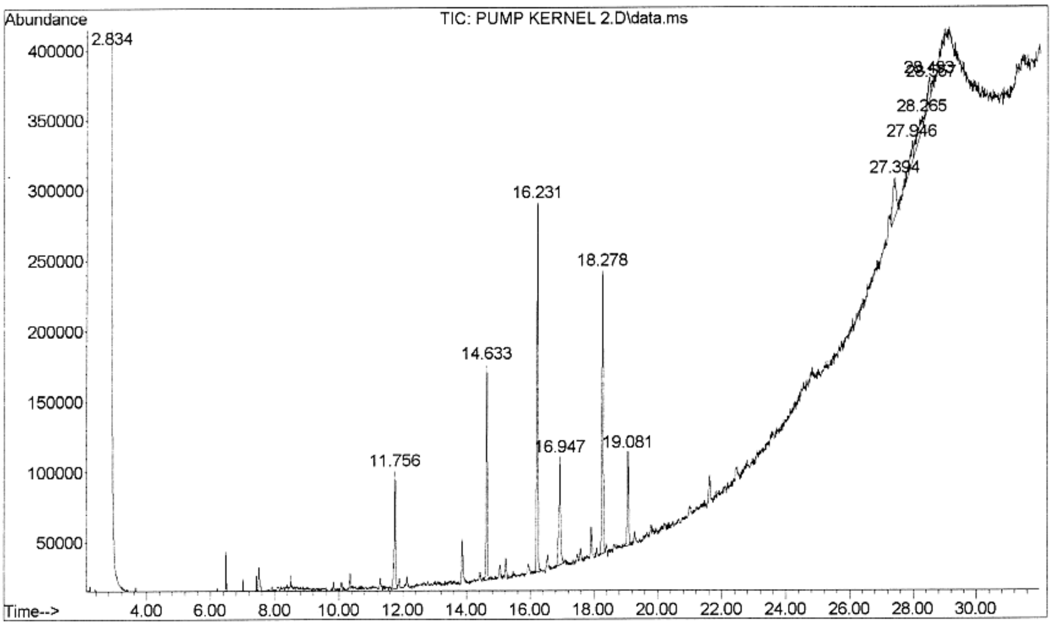

```
                           Library Search Report

  Data Path : D:\Data\LEMON OIL\PSM BIO OIL050309\
  Data File : MCSOCARP FIBER 2.D
  Acq On    :  5 Mar 2009  16:21
  Operator  : HAFIZAH
  Sample    : MCSOCARP FIBER 2
  Misc      :
  ALS Vial  : 3   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   2.845 75.50 C:\Database\NIST05a.L
                 Methylene Chloride                   1499 000075-09-2 95
                 Methylene Chloride                   1498 000075-09-2 94
                 Methylene Chloride                   1497 000075-09-2 91

  2  16.945  0.38 C:\Database\NIST05a.L
                 Diethyl Phthalate                   72412 000084-66-2 98
                 Diethyl Phthalate                   72414 000084-66-2 96
                 Diethyl Phthalate                   72413 000084-66-2 91

  3  18.281  0.83 C:\Database\NIST05a.L
                 11-Octadecenoic acid, methyl ester 122316 052380-33-3 99
                 9-Octadecenoic acid, methyl ester, 122326 001937-62-8 99
                  (E)-
                 9-Octadecenoic acid (Z)-, methyl e 122323 000112-62-9 99
                 ster

  4  24.369  0.04 C:\Database\NIST05a.L
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100941 017455-13-9 70
                 ane
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100939 017455-13-9 68
                 ane
                 Octaethylene glycol monododecyl et 186450 003055-98-9 64
                 her

  5  24.615  0.13 C:\Database\NIST05a.L
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100942 017455-13-9 53
                 ane
                 Hexaethylene glycol monododecyl et 179948 003055-96-7 52
                 her
                 Pentaethylene glycol monododecyl e 172700 003055-95-6 52
                 ther

  6  24.701  0.04 C:\Database\NIST05a.L
                 Octaethylene glycol monododecyl et 186450 003055-98-9 68
                 her
                 1,4,7,10,13,16-Hexaoxacyclooctadec 100938 017455-13-9 53
                 ane
                 15-Crown-5                          70736 033100-27-5 53

  7  27.563 11.73 C:\Database\NIST05a.L
                 Hexagol                            112857 002615-15-8 83
                 Octaethylene glycol                161142 1000289-34-2 83

KAMAL PSM.M Wed Apr 15 11:12:17 2009 CHEMSTATION                Page: 1
```

```
                         Library Search Report

  Data Path : D:\Data\LEMON OIL\PSM BIO OIL050309\
  Data File : MCSOCARP FIBER 2.D
  Acq On    :  5 Mar 2009  16:21
  Operator  : HAFIZAH
  Sample    : MCSOCARP FIBER 2
  Misc      :
  ALS Vial  : 3   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
________________________________________________________________________________
                   Hexagol                             112858 002615-15-8 83

  8  27.606 10.39 C:\Database\NIST05a.L
                   Hexagol                             112859 002615-15-8 91
                   Hexagol                             112858 002615-15-8 83
                   Octaethylene glycol                 161142 1000289-34-2 83

  9  28.471  0.96 C:\Database\NIST05a.L
                   Octaethylene glycol                 161142 1000289-34-2 72
                   1,4,7,10,13,16-Hexaoxacyclooctadec 100942 017455-13-9 53
                   ane
                   Pentaethylene glycol                 83339 004792-15-8 53
```

PUMP KERNEL SHELL (PKS)

```
File        :D:\Data\LEMON OIL\PSM BIO OIL050309\PUMP KERNEL 2.D
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
```



```
                           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
```

```
                         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)-
```