CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil, coal, and natural gas are collectively known as fossil fuels. In United State, 85% of energy produced comes from burning these fuels. High dependency of fossil fuel in industry and automobile leads to the several of major problem such as energy crisis and environmental pollution. Byproduct is produced by burning the fuels to create energy. The most by product produced are carbon dioxide and nitrous oxide, greenhouse gases that are major contributors to global warming and acid rain. The increasing energy demands speed up the depleting of fossil fuels which are harder to retrieve. The solution for the above problems can be resolved by a renewable, alternative energy such as biomass.

The term "biomass" refers to organic matter that has stored energy through the process of photosynthesis. The sources of biomass fuel come in the form of wood chip, empty fruit bunches (EFBs), plant waste and crop residue. Moreover, it is one of the most abundant renewable resources. It has become one of the most commonly used renewable sources of energy in the last two decades, second only to hydropower in the generation of electricity. Based on the figure below, the usage of biomass as a renewable energy is expected to increase every year.

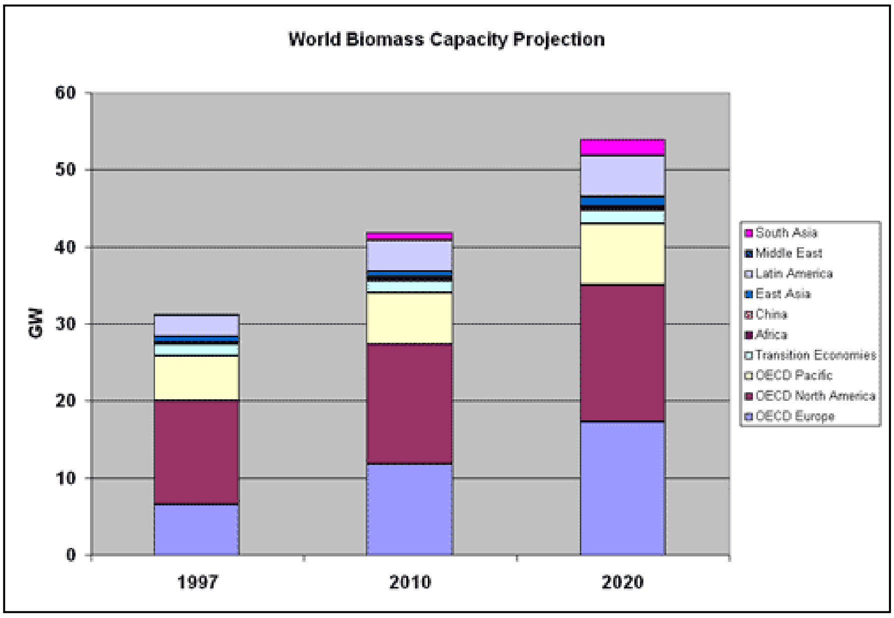


Figure 1: World Biomass Capacity Projection

The biomass can be converted to the oil-liquid form which is known as bio-oil by a pyrolysis process. According to Park et al. (2009) bio-oil has attracted considerable interest as one of the promising renewable energy resources because it can be used as a feedstock in conventional petroleum refineries for the production of high value chemicals or next-generation hydrocarbon fuels. However, due to the complexity of the structure of bio-oil and unstable properties, it is not suitable to directly use the bio-oil as fuel for commercial equipment and industrial process. It is necessary to study the characteristics of bio-oil to develop technologies to convert bio-oil to more suitable form and multipurpose.

1.2 Problem statement

According to Ozbay et al. (2007), the distribution of compounds in bio-oil mostly depends on the types of biomass used and on the processes severity which are temperature, residence time and heating rate profiles. It can be said that different types of bio-oil has a different properties and characteristics caused by the distribution of compound in bio-oil. Moreover, the excess oxygenated compounds present in bio-oil impart to the instability of characteristics of bio-oil such as high viscosity, low pH and temperature sensitivity. It is very important to study the physical and chemical characteristics of bio-oil before further technology development can be made.

Saleh (2007) has stated that Malaysia is still basically an agricultural country though it is fast developing into an industrial country. There are abundant biomass resources in Malaysia. However, utilization of biomass is inefficient in Malaysia and without proper handling of biomass will not only causes environmental pollution but also waste resources. Utilizing of biomass will help to reduce the cost of plant waste management and at the same time develop an alternative fuel.

Furthermore, no study has been done yet on the chemical and physical characteristics of bio-oil from EFBs. Most of the researchers focused on the study of bio-oil from hardwood and softwood. Thus, this study is being conducted in order to obtain the physical and chemical characteristics of bio-oil from EFBs.

1.3 Objectives of study

There are few objectives that have been identified and are related to the commencement of this project. All of these objectives need to be accomplished as the benchmark of project completion. The objectives are:

1) To study and conduct the experiment of bio-oil to know the chemical and physical characteristics of bio-oil from EFBs.
2) To analyze results obtained from the experiments.
3) To compare chemical and physical characteristics of bio-oil from EFBs with other types of bio-oil.

1.4 Scope of study

The project is limited to the bio-oil produced from EFBs by pyrolysis process. The bio-oil is divided into two fractions which are upper layer and lower layer. Both samples will be tested and undergo the same experiment.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass: Source of EFBs in Malaysia

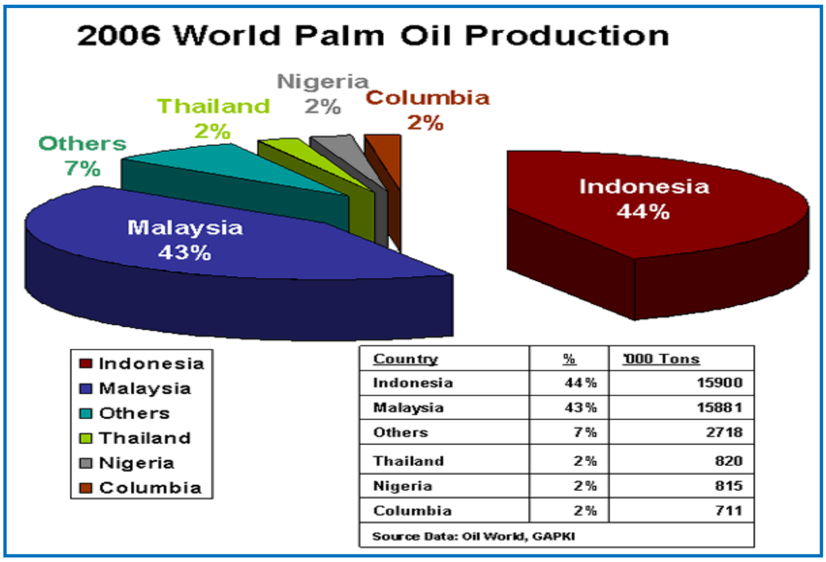
According to McKendry (2001), the conversion of biomass to energy encompasses a wide range of different types and sources of biomass, conversion options, and end - use applications and infrastructure requirements. Biomass can be derived from the numerous types of plant such as corn and sugarcane, plant residue such as EFBs and straw, and from biomass wastes such as sludge from organic industrial waste and organic domestic waste or the wastes themselves.

EFBs is stand for Empty Fruit Bunches. EFBs are available in large quantities in oil palm factory. Based on Siregar et al. (2007), every tonne of crude palm oil produced generates also one tonne of EFBs. EFBs are 20% more than the fruits weight. This represents huge quantities of organic matter that can be used as biomass to be converted to bio-oil. EFBs are commonly utilized as fertilizer and power generation in palm process mill. In Malaysia, EFBs is utilized as fuel for power boiler and also turns to construction product which is roof tile but it is yet to utilize EFBs as oil fuel.

Figure 2: An EFBs

Figure 3: EFBs in fibrous form

Moreover, Malaysia is rich with palm oil and is well known as second the largest supplier of palm oil after Indonesia in the world as can be seen in the Figure 4 below (USDA.GOV (2009), MPOB (2009), and M.T. Lim, Z. Alimuddin (2008)). Hence, EFBs is an abundant resource in Malaysia and the usage of EFBs can be diversified by converting to bio-oil.



Country	%	'000 Tons
Indonesia	44%	15900
Malaysia	43%	15881
Others	7%	2718
Thailand	2%	820
Nigeria	2%	815
Columbia	2%	711

Source Data: Oil World, GAPKI

Figure 4: 2006 World Palm Oil Productions

2.2 Chemical Composition of Biomass

The chemical composition of biomass varies among species, but plants consist of about 25% lignin and 75% carbohydrates or sugars. The carbohydrate fraction consists of many sugar molecules linked together in long chains or polymers. Two larger carbohydrate categories that have significant value are cellulose and hemi-cellulose. The lignin fraction consists of non-sugar type molecules. Nature uses the long cellulose polymers to build the fibers that give a plant its strength. The lignin fraction acts like a "glue" that holds the cellulose fibers together. Figure 5 shows the chemical composition of biomass.

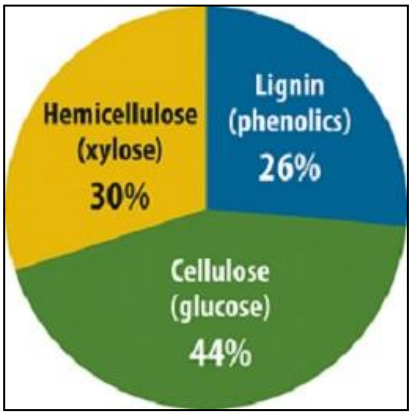


Figure 5: Chemical Composition of Biomass

Each composition degraded at different degree of temperature. For cellulose, degradation occurs at 250-350°C to produce anhydrocellulose and levoglucosan. Hemicellulose or also known as polyose decomposes at temperature of 200-260°C producing more volatiles, less tar and less chars compared to cellulose. Much of acetic acid released from wood during pyrolysis is attributed to deacetylation of the hemicelluloses. The third major component which is lignin decomposed at 280-500°C. pyrolysis of lignin resulted in producing phenols via the cleavage of ether and carbon-carbon linkages. Residual char is produced more during lignin pyrolysis than cellulose. Below is the summary of the thermal degradation steps.

Thermal degradation of hemicelluloses > cellulose > lignin.

2.3 Pyrolysis Process

Pyrolysis is a form of heating process in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F). Biomass decomposes to produce aerosols, vapors, and char. A dark brown liquid bio-oil is produced after cooling and condensation of vapors and aerosols. According to Mohan et al. (2005), no waste generated from pyrolysis of biomass as the bio-oil and solid char can each be used as a fuel and the gas can be recycled back into the process.

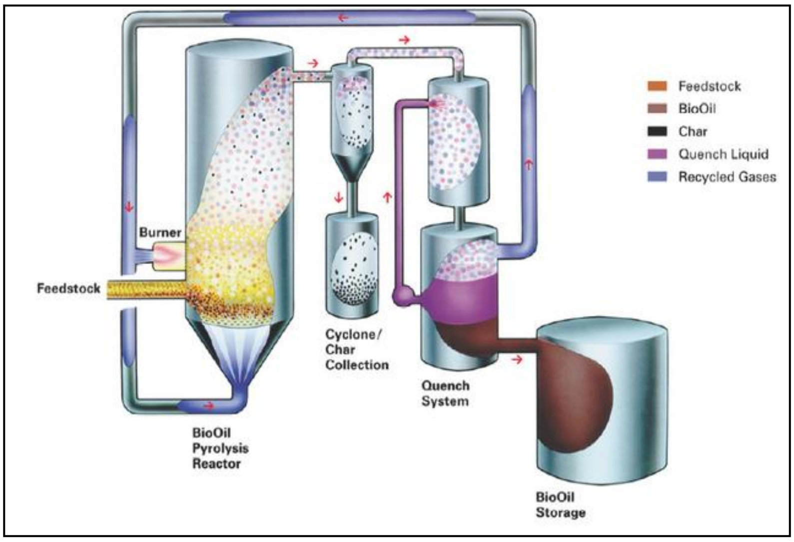


Figure 6: Process of Producing Bio-oil from Biomass

Figure 6 shows the example of pyrolysis process to produce bio-oil. The biomass is injected using a feedstock injector into a reactor. The burner heats up the biomass up to 500°C in the reactor. Each component of biomass pyrolyzes at different rate and temperature. The biomass will be converted into vapor and char and move to the char collection system. Then, char will be collected at the bottom of the char collection system while the vapor will proceed to the quench system. In the quench system, the vapor will cool down and condense to bio-oil. The bio-oil will be collected in the bio-oil storage and the gas will be recycled back into the reactor.

2.4 Bio-oil

Bio-oil, pyrolysis oil, biomass pyrolysis oil, bio-crude are all refer to the liquid product from the pyrolysis process of biomass. Bio-oil is a dark-brown liquid, high viscous, easily to evaporate with a smoky odor. Bio-oil is derived from the rapid and depolymerization of cellulose, hemicelluloses and lignin in biomass with a rapid increase in temperature. It consists of several compounds, mostly is water and oxygen, and organic compound such as acid, alcohol, notably aldehydes, ketones, carboxylic acids, alkenes, guaiacol-type molecules and many more.

According to Mohan et al. (2005), bio-oil ages after it is recovered. It can be observed from the changes of viscosity, phase separation and volatility. This instability is occurred because of breakdown in the stabilized microemulsion and to chemical reactions, which continue to proceed in the oil. The undesirable physical changes of bio-oil are caused by aldehydes, ketones and other compounds that can react via aldol condensation to form larger molecule during storage and handling. It is believed that temperature is an important variable in aging the bio-oil.

Apparently, bio-oil has a number of potential applications such as fuel for electricity generation, turbine and boiler. To date, most attention has been focused on bio-oil potential as a liquid fuel. However, bio-oil utilization for liquid fuel applications has been limited by the combined effect of high oxygen and water contents. Below is the figure of potential application of bio-oil investigated by Hyun et al. (2009).

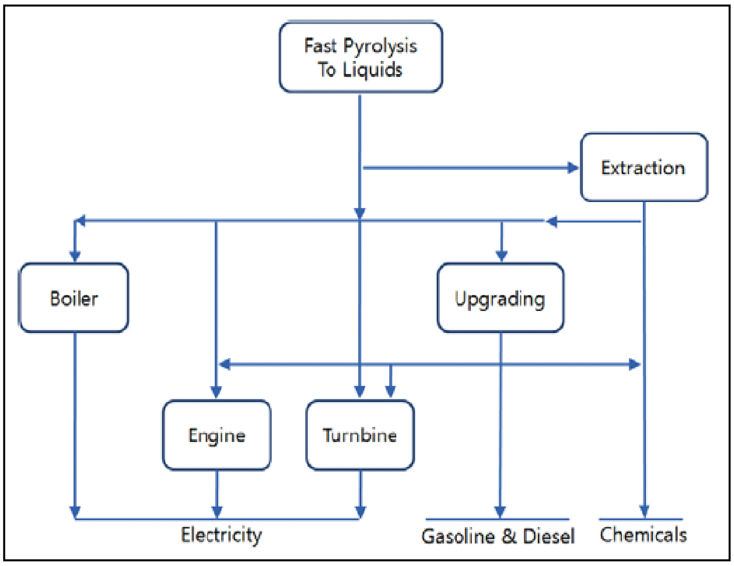


Figure 7: Potential Application of Bio-oil

2.5 Properties of Bio-oil

According to Q.Lu et al. (2009), 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 and pressure. In addition, bio-oils multi-component mixtures of different size molecules derived from depolymerization and fragmentation of cellulose, hemicellulose and lignin. Therefore, properties of bio-oil are differently according to their feed stock.

2.5.1 Water Content

Bio-oil contains high percentage of water compared to heavy fuel oil. Amount of water percentage in bio-oil is varying in the range of 15-30% while heavy fuel oil only has 0.1% of water. Excess of water in bio-oil originates from the water present in the biomass feedstock and reaction water that is dependent on the process condition. The presence of high value of water leads to the several of problems such as complex effect on viscosity, lower heating value, and homogeneity. From the positive aspects, water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of bio-oil in the engine. Dinesh et al. (2007) recommend Karl Fischer titration for analyzing water in bio-oil.

2.5.2 Oxygen Content

Amount of oxygen content in bio-oil is a primary issue of differences in bio-oils and hydrocarbon fuel. Normally, bio-oil contains 30-40% of oxygen depending on the feedstock and pyrolysis conditions. Bundles of organic compounds in bio-oil which have been classified into five broad categories; hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acid and phenolic compound, impart to the presence of high oxygen percentage in bio-oil. The oxygenated compound in bio-oil affects the characteristic of bio-oil which leads to mostly on the negative issues. According to Zhang et al. (2006), the high oxygen content leads to the lower energy density than the conventional fuel by 50% and immiscibility with hydrocarbon fuels also. There are several problems more that arise from the high oxygen content in bio-oil such as low heating value, corrosiveness and instability of bio-oils.

2.5.3 Acidity

Presence of carboxylic acid such as acetic and formic acid, contributes to the acidity of bio-oil. The pH value of bio-oil is varies in the range of 2.0-3.0. Bio-oil is very corrosive and without proper handling it will lead to corrosion of vessels and pipe work. Careful material selection must be accounted to avoid further loss such as high maintenance cost.

2.5.4 Caloric value

Calorific value defines the amount of heat released from the complete combustion of a specific amount of fuels with oxygen under standard condition. According to Mohan et al. (2007), calorific value of bio-oils on a volume basis is 60% of the calorific value of hydrocarbon oils, because of the high oxygen content, the presence of water and the higher bio-oil density. However, combustion tests showed that the calorific value of bio-oils is capable to replace heavy and light fuel oils in industrial boiler applications. Further development of bio-oil is needed to be done to utilize as transportation fuel. Moreover, the calorific value of bio-oil is dependable to the feedstock. Usually the bio-oils of oil plants have a higher calorific value compared with those of straw, wood or agricultural residues (Zhang, (2006)). Calorific value will be best measured by using bomb calorimeter.

2.5.5 Ash Content

Ashes resulted from combustion of bio-oil are very harmful to the engines and machinery equipment. The presence of ash in bio-oil can cause erosion, corrosion and kicking problems in the engines and the valves. If the ash content is higher than 0.1 wt% the effect can be worsen. Moreover, the alkali metal in the ash is more problematic. According to Mohan et al. (2007), alkaline metals identified in bio-oil are originally from biomass feedstocks. The amount of ash content in bio-oil can be obtained by weighing the collected residue of bio-oil after burning it at 700 °C for 3 hours. Table 1 shows the typical mineral components in biomass.

Table 1: Typical Mineral Components in Biomass

Element	Percentage of Dry Matter
Potassium	0.1
Sodium	0.015
Phosphorous	0.02
Calcium	0.2
Magnesium	0.04

2.5.6 Viscosity and Aging

The viscosity of bio-oils can vary over a wide range (35-1000 cP at 40 °C) depending on the feedstock and process conditions, and especially on the efficiency of collection of low boiling components. It decreases at higher temperatures much faster than for petroleum-derived oils, so that even very viscous bio-oils can be easily pumped after a moderate preheating. A significant reduction in viscosity can also be achieved by addition of polar solvents such as methanol or acetone. An undesired effect, especially observed when the oils are stored or handled at higher temperature, is the viscosity increase with time results from chemical reactions between various compounds present in the oil, leading to the formation of larger molecules. There is also evidence of reaction with oxygen from air.

CHAPTER 3

METHODOLOGY

3.1 Procedure Identification

There are several procedures need to be completed to accomplish this project. Thus to study the chemical and physical characteristics of bio-oil from EFBs, the first step will be to identify the procedures that need to be done accordingly. As for that, the following procedure has been identified and will be used.

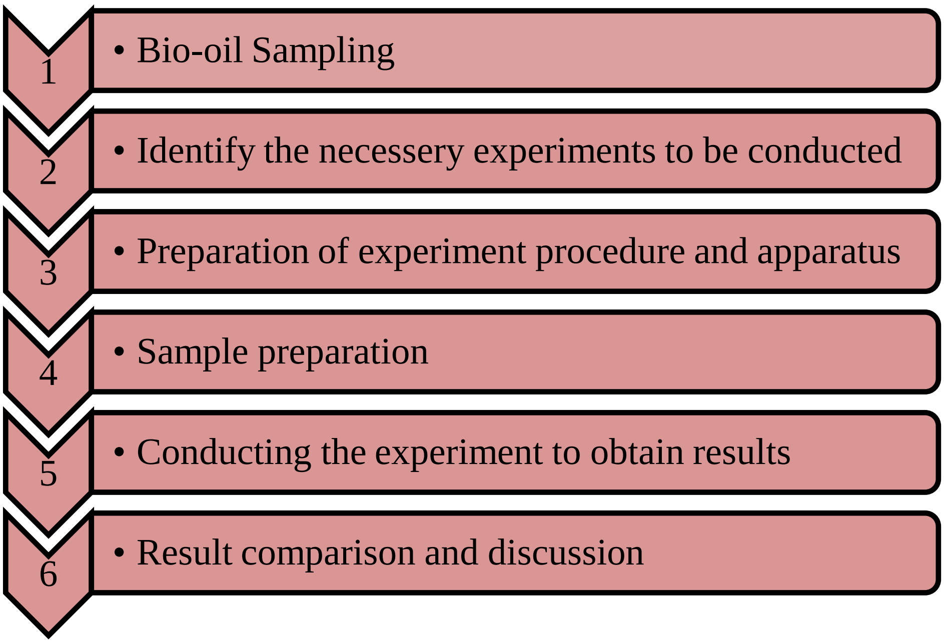


Figure 8: Procedure Identification

3.2 Bio-oil Sampling

The bio-oil is divided into two fractions which are upper layer and lower layer. The lower layer represents a heavy component of bio-oil and the upper layers represent the light component. Experiments will be conducted for both layer; upper layer and lower layer.

3.3 Identified Characteristics Experiments

The purpose of this experiment is to obtain the data for the properties of bio-oil from EFBs in order to study the chemical and physical characteristics and compare to other type of bio-oil. Below is the list of the experiment that will be conducted for bio-oil characteristic experiments.

1) Density test
2) Ash content test
3) pH test
4) Calorific value test
5) Water content test
6) CHNS
7) GC-MS

3.4 Preparation of experiment procedures and apparatus

3.4.1 Density

Density of bio-oil is high and density measuring instrument such as density meter and pycnometer cannot be used. Thus, an alternative way is identified based on the density formula;

$$\text{Density}, \rho = \text{mass (kg)}/\text{volume (L)}$$

Apparatus:

1) 50mL beaker
2) Analytical balance

Experiment Procedure:

1) Weigh an empty 50mL beaker using analytical balance and take the reading.
2) Fill the bio-oil into beaker up to 50mL.
3) Leave the bio-oil in the beaker for a moment to let it settle down.
4) Add in more bio-oil if the level is still below 50mL. Make sure it reaches exactly 50mL.
5) Weight the bio-oil and take the reading

Table 2: Template of Result for Density Test

Type of Raw Material	Weight of 50mL Beaker (g)	Weight of Bio-oil + Beaker (g)	Weight of Bio-oil (g)
Upper Layer			
Lower Layer			

Density, ρ = Mass of Bio-oil (g)/50mL

3.4.2 Ash Content

Apparatus:

1) Furnace
2) Crucible
3) Analytical balance

Experiment Procedure:

1) Weigh an empty crucible and take a reading.
2) Fill a small amount of bio-oil into the crucible and weigh it again.
3) Set the temperature to 700°C and retention time to 180 minutes at the furnace.
4) Insert the crucible filled with bio-oil into the furnace and leave it for 3 hours.
5) Open the lid of furnace and let the crucible cool down.
6) Take out the crucible from furnace and weigh the crucible with the ash.

Table 3: Template of Result for Ash Content Test

Bio-oil	Weight of Crucible (g)	Weight of Crucible + Bio-oil (g)	Weight of Bio-oil (g)	Weight of Crucible + Ash (g)	Weight of Ash (g)
Upper Layer					
Lower Layer					

$$\text{Wt \% of Ash} = \frac{Weight\ of\ Ash\ (g)}{Weight\ of\ Bio-oil\ (g)} \text{ X } 100\%$$

3.4.3 pH Test

The pH for liquid product will be measure directly by using pH meter. Data will be recorded into table and discussed.

Table 4: Template of Result for Ash Content Test

Bio-oil	pH of Bio-oil
Upper Layer	
Lower Layer	

3.4.4 Calorifc value Test

Apparatus:

1) Bomb Calorimeter

Experiment Procedure:

1) Weigh a clean, dry ignition cup and push tare.
2) Insert bio-oil in the ignition cup and weigh again.
3) Place the bomb head on its stand and put the ignition cup in place
4) Measure and cut a length of fuse wire
5) Loop the wire between the electrodes so that it gently rests on the bio-oil but does not contact the metal cup
6) place the bomb head in the bomb and screw the cover ring in place tightly
7) Close the outlet valve on the bomb head until it is finger tight.
8) Position the bucket inside the calorimeter jacket.
9) Insert the weigh of sample and push the start button

3.4.5 Water Content Test

Apparatus:

1) Karl Fischer Titration

Experiment Procedure:

1) Weigh an empty sample bottle and push tare
2) Insert small amount of bio-oil into the sample bottle
3) Seal the sample bottle with aluminum foil and rubber
4) Place the sample bottle on the Stromboli
5) Insert the weigh of sample and start the titration

3.4.6 CHNS

Apparatus:

1) CHNS Analyzer

Experiment Procedure:

1) Tare a silver capsule which contains a sorbit pad
2) Add bio-oil into the capsule using a micro-pipette.
3) Crimp and fold the capsule
4) Weigh the sample again
5) Insert the weigh value into the CHNS analyzer
6) Analyze the sample

3.4.7 GC-MS

Apparatus:

1) GC-MS analyzer

Sample preparation:

1) Insert bio-oil into measuring cylinder up to 2mL.
2) Leave the bio-oil for a few minutes to settle down.
3) Add in bio-oil if the level still below 2mL. Make sure it is reach exactly 2mL.
4) Fill the measuring cylinder with Tetrahydrofuran(THF) until it reach 10mL.
5) Cover the measuring cylinder with aluminum foil.
6) Gently shake the measuring cylinder until the mixtures are well mixed.

Experiment Procedure:

1) Modify method for the new solvent delay.
2) Run method by clicking on “Method”, then “Run Method”. The software will give a dialog box signaling that the instrument is ready.

3) Press the [Prep Run] key on the GC instrument. Wait until the screen on the GC signals that it is ready for an injection.

4) Rinse the syringe with 5 volumes of pentane. Rinse the syringe with 5 volumes of the mixture.

5) Load the syringe with 1 µL of air, then 2 µL diluted bio-oil and then pull the plunger all the way back to load about 7 µ of air. This gets the sample out of the syringe needle which will avoid volatilization of sample from the needle. Inject the sample and press [START] on the GC.

6) The software will then present a dialog box concerning the solvent delay. DO NOT override the solvent delay. After clearing this dialog box, the chromatogram will begin to plot, as soon as the solvent delay time is over.

7) When the run is complete the software will process the chromatogram and the associated mass spectral data. It will then output a library search report.

CHAPTER 4
RESULT AND DISCUSSION

4.1 Density

Table 5, shows the result of density test for bio-oil from EFBs. The density of bio-oil is normally higher than water. Surprisingly, the density of upper layer is higher than lower layer. The density of upper layer which is from a light fraction of bio-oil is 1.1943 g/cm^3 while the density of lower layer which is from a heavy fraction of bio-oil is 1.0548 g/cm^3. It is believed that the bio-oil of lower layer was affected by aging process. According to Dinesh Mohan et al. (2007), bio-oil contains aldehydes, ketones, and other compounds that can react via aldol condensations during storage or handling to form larger molecules. These reactions cause undesirable changes in physical properties and specifically it can cause a formation of larger molecules

Table 5: Density of Bio-oil from EFBs

Bio-oil	Density(g/cm^3)
Upper Layer	1.1943
Lower Layer	1.0548

Figure 9 shows the comparison of density with different types of bio-oil. The density of bio-oil is in the range of 1.29 to 1.055 g/cm^3. It is clearly can be noticed that the density of bio-oil is higher than water and hydrocarbon fuel. Bio-oil is riches with carbon and oxygen molecules which contribute to the high density value in bio-oil. However the density of bio-oil may be changed as the instability characteristics of bio-oil itself. Improper storage condition of bio-oil may encourage the condensation of reactive compounds in bio-oil to form larger molecule during storage resulting to higher density of bio-oil. Other than that, suitable chemical can be blended together with bio-oil to control or reduce the instability of bio-oil to maintain the density.

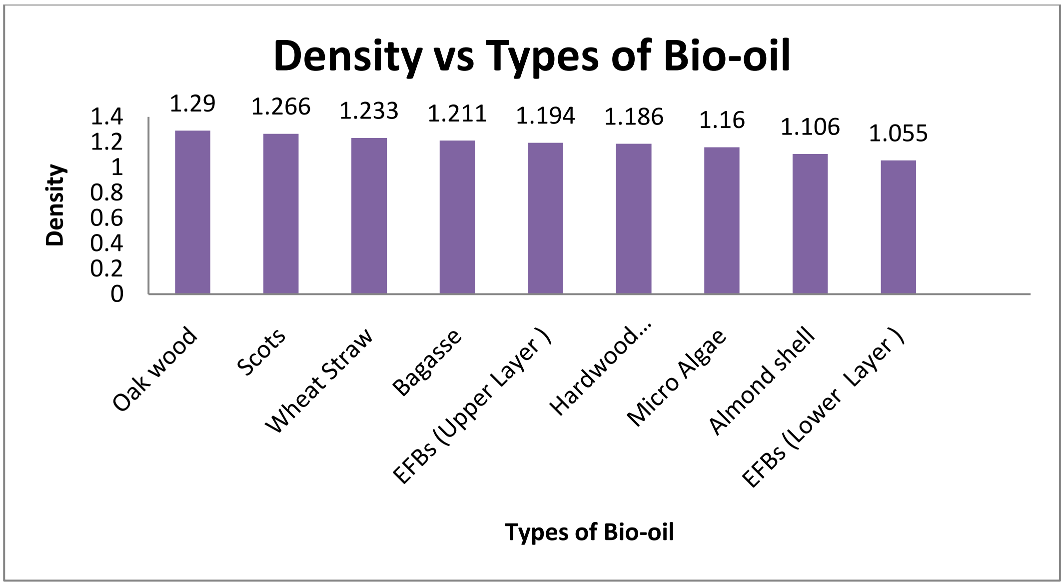


Figure 9: Comparison of Density of Bio-oil With Various Types of Bio-oil

4.2 Ash Content

Ash content is the non-combustible residue left after one sample is burnt. It represents the bulk mineral matter after carbon, oxygen, sulfur and water has been driven off during combustion. High value of ash content could leads to erosion and deposition of metal in engine. Table 6 show the ash content of bio-oil from EFBs. The upper layer has a higher value which 0.3133 wt % of ash content while lower layer contains 0.0529 wt%. It is believed that the upper layer of bio-oil contains of high mineral element such as potassium and calcium.

Table 6: Ash Content of Bio-oil from EFBs

Bio-oil	Ash Content (Wt%)
Upper Layer	0.3113
Lower Layer	0.0529

Figure 10 below shows comparison of ash content of bio-oil from EFBs with other types of bio-oil. From the graph, it can be concluded that ash content in bio-oil from biomass is the highest follows by bio-oil from bagasse and bio-oil from EFBs (upper layer). Lower layer of bio-oil from EFBs, has the second lowest of ash content, while bio-oil from rapeseed, almond shell and acacia have zero ash content.

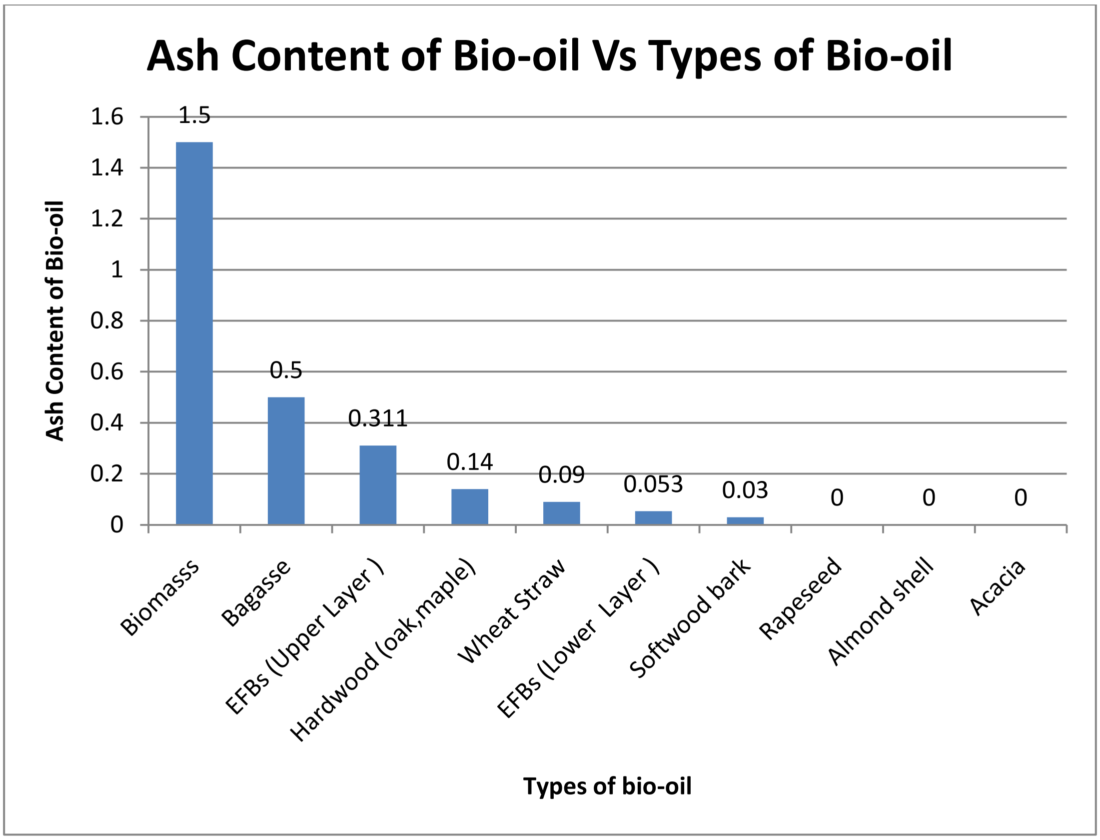


Figure 10: Comparison of Ash Content of Bio-oil With Various Types of Bio-oil

The dry matters in ash content are originated from the biomass feedstock. According to Sukiran (2008), the highest content of organic matter in EFBs is Potassium which is 2.22%. Nitrogen contributes 0.44% of organic matter in EFBs. Both Calcium and Magnesium contribute 0.36% of dry matter. Phosphorus is the lowest content of organic matter in bio-oil which is 0.14%. The mineral can be reduced my prewash the biomass with acid solution and rinse with water. Table 7 is the summarization of nutrient content of EFBs.

Table7: Nutrient content of EFBs

Element	Percentage of dry matter
Potassium, K	2.24
Nitrogen, N	0.44
Phosphorus, P	0.14
Calcium, Ca	0.36
Magnesium, Mg	0.36

4.3 pH test

pH of bio-oil was stated in the literature review varies in the range of 2.0-3.0.However the pH of bio-oil from EFBs is above that range. The pH of upper layer is 3.23 while the lower layer is 3.30. The upper layer of bio-oil is more acidic than the lower layer. From the result, it can be concluded that the upper layer of bio-oil is riches with acid compound compared to the lower layer.

Table 8: pH of Bio-oil from EFBs

Bio-oil	pH
Upper Layer	3.23
Lower Layer	3.30

Figure 12 shows the comparison of pH of Bio-oil with different types of bio-oil. The pH value of bio-oils is in the range of 5.5 to 2.6. There is only a slightly pH different of upper layer and lower layer of bio-oil.

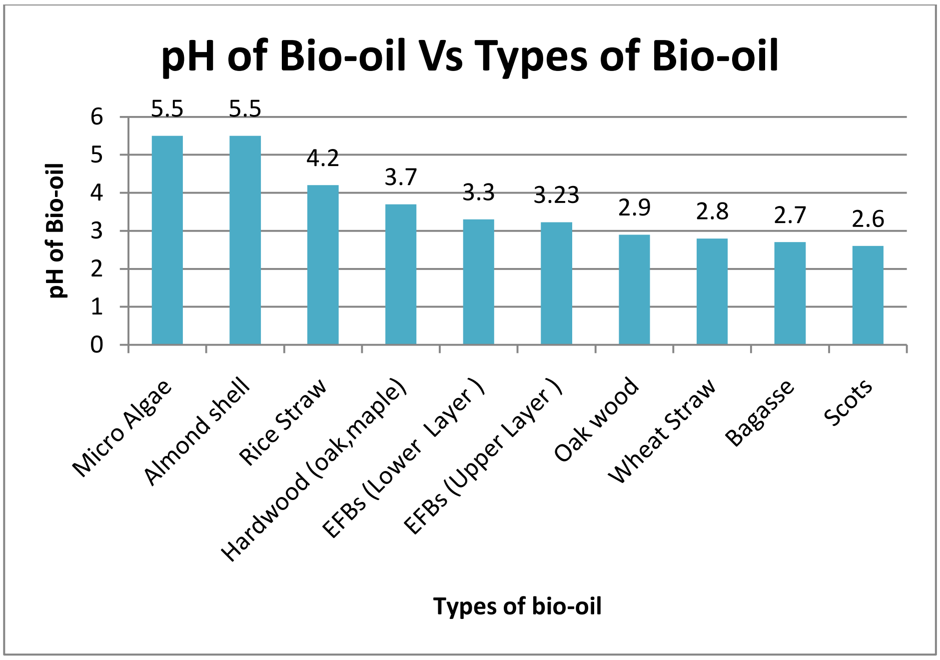


Figure 11: Comparison of pH of Bio-oil With Various Types of Bio-oil

4.4 Calorific Value

Calorific value of bio-oil is lower than the hydrocarbon fuel. This is due to the high water content in bio-oil. Calorific value of upper layer is 24.6 MJ/Kg while the lower layer 33.54 MJ/Kg. The upper layer has a lower value of calorific than the lower layer because the upper layer contains higher amount of water compared to lower layer.

Table 9: Calorific value of Bio-oil from EFBs

Bio-oil	Calorific Value (MJ/Kg)
Upper Layer	24.6
Lower Layer	33.54

Figure 12 shows the comparison of calorific value of upper and lower layer of bio-oil with other types of bio-oil. Bio-oil from rapeseed has the highest value of calorific value which is 38.4 MJ/Kg. It was stated in the literature review that existence of water and will affect the calorific value of bio-oil. The calorific value also can be affected by number of carbon molecule in bio-oil. Based on figure 19; Water Content of Bio-oil Vs Types of Bio-oil, the water content of bio-oil from rapeseed is zero. Moreover, the bio-oil from rapeseed has the second highest of carbon percentage which is 74.4%. From table 9, the relationship of calorific value with water content and carbon content can be clearly seen and it also apply to the lower layer and upper layer of bio-oil from EFBs.

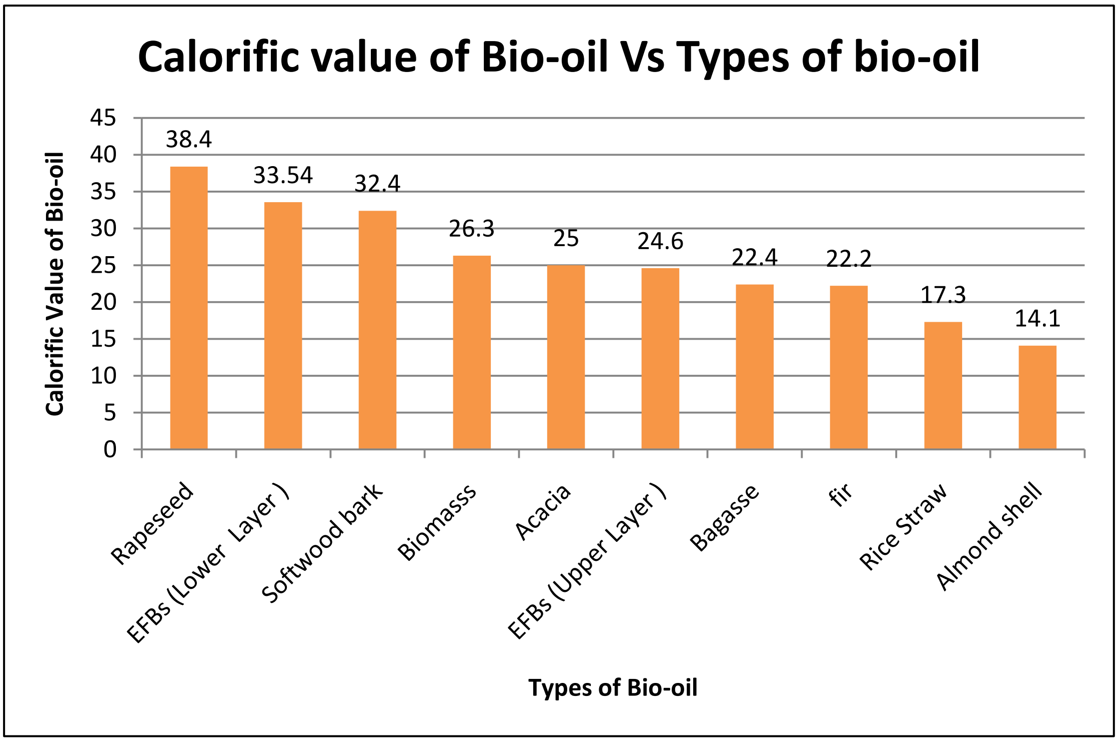


Figure 12: Comparison of Calorific Value of Bio-oil With Various Types of Bio-oil

Table 10: Relationship of Calorific Value with carbon content in bio-oil

Characteristics	Rapeseed	Lower Layer(EFBs)	Upper Layer (EFBs)
Calorific (MJ/Kg)	38.4	33.54	24.6
Water Content (wt %)	0	22.41	47.178
Carbon Content (wt %)	77.56	65.37	50.72

In order to get more accurate calorific value data of bio-oil, the theoretical calculation also has been made to compare the calorific value with the value obtained from experiment. Several correlations for calorific value and elemental compositions were chosen to get more clear view and accurate data of calorific value. The equation used to get the calorific value from the percentage of elemental composition in bio-oil is stated below. Table 10 shows the value of coefficient for each types of correlation used in this project.

Calorific Value, HHV [MJ/Kg] = a X Carbon + b X Hydrogen + c X Oxygen + d

Table 11: Correlation used to calculate calorific value

Types of correlation	**Coefficient**			
	a	**b**	**c**	**d**
Dulong	0.3383	1.443	-0.1804	0
Dermibas	0.335	1.423	-0.154	0
RITE	0.2698	0.0499	0	6.1044
Seyler	0.519	1.625	0.001	-17.87
Tilman	0.4373	0	0	-0.3059
Tilman (modified)	0.4373	0	0	-1.6701
Abe	0.3391	1.434	-0.097	0

Six graphs have been plotted for each type of correlations to compare between the calorific value obtained from experiment and calculation. The value obtained from experiment is labeled as actual HHV. From the graphs below, Abe’s correlation is the best correlation to calculate the calorific value for bio-oil from EFBs as the value calculated by using Abe’s correlation has only a slight different with the value obtained from experiment. Since that the error of value obtained from experiment and calculation has only a small error, the calorific values for upper layer and lower of bio-oil from EFBs measured in experimental work are acceptable.

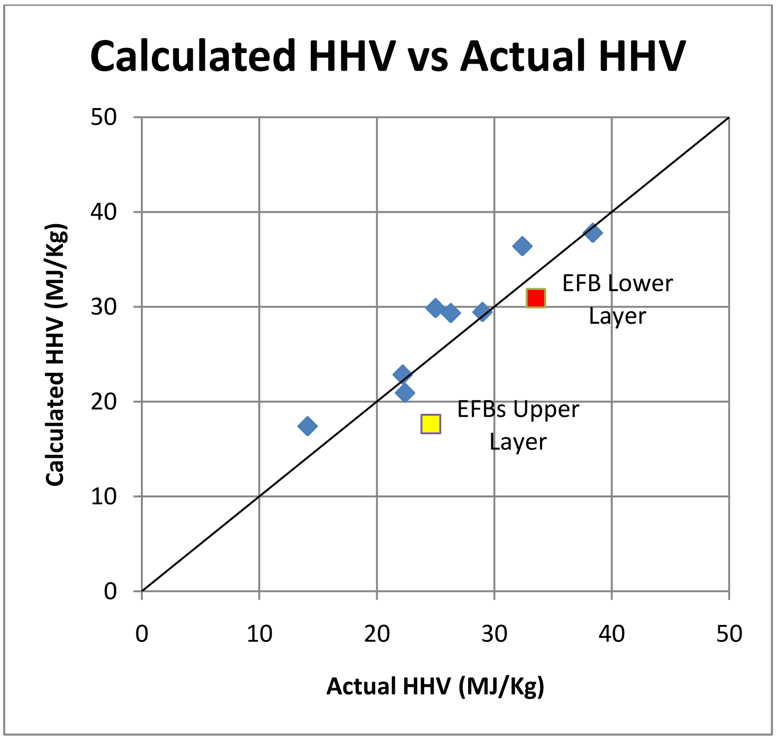


Figure 13: Comparison of Calorific Value Obtain from Experiment and Dulong’s Correlation

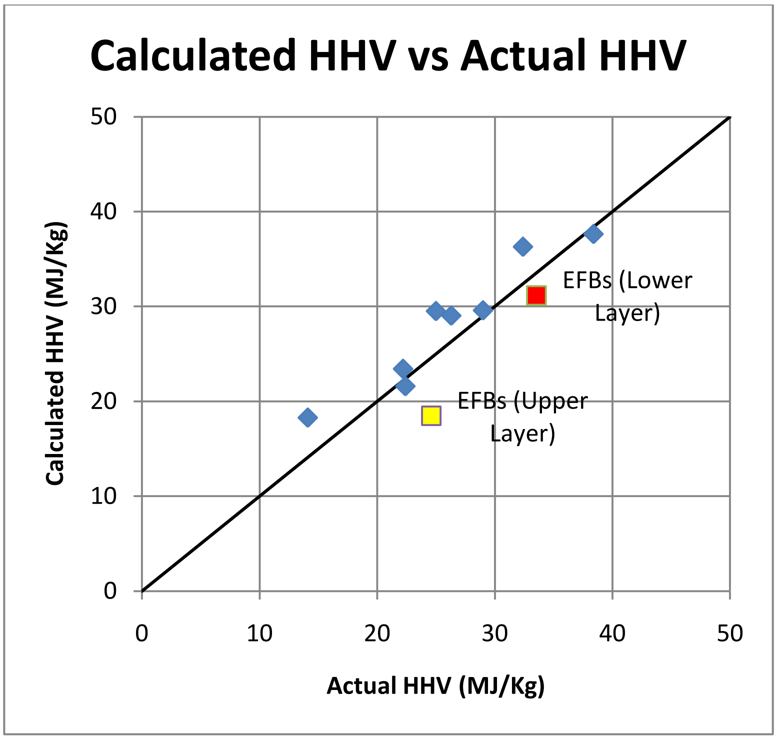


Figure 14: Comparison of Calorific Value Obtain from Experiment and Dermibas's Correlation

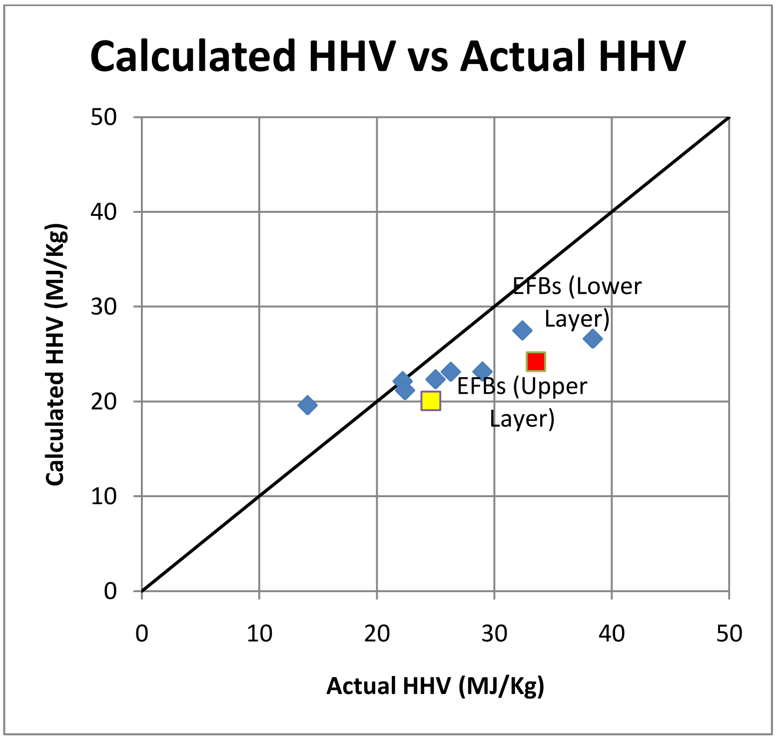


Figure 15: Comparison of Calorific Value Obtain from Experiment and RITE's Correlation

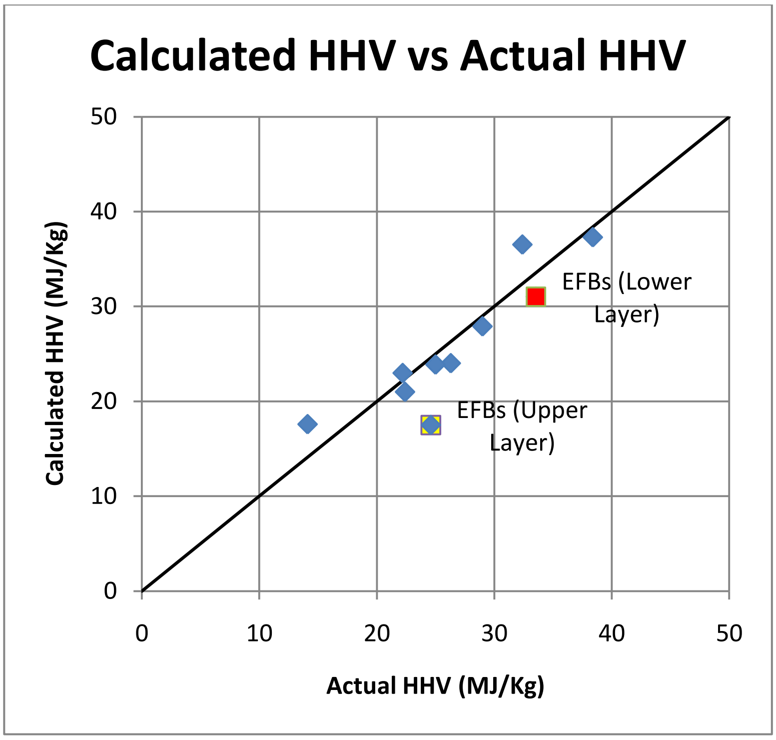


Figure 16: Comparison of Calorific Value Obtain from Experiment and Seyler's Correlation

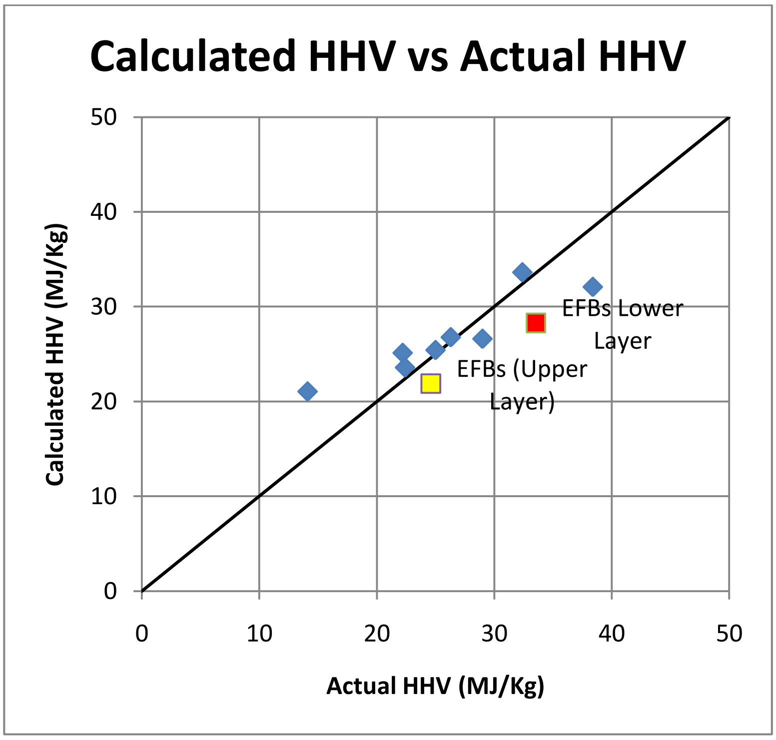


Figure 17: Comparison of Calorific Value Obtain from Experiment and Tilman's Correlation

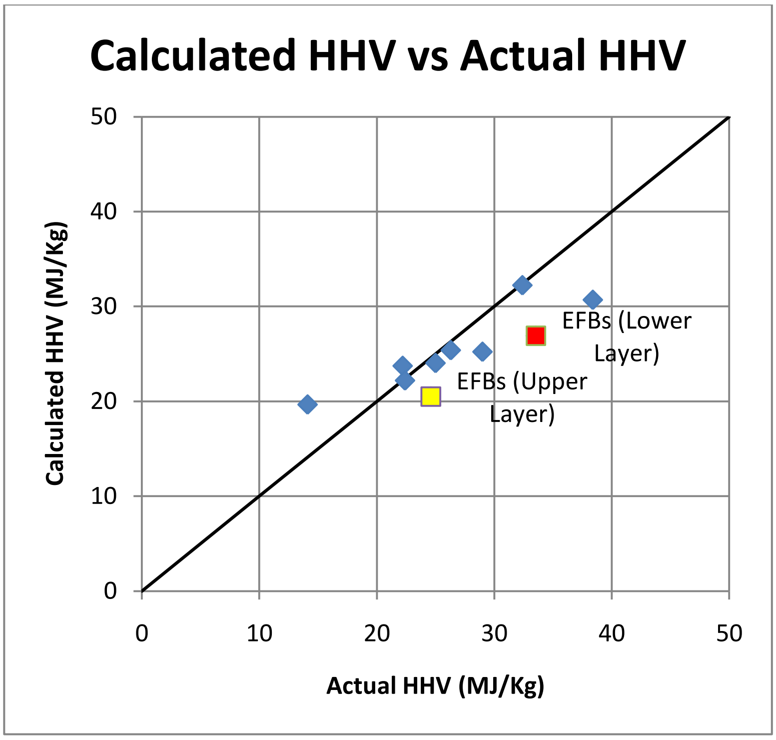


Figure 18: Comparison of Calorific Value Obtain from Experiment and Tilman (Modified)'s Correlation

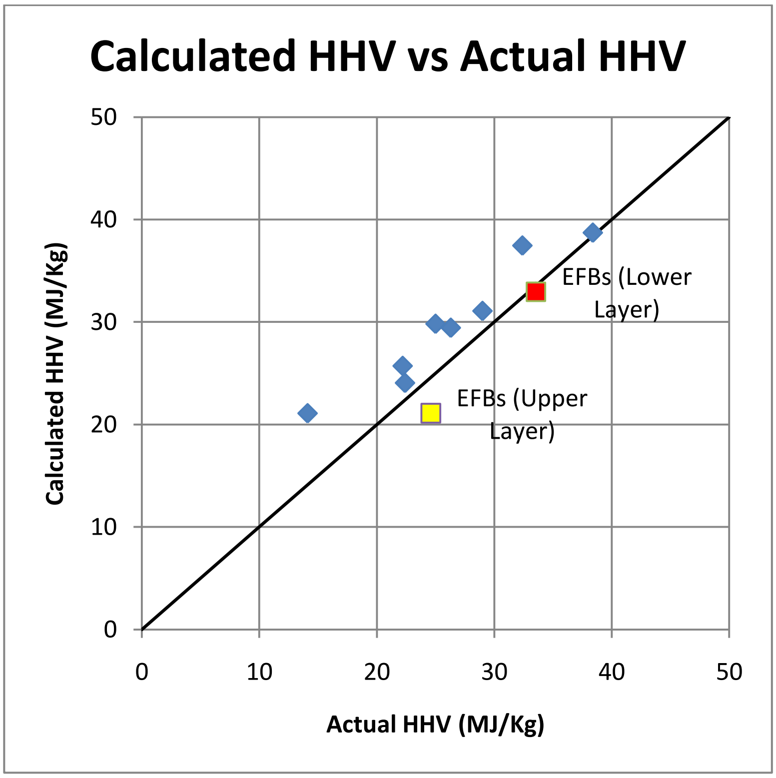


Figure 19: Comparison of Calorific Value Obtain from Experiment and Abe's Correlation

4.5 Water Content

One of the major problems of bio-oil is it contains of high water content. This can be proved by the result of water content test of bio-oil from EFBs. The upper layer contains 47.18 wt% of water while the lower layer is 22.44 wt%. Although the high water contain ease the handling of bio-oil, but it is reduce the performance of bio-oil as fuel by lowering the calorific value. The relationship between water content and calorific value has already been explained in the calorific value section.

Table 12: Water Content of Bio-oil from EFBs

Bio-oil	Water Content (Wt %)
Upper Layer	47.18
Lower Layer	22.44

Eight types of different bio-oil are used to compare the value of water content with bio-oil from EFBs. Figure 20 shows that, among of all the bio-oils the upper layer of bio-oil from EFBs, contains the highest water content. Water content of lower layer of bio-oil from EFBs is in the average range of 24-20 wt%.

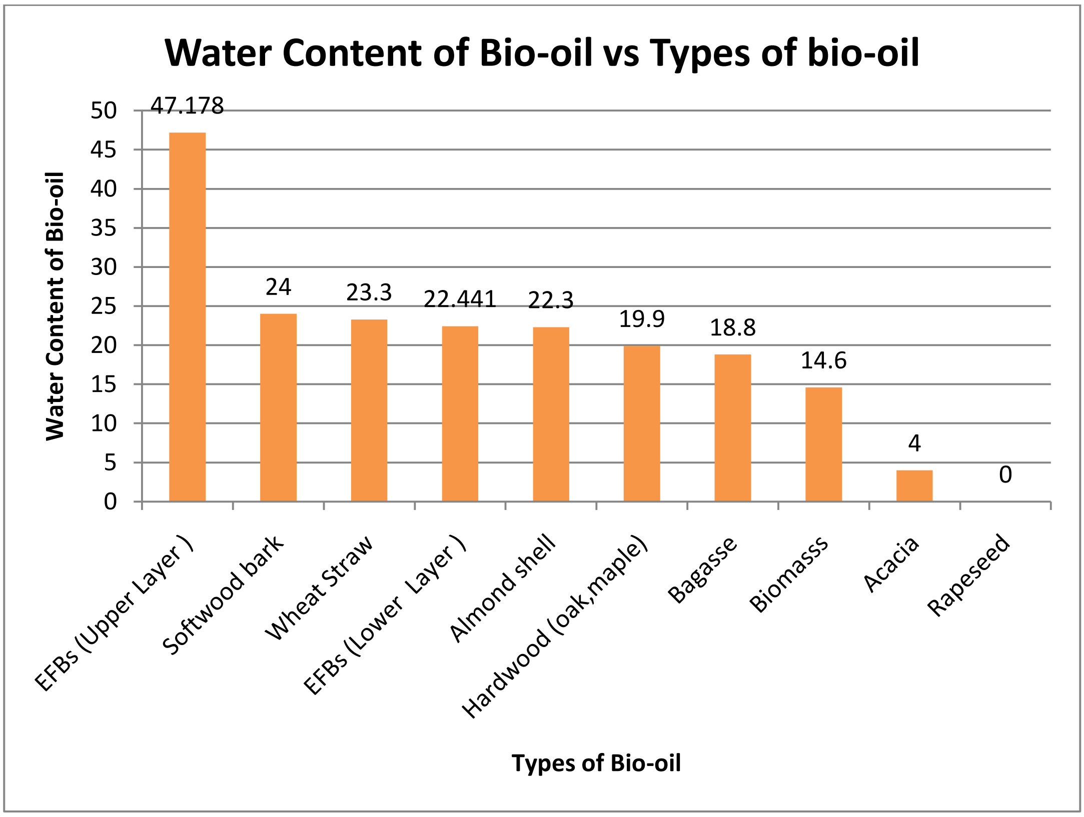


Figure 20: Comparison of Water Content of Bio-oil With Various Types of Bio-oil

4.6 CHNS and Oxygen Content

Table 13 shows the carbon, hydrogen, nitrogen, sulfur and oxygen content for both upper layer and lower layer. Carbon, hydrogen, nitrogen and sulfur contents are obtained from the CHNS analyzer. The oxygen content was calculated by subtracting 100 with total of oxygen, hydrogen, nitrogen and ash content. From the result, the lower layer has higher carbon content; 65.37 wt% compared to upper layer; 50.72 wt%. Bio-oil has a potential to substitute hydrocarbon fuel since the carbon content is quite high. Furthermore, the bio-oil contains low sulfur content. However, bio-oil has high oxygen content which imparts to the unwanted characteristics. The upper layer has 41.58 wt% of oxygen while the lower layer has 24.77. The oxygen content in bio-oil is contributed mostly by water and other oxygenated compound in bio-oil.

Table 13: Composition of Bio-oil from EFBs

Component	C (wt %)	H (wt %)	N (wt %)	S (wt %)	O (wt %)
Upper Layer	50.72	5.536	1.704	0.146	41.58
Lower Layer	65.37	9.197	0.571	0.037	24.77

Figure 21 shows the comparison of carbon, hydrogen, nitrogen and oxygen in various types of bio-oil. Value of sulfur is too low and has been neglected. The graph was arranged based on the highest carbon to the lowest carbon in bio-oil. From the figure below, obviously that when the carbon content is high the oxygen is low. The trend can be seen clearly from the bio-oil from softwood bark to bio-oil from almond shell, when the carbon content is getting lower, the oxygen content is getting higher.

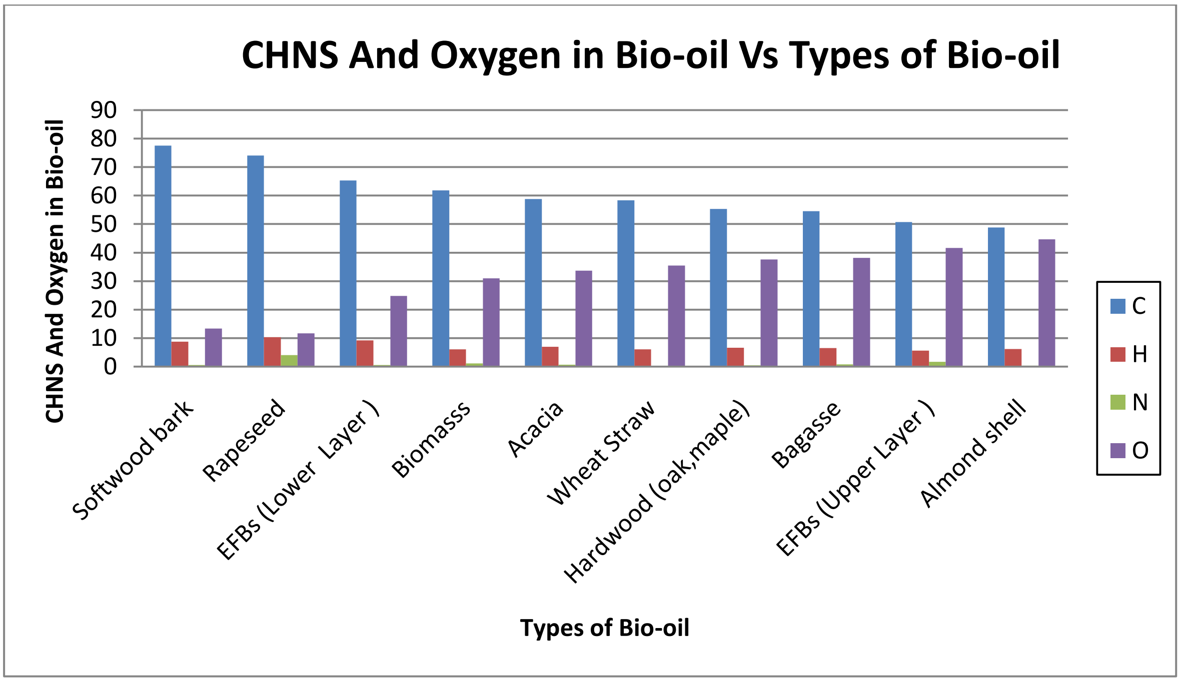


Figure 21: Comparison of CHNS and Oxygen of Bio-oil With Various Types of Bio-oil

4.7 GC-MS

Based on the result of GC-MS, 27 peaks are detected in upper layer and 42 peaks are detected in lower layer of bio-oil from EFBs. Each peak is represents an organic compound. GC-MS will give information regarding the compound detected at each peak such as molecule weight, molecule formula and bunches of possible compound name. Figure 22 and 23 show peak for upper and lower layer of bio-oil from EFBs. Organic compounds that have been detected in sample are categorized into different hydrocarbon group of organic compounds such as ester, alcohol, carboxylic acid and ketone.

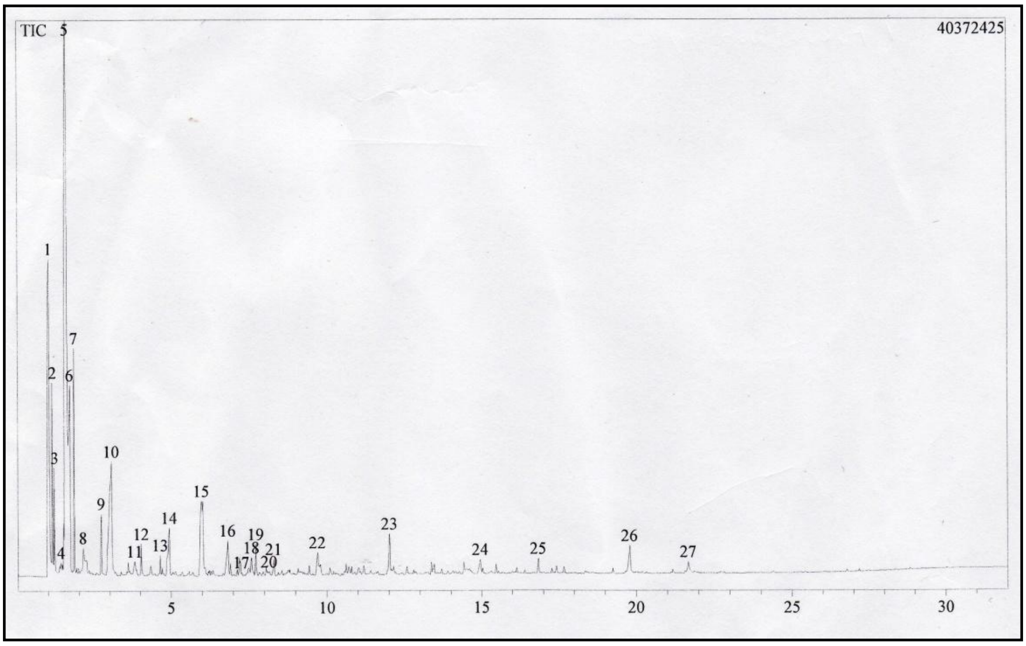


Figure 22: Peaks of Upper Layer of Bio-oil From EFBs

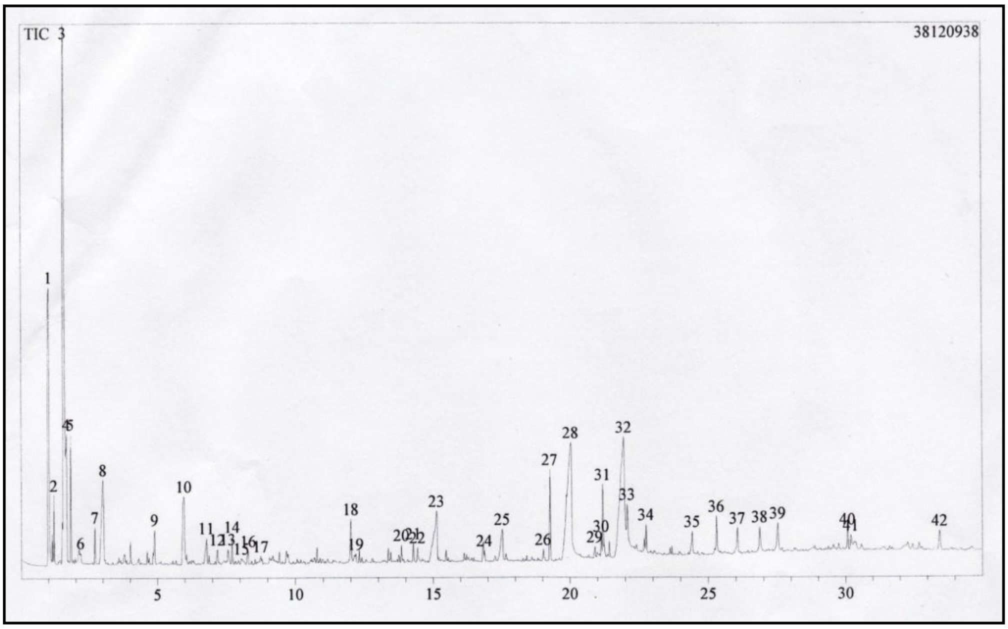


Figure 23: Peaks of Upper Layer of Bio-oil From EFBs

Figure 24 shows the hydrocarbon group and the percentage in upper layer of bio-oil from EFBs. Ketone is the major organic compound exists in upper layer with 36%. It is follows by carboxylic acid which contributes 20% of organic compounds. There are 8 % of aldehydes and furan in upper layer. Alcohol, amine and benzene share the same percentage which is 4%.

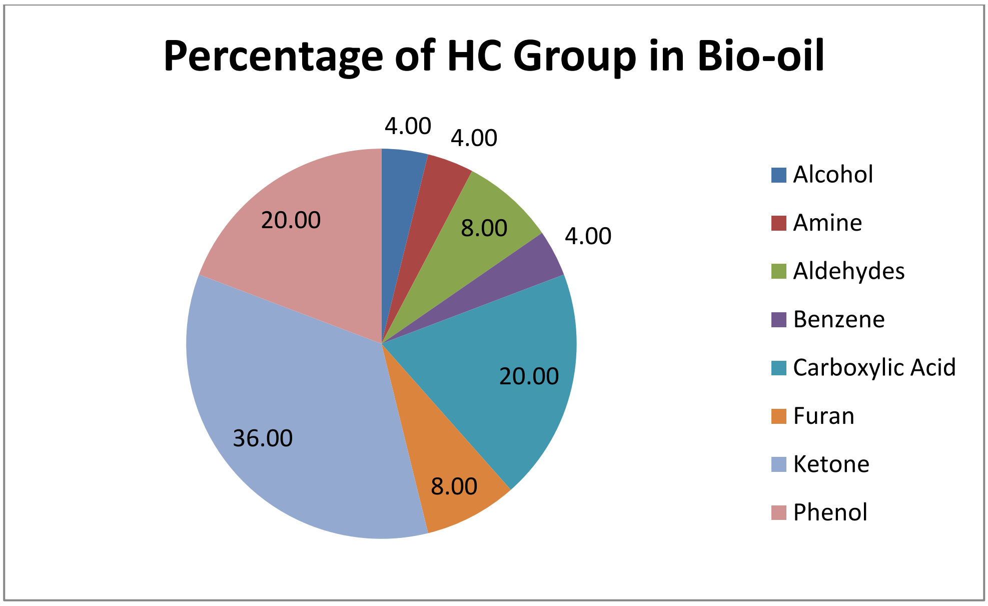


Figure 24: Percentage of Hydrocarbon Group in Upper Layer

Figure 25 shows the hydrocarbon group and the percentage in lower layer of bio-oil from EFBs. There are 11 hydrocarbon groups detected in lower layer of bio-oil from EFBs. The major hydrocarbon group is carboxylic acid with 34.15%. 14.93% of lower layer are coming from ester and phenol group. Benzene group is existed at 7.32% and furan is at 4.88%. Alcohol, aldehydes, alkane and alkene group contribute 2.44% in lower layer of bio-oil from EFBs.

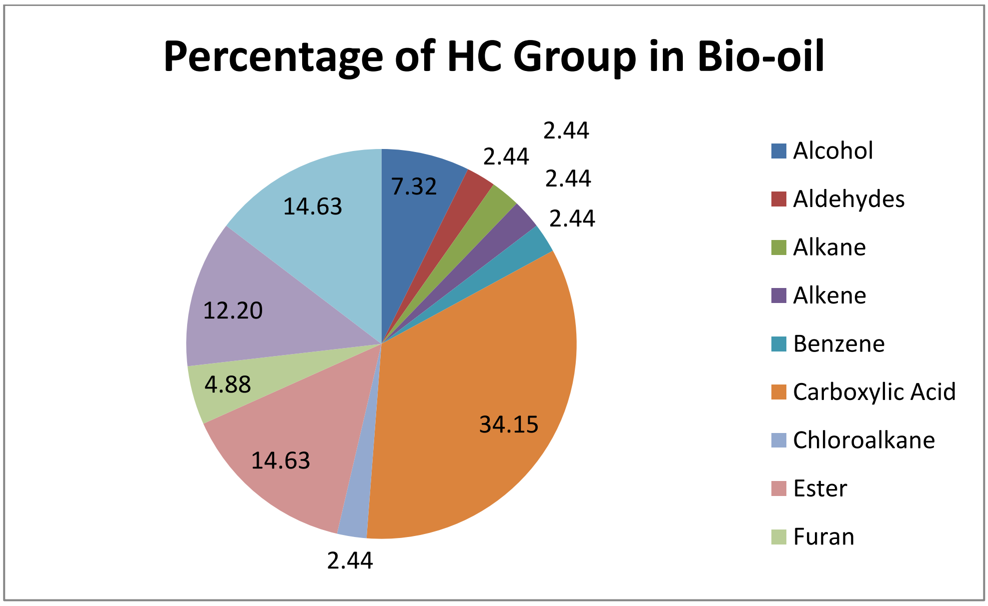


Figure 25: Percentage of Hydrocarbon Group in Lower Layer

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This research has investigated the physical and chemical characteristics of bio-oil from EFBs. Throughout the research period all the information was gathered from all reliable resources such as article, journals and online resources. The main focus of this project to investigate the properties of bio-oil; density, calorific value, pH, ash content, water content, CHNS, and analyzing the organic compound in bio-oil from EFBs. Therefore the knowledge and experience in chemical engineering study has fully utilized to conduct the experiment and research. The research is conducted by using various types of equipment and apparatus according to the characteristic of bio-oil that need to be studied.

Data obtained from the experimental works have been analyzed and compared with properties of several types of bio-oil. Thus, this project has fully completed and met the objectives.

The carbon content in bio-oil from EFBs is in the range of 50-65%. Hence, the bio-oil from EFBs has a potential to be a renewable energy source since the high content of carbon in bio-oil encourages toward high calorific value. However, the water and oxygen content reduced the effectiveness of bio-oil as a fuel and also imparted to several unwanted characteristics. The pH of bio-oil is in the range of 3.0-3.3 which is acidic making it is not suitable to be directly used in engine and machinery. High water in bio-oil is making it less viscous and easily to handle. Since that there are advantages and disadvantages in property of bio-oil, a further study and treatment need to be done according to the purpose of bio-oil so it can be marketable. Moreover, utilization of bio-oil from EFBs could reduce the environmental pollution and waste of EFBs resources.

5.2 Recommendation

During the storage of upper layer of bio-oil from EFBs, the sample had undergone aging process. According to Dinesh Mohan et al. (2007), bio-oil contains aldehydes, ketones, and other compounds that can react via aldol condensations during storage or handling to form larger molecules. This phenomena has ruined the sample, thus the accurate date cannot be obtained from the experiment. For example, when the density test is conducted, the upper layer of bio-oil has already formed larger molecules. Therefore, the density result of upper layer of bio-oil is higher than lower layer of bio-oil. To avoid this uncertainty of result, the bio-oil must be kept properly in a storage bottle with low temperature. Furthermore, the experiment to study the characteristics of bio-oil should be repeated monthly, so the aging process of bio-oil could be monitored.

There is only a part of characteristics of bio-oil from EFBs that had been studied. There are several experiments which are important to determine the characteristics of bio-oil from EFBs such as pour point, viscosity and flash point. Flash point is important to know the lowest temperature that bio-oil can vaporize to form an ignitable mixture in air. Combustion in an engine is driven by a spark. The fuel should be premixed with air within its flammable limits and heated above its flash point, then ignited by the spark plug. So, the information from flash point experiment will help to determine whether the bio-oil is suitable to be used in normal diesel engine.

Since that the characteristics of bio-oil from EFBs has been gathered, it is recommend to proceed this project with upgrading bio-oil to stabilize the bio-oil. From the experimental work, the bio-oil has excess content of oxygen. Presence of excess oxygen in bio-oil is making it unstable. According to Courtney et. al. (2008), the quality of bio-oils can be improved by the partial or total elimination of the oxygenated functionalities present.

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APPENDICES

RAW DATA FOR DENSITY TEST

Volume = 50mL=50cm3

Lower Layer

Sample	Weigh Beaker	Beaker + Sample	Sample	Density	Average (g/cm3)
H1	99.8	150.83	51.03	1.0206	1.0548
H2	97.25	150.93	53.68	1.0736	
H3	97.2	150.71	53.51	1.0702	

Upper Layer

Sample	Weigh Beaker	Beaker + Sample	Sample	Density	Average (g/cm3)
L1	97.24	154.14	56.9	1.138	1.1943
L2	97.23	159.02	61.79	1.2358	
L3	97.25	157.71	60.46	1.2092	

RAW DATA FOR PH TEST

<u>Lower Layer</u>

Sample	**PH**	**Average**
H1	3.30	3.30
H2	3.30	
H3	3.29	

<u>Upper Layer</u>

Sample	**PH**	**Average**
L1	3.24	3.23
L2	3.22	
L3	3.23	

RAW DATA FOR CHNS

Upper Layer

Sample	Weigh (g)	C %	H %	N %	S %
1	1.746	50.17	5.815	1.683	0.203
2	1.523	50.27	5.323	1.706	0.131
3	1.977	51.73	5.470	1.724	0.104

Lower Layer

Sample	Weigh (g)	C %	H %	N %	S %
1	1.715	65.43	9.221	0.571	0.038
2	1.881	65.97	9.278	0.598	0.041
3	1.885	64.72	9.092	0.543	0.031

RAW DATA FOR CALORIFIC VALUE

Lower Layer

Sample	**Weigh (g)**	**Result (J/g)**	**Average (J/g)**
H1	0.1580	35622	33536.33
H2	0.1760	34093	
H3	0.1882	30894	

Upper Layer

Sample	**Weigh (g)**	**Result (J/g)**	**Average (J/g)**
L1	0.1901	24963	24595
L2	0.1908	24118	
L3	0.1882	24704	

RAW DATA FOR ASH CONTENT

Lower layer

Sample	CW (g)	Sample (g)	Sample + CW (g)	Ash + CW (g)	Ash (g)	Wt %	Wt% Average
H1	36.5364	4.7515	41.2879	36.5380	1.6E-3	0.0336	0.0529
H2	38.2802	4.9920	43.2722	38.2813	1.1E-3	0.022	
H3	36.3275	4.8660	41.2135	36.3325	5E-3	0.103	

Upper layer

Sample	CW (g)	Sample (g)	Sample + CW (g)	Ash + CW (g)	Ash (g)	Wt%	Wt% Average
L1	37.7555	4.9102	42.6657	37.7650	9.5E-3	0.193	0.3113
L2	38.3343	4.8756	43.2099	38.3559	0.0216	0.443	
L3	33.0622	4.8963	37.9585	33.0768	0.0146	0.298	

RAW DATA FOR WATER CONTENT

Lower layer

Sample	Weigh (g)	ppm	%	Average
H1	0.0327	170195.4	17.02	22.441
H2	0.0399	321174.4	32.117	
H3	0.0478	181855.6	18.186	

Upper Layer

Sample	Weigh (g)	ppm	%	Average
L1	0.0316	440935.9	44.094	47.178
L2	0.0520	456509.4	45.651	
L3	0.0302	517881.5	51.788	

RAW DATA FOR GCMS

Upper Layer

No. Peak	Molecular Structure	Compound Name	Group	No	SI	Ref
1	H_2O	Water	Water	1	86	1,2
2	$C_4H_{11}N$	2-methyl-2-Propanamine	Amine	1	73	1,2,3
3	$C_3H_6O_2$	Propanoic Acid	Carboxylic Acid	1	87	1
4	$C_4H_6O_2$	Butanedial	Aldehydes	1	70	1
5	C_4H_80	Tetrahydro-Furan	Furan	1	94	1,2,3
6	$C_2H_4O_2$	Acetic acid	Carboxylic Acid	1	97	1,2,3
7	$C_3H_6O_2$	1-hydroxy-2-propanone	Ketone	1	94	1,2,3
8	$C_4H_8O_2$	1 -methoxy-2-propanone	Ketone	1	80	1
9	$C_4H_8O_3$	1 -hydroxy-2-butanone	Ketone	1	93	1,2,3
10	$C_4H_8O_2$	Tetrahydro-2-furanol	Furan	1	93	1,2
11	$C_3H_6O_2$	1 -hydroxy-2-propanone	Ketone	1	91	1
12	$C_5H_8O_3$	1-(acetyloxy)-2-propanone	Ketone	1	93	1
13	C_6H_8O	2-methyl-2-cyclopenten-1-one	Ketone	1	93	1,2
14	C_4H6O_2	Butylrolactone	Ketone	1	91	1,2,3
15	C_6H_6O	Phenol	Phenol	1	92	1,2,3
16	$C_6H_8O_2$	3-methyl-1,2-cyclopentanedione	Ketone	1	94	1
17	$C_{10}H_{12}O_3$	acetate-9-oxabicyclo[3.3.1]nonan-2-ol	Alcohol	1	78	1
18	C_7H_8O	3-methyl-Phenol	Phenol	1	89	1,2,3
19	$C_7H_8O_2$	Mequinol	Phenol	1	92	1,3
20	$C_6H_{10}O$	5-hexen-2-one	Ketone	1	83	1
21	$C_8H_{14}O$	2-methyl-2-heptenal	Aldehydes	1	86	1,2
22	$C_6H_6O_2$	1,2-Benzenediol	Benzene	1	84	1,2,3
23	$C_8H_{10}O_3$	2,6-dimethoxy-Phenol	Phenol	1	88	1,2
24	$C_{12}H_{24}O_2$	Dodecanoic acid	Carboxylic Acid	1	93	1,2,3
25	$C_{11}H_{14}O_3$	2,6-dimethoxy-4-(2-propenyl)-Phenol	Phenol	1	90	1,2,3
26	$C_{16}H_{32}O_2$	n-hexadecanoic acid	Carboxylic Acid	1	95	1
27	$C_{18}H_{34}O_2$	Oleic acid	Carboxylic Acid	1	93	1

Lower Layer

No. Peak	Molecular Structure	Compound Name	Group	No	SI	Ref
1	H_20	Water	Water	1	87	1,2
2	$C_3H_6O_2$	Methyl acetate	Ester	1	88	1
3	C_4H_8O	Tetrahydrofuran	Furan	1	95	1,2,3
4	$C_2H_4O_2$	Acetic acid	Carboxylic Acid	1	95	1,2,3
5	$C_3H_6O_2$	1-hydroxy-2-propanone	Ketone	1	93	1,2,3
6	$C_3H_6O_2$	Propanoic acid	Carboxylic Acid	1	94	1,2,3
7	$C_4H_8O_2$	1-hydroxy-2-butanone	Ketone	1	94	1,2,3
8	$C_4H_8O_2$	Tetrahydro-2-furanol	Furan	1	94	1,2
9	$C_4H_6O_2$	Butyrolactone	Ketone	1	90	1,2,3
10	C_6H_6O	phenol	Phenol	1	93	1,2,3
11	$C_6H_8O_2$	3-methyl-1,2-cyclopentanedione	Ketone	1	96	1
12	C_7H_8O	2-methyl-Phenol	Phenol	1	93	1,2,3
13	C_7H_8O	3-methyl-Phenol	Phenol	1	91	1,3
14	C_7H_8O	Mequinol	Phenol	1	93	1
15	$C_3H_6O_2$	Oxiranemethanol	Alcohol	1	78	1,2,3
16	$C_8H_{14}O$	2-methyl-2-heptenal	Aldehydes	1	86	1,2
17	$C_8H_{10}O$	2,3-dimethyl-Phenol	Phenol	1	91	1,3
18	$C_8H_{10}O_3$	2,6-dimethoxy-Phenol	Phenol	1	87	1,2,3
19	$C_{10}H_{20}O_2$	n-Decanoic acid	Carboxylic Acid	1	91	1
20	$C_{15}H_{32}$	Pentadecane	Alkane	1	97	1,2
21	$C_{13}H_{26}O_2$	Tridecanoic acid	Carboxylic Acid	1	95	1,2,3
22	$C_{10}H_{14}O_3$	1,2,3-trimethoxy-5-methyl-benzene	Benzene	1	73	1,2
23	$C_{12}H_{24}O_2$	Dodecanoic acid	Carboxylic Acid	1	94	1,2,3
24	$C_{15}H_{30}O_2$	Methyl tetradecanoate	Ester	1	94	1,2
25	$C_{14}H_{28}O_2$	tetradecanoic acid	Carboxylic Acid	1	95	1,2,3
26	$C_{17}H_{34}O$	2-Heptadecanone	Ketone	1	96	1,2
27	$C_{17}H_{34}O_2$	heptadecanoic acid	Carboxylic Acid	1	96	1,2
28	$C_{16}H_{32}O_2$	Hexadecanoic acid	Carboxylic Acid	1	95	1,3
29	$C_{12}H_{22}O_2$	Allyl nonanoate	Ester	1	88	1
30	$C_{19}H_{34}O_2$	methyl-9,12-hexadecadienoate	Ester	1	91	1
31	$C_{19}H_{36}O_2$	methyl-trans-9-octadecenoate	Ester	1	95	1,2

32	$C_{18}H_{34}O_2$	9-Octadecenoic acid	Carboxylic Acid	1	94	1
33	$C_{18}H_{36}O_2$	Octadecanoic acid	Carboxylic Acid	1	94	1
34	$C_{16}H_{31}ClO$	Palmitoyl Chloride	Chloroalkane	1	83	1
35	$C_{21}H_{40}O_3$	2-methoxyethyl octadec-9-enoate	Ester	1	88	1,2
36	$C_{19}H_{38}O_4$	2,3-dihydroxypropyl ester-hexadecanoic acid	Carboxylic Acid	1	88	1,2
37	$C_{23}H_{42}O_6$	2-(acetyloxy)-1-[(acetyloxy)methyl] ethyl ester-Hexadecanoic acid	Carboxylic Acid	1	84	1,2
38	$C_{21}H_{40}O_4$	2,3-dihydroxypropyl ester-9-Octadecenoic acid (Z)	Carboxylic Acid	1	89	1,2
39	$C_{25}H_{44}O_6$	2-(acetyloxy)-1-[(acetyloxy)methyl] ethyl ester-9-Octadecenoic acid	Carboxylic Acid	1	87	1,2
40	$C_{29}H_{50}O$	Gamma-sitosterol	Alcohol	1	83	1
41	$C_{29}H_{50}O_2$	Vitamin E	Alcohol	1	94	1,2
42	$C_{29}H_{48}$	Stigmastan-3,5-dien	Alkene	1	86	1

Project Gantt Chart for Final Year Project 1

	PROJECT ACTIVITIES	WEEK													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project/Topic Selection	▨	▨												
2	Data Gathering Research and discussion on topic Preparation for preliminary report	▨	▨	▨	▨										
3	Research on Bio-oil. Define objective and scope of study. Research on Bio-oil Characteristics				▨	▨	▨	▨	▨						
4	Identify the experiment that need to be conducted					▨	▨	▨	▨	▨					
5	Update on literature review					▨	▨	▨	▨	▨					
6	Submission of preliminary report.				▨										
7	Seminar 1.											▨	▨		
8	Prepare the experiment procedure										▨	▨	▨	▨	▨
9	Read books regarding project. Update literature review. Preparation and data gathering for final report and interim report.								▨	▨	▨	▨	▨	▨	▨
10	Submission of Final Draft Report	21st October 2009													
11	Submission of Interim Report	30th October 2009													
12	Oral Presentation	30th November - 4th December 2009													

Project Gantt Chart for Final Year Project 2

	PROJECT ACTIVITIES	WEEK													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Experimental works	▨	▨	▨	▨	▨	▨								
2	Analyzing data and repeating experimental work					▨	▨								
3	Preparing report for Progress Report 2							▨	▨	▨					
4	Experimental work in progress			▨	▨	▨	▨	▨	▨	▨	▨				
5	Result obtained from experiments and being discussed							▨	▨	▨	▨	▨			
6	Study on the results obtained	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			
7	Poster Presentation										▨	▨			
8	Preparing report for Draft and Final Report (Soft Cover)												▨	▨	▨
9	• Submission of Final Report (Soft Cover)	7th May 2010													
10	• Submission of Final Report (Hard Cover)	25th June 2010													
11	• Oral Presentation	7th June - 11th June 2010													