Studies on Physical and Chemical Properties of Bio Oil During Storage

by

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Dissertation submitted in partial
fulfilment of the requirements for
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(Hons) (Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
Universiti Teknologi PETRONAS
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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____
(AP DR SUZANA YUSUP)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

WAN NORSURIA BT WAN SHUKRI

ABSTRACT

Pretty soon, the earth is expected to run short of its present sources of energy like petroleum, coal and charcoal. This is the reason why researchers all over the world are putting on their thinking hats to find new and feasible sources of renewable energy. Bio oil is one solution for the shortage of fuel in coming years and high consumption of fuel all over the globe. This project will investigate the physical properties and chemical composition of bio oil in time of storage. Science people now are trying to upgrade bio oil to make full use of it and discard composition that affects bio oil storage. This project starts with investigation of bio oil properties and safety precaution when we know the characteristics of bio oil. All these data give comprehensive study on stability of bio oil. The findings will be useful to check stability of bio oil from EFB (empty fruit bunches) involving pH, density, ash content, CHNS analysis, calorific value and viscosity. The methodology of all the experiments will be taken from American Standard Test Methods (ASTM) references. Bio oil characteristics will be investigated in time of storage in 5 months. The readings will be repeated for 2 or 3 times. And the pattern of each characterization will show how aging affect bio oil stability. This project provides evidence that bio oil need further upgrading to avoid instability during storage.

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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: PROJECT METHODOLOGY

CHAPTER 4: RESULT AND DISCUSSION

CHAPTER 5: CONCLUSION

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background Of Study

Bio oil is one solution that can replace the non-renewable source of energy that we have now. It has a few advantages in substituting present fuel. Bio oil has a significant advantage in transportation. If tanker ship of fossil fuel sinks and cause spillage, the fuel will spread and cause huge disaster in water pollution and country has to spend a lot of money to handle this issue. But for pyrolysis oil, it will not spread and but separate into heavy organic fraction that will sink and aqueous fraction will be diluted and is very bio-degradable.

Bio oil is a fossil fuel substitute that can pump well, burn readily and ignite once it is atomized. Bio oil was produced by pyrolysis oil. The EU has set energy targets at 10% of energy production and 22% of electricity generation from renewable sources by 2010. Bio oil produced from pyrolysis process. Pyrolysis is the heating of biomass in the absence of oxygen, vaporized and condensed to produce liquid fuel and charcoal. The direct use as fuel and replacement of fuel for possible future, bio oil will require upgrading to improve its stability.

Bio oil has high chance to be renewable energy source to generate power, produce chemicals and as fuel replacement for transport. The investigation of its properties will be done in this project using laboratory equipment and see its stability in time of storage.

1.2 Problem Statement

1.2.1 Problem Identification

Bio oil is another source of renewable energy that can be used in the future with a few improvements. But to upgrade bio oil, we need to investigate the bio oil itself and know what affect its stability during storage. Through this project, people will know the appearance of bio oil in term of smell and look. Safety precautions also will be taken in place when properties of bio oil are taking into account.

Both chemical and physical properties of bio oil will be measured in this project. ‘Physical properties’ means properties that can be measured without changing the chemical identity of bio oil. Examples of physical properties are pH, viscosity, heating value and density. And ‘chemical properties’ is properties that can be measured when we change bio oil chemical identity by react bio oil with other chemical substances. But in this project, we will be focusing on the chemical composition of the bio oil from empty fruit bunches.

1.2.2 Significant of Project

Upgrading process also will try to get rid of the component which deteriorates the stability of bio oil during storage. This project is significant because people now are trying to research more about renewable sources to generate power in the coming future especially bio oil so they can further upgrade it and improve its characteristics. In addition to it, renewable biomass sources can be converted to fuels and are a logical choice to replace oil.

Published materials help a lot in reviewing and get acquainted with the subject in project and were presented in Chapter 2.This investigation will strengthen the evidences found in literature saying that stability of bio oil and its suitability to be used as transportation fuel and other alternatives. The stability of the bio oil can be improved by upgrading process such as esterification and reactive rectification using catalyst. The upgrading will improve the properties that affect the stability of bio oil. The stability of bio oil can be seen as time passes by, whether the stability is improving or deteriorating within time. That is why this investigation must be updated every time to see its characteristics in stability.

1.3 Objectives And Scope Of Study

1.3.1 Objectives

The objectives of this study are:

1. To investigate physical and chemical properties of bio oil during storage and its stability as time passes by.
2. To identify what components and properties that affects most the stability and must be discarded in upgrading to improve its characteristics for storage and transportation.

1.3.2 Scope of Study

As outlined in the objectives, the purpose of this project is to investigate the properties of bio oil. Equipments like viscometer and GC-MS (gas chromatography-mass spectrometry) will be used in this study for 2 or 3 times to see the pattern of properties with time. Physical properties include analyzing the components in bio oil, water and ash content, viscosity, heating, pH value and density while chemical part focusing on chemical composition of the bio oil such as CHNS and GC-MS characterization. And all these characteristics will be checked time by time in 5 months to see how it affects the bio oil stability. All equipments and experimental procedures will be further explained in Chapter 3. While Chapter 4 will present comparison between findings and from literature review referred.

1.3.3 The Relevancy of Project

By deriving more energy from renewable feedstocks, many countries might be able to significantly decrease their reliance on foreign petroleum. For this reason, efforts have been made to develop new processes for converting renewable biomass to energy. Biomass, which comprises 47% of the total renewable energy consumption, is the single-largest renewable energy resource currently being used. Most processes that convert biomass to liquid fuels begin with pyrolysis followed with upgrading.

The fast pyrolysis of biomass in the absence of oxygen has the potential to contribute to the world's need for liquid fuels and, ultimately, for chemicals production. Bio oil has great potential to be used as a fossil fuel replacement where it has customers in the local, regional and national electrical utilities that operates either with partial or complete fuel substitution. The uses of bio oil in industrial applications are numerous. Today, environmental guidelines are becoming stricter and people are always up-to-date in contributing products for better performance and environmentally friendly.

Around the world, humans burn over 8.7 billion tonnes of biomass annually, which can be potentially converted into a high-density fuel source, bio oil. With this abundance of feedstock, bio oil is a viable alternative to protect the environment and is a strong alternative for the industrial fuels markets. So, bio oil properties project can further help people knowing bio oil and know its functions in many industries. This project also will help scientists and researchers in upgrading bio oil stability to improve its functions as renewable energy source.

CHAPTER 2

LITERATURE REVIEW

2.1 Analysis of Literature

There are many articles regarding bio oil properties but has differences in feedstocks derivation. Bio oil can be derived from various feedstocks such as rapeseed cake, corn stove and many more type of biomass. Renewable energy should be more explored considering the fact that limited fossil fuels are nearly exhausted and increasing consumption of energy [6]. So, bio oil is one of the solutions that are actively studied for the time being. In the article, it stated that bio oil is multi-component mixtures of different sizes molecules derived from depolymerisation and fragmentation of cellulose, hemicelluloses and lignin. It was also found out that bio oil has high content of water about 15-30% and be the cause to the lower heating value but at the same time, reduce the viscosity of bio oil. While ash content in bio oil will result in kicking problems in engine and even deterioration.

Bio oil was produced by fast pyrolysis process. Fast pyrolysis is a thermal decomposition process that occurs in the absence of oxygen where the biomass is rapidly heated [9]. The advantages of biomass sources which are CO_2 neutral, has low containment of sulphur and nitrogen and environmental friendly [1]. This pyrolysis oil has advantages in transport and combustion. So, from there, further investigation was carried out which including the study of properties of bio oil. They mentioned that bio oil has instability that will affect the corrosiveness and viscosity. It was found out that bio oil contains mostly oxygenated organics.

The methodology that can be used in the properties investigation has been identified [5]. The methodology was taken from standard test methods that was approved and used around the globe. Table 2.1 below shows some of the methods that been used.

Table 2.1: Methodology

PROPERTIES	**METHODS**
Water Content	ASTM D 1744 -Using Karl Fischer titration method
Ash Content	ASTM D 482 -Heating in furnace until carbon and ash remain
Viscosity	ASTM D 88
Composition	Column chromatography using GC-MS
pH	ASTM D 974

But the methods taken are only water content method and ash content method due to problems regarding equipment used and unavailability. Table 2.2 shows other properties investigation methods for bio oil produced from empty fruit bunch [17].

Table 2.2: Methodology for EFB bio oil

PROPERTIES	**METHODS**
Water Content	ASTM D 4928
Ash Content	ASTM D 482 -Heating in furnace until carbon and ash remain
High calorific value	ASTM D 5865
C,H and N Content	ASTM D 5373 -using CHNS analyzer
pH	pH meter
Color and odor	Visual and smell

Basically, from this article, all methods were taken except for water content because ASTM D 1744 using Karl Fischer method is preferable. There are also cross-referencing in these two literature reviews found for bio oil properties.

Complete chemical characterization of bio oil is difficult to be done because of presentation of pyrolytic lignins that cannot be determined by gas-chromatography [3]. And chemical compositions of bio oil depend a lot on feedstocks and pyrolysis conditions. This article also prefer Karl Fischer titration method for water content determination of bio oil and stated that water is one component that is very hard to be removed.

Instability of bio oil happened due to slow increase of viscosity during storage and evaporation of volatile components in the air [10]. Bio oil experienced chemical reactions which are aldehydes, the most unstable component can react with water and alcohol while acids can react with alcohol to form esters [11].

Due to reactions stated, most characteristics of bio oil have changed in time of storage because of ageing such as increase in water content and viscosity. Viscosity, density and flash point show increment while decrease in heating value. Further studies are suggested in the future to improve the properties of bio oil [3].

Chemical characterization, the bio-oil contains higher-molecular-weight species and it contains polar, nonvolatile components [4]. Whole pyrolysis liquids can be analyzed by GC-MS (volatile compounds). While, physical properties of bio oil are different in a way that stated below in each of the properties that will be investigated. Below are some of the general views of physical properties of bio oil:

i. Karl-Fischer titration is recommended for analyzing water in pyrolysis liquids. Water standards and water addition method are suggested for calibration.
ii. pH determination is recommended and the pH level should be reported to one decimal place. Accurate determinations of acidity changes are needed and require frequent calibration.
iii. It might be necessary to calibrate the gas and liquid chromatographic systems, using standard solutions of known amounts of compounds during chemical characterization.

As bio oil is very viscous, it is hard to be injected into GC-MS for component analysis. So, it must be diluted first using solvent. T.H.F (Tetrahydrofuran) was used as solvent to dilute bio oil for chemical analysis [8].

2.2 Cross Referencing

2.2.1 Methodology in Literature Review

These methods were taken from production and characterization of bio-oil and biochar from rapeseed cake [5] compared with bio oil produeced by softwood bark [4]. There are a few cross-referencing in methodology of how characterization of CHNS analysis. These cross-referencing will be later compared with the availability of equipment in UTP. Table 2.3 below shows a few cross referencing in project methodology.

Table 2.3: Cross referencing methodology

PROPERTY	**METHODS**		
	RAPESEED CAKE BIO OIL [4]	**SOFTWOOD BARK [3]**	**EFB OIL [16]**
Component	GC-MS	N/A	N/A
CHNS	ASTM D 5291-02	ASTM D 5291	ASTM D 5373
Water Content	Karl Fischer Titration Method (ASTM D 1744)	ASTM 203	ASTM D 4928
Ash Content	ASTM D 482	N/A	ASTM D 482
Viscosity	ASTM D 88.	ASTM D 445	N/A
Gross Calorific Value	ASTM D 3286-91a LECO AC 350 instrument	N/A	ASTM D 5865
Density	ASTM D 1298	ASTM D 4052	N/A
pH	ASTM D 974.	pH meter	pH meter

2.2.2 Results Based On Literature Review

Table 2.4 below shows cross referencing for methodology that has been used in bio oil investigation.

Table 2.4: Cross referencing results

PROPERTY	**RAPESEED CAKE BIO OIL** [4]	**SOFTWOOD BARK** [3]			**EFB OIL** [16]
		UPPER LAYER	**BOTTOM LAYER**	**WHOLE**	
CHNS (wt %)					
C	73.74	74.1	61.3	62.3	68.26
H	10.69	8.5	6.5	7	8.02
O	10.51	17	31.3	29	21.57
S	0.11	0.3	0.07	0.07	0.03
N	4.65	0.05	0.6	1.1	2.02
Ash	0.30	0.1	0.3	0.3	0.1
Water Content (v%)	0.001	3.5	14.6	13.0	N/A
Viscosity	50.0 °C,= cSt 38	88	66	62	50.0 °C,= cSt 13.52
Gross Calorific Value (MJ/kg)	36.4	34.3	26.4	27.9	31.4
Density	993 kg/m3 (15°C)	1089 (28°C)	1222 (28°C)	1188 (28°C)	1.031
pH	Total acid value, mg KOH/g =75	3.03	2.98	3.00	3.6

2.3 Current Technologies

Bio oil contains low molecular weight acids and other volatile components and is a complex mixture highly oxygenated. The molecules in bio oil nearly involve all kinds of oxygenated organics such as esters, phenols, ketones and alcohols.

In order to investigate properties of bio oil, many tests have been done using the standard test methods. Table 2.5 shows current technologies that have been used in investigating bio oil properties.

Table 2.5: Methodology with current technology

PROPERTY	EQUIPMENT	METHOD
Component	GC-MS	
CHNS	CHNS Analyzer	ASTM D 5291-02
Water Content	METTLER TOLEDO (DL39 titrator with Stromboli, drying unit and optional air pump)	
Ash Content	Chamber furnace Porcelin container	ASTM D 482
Viscosity	SYP-IA Viscometer / Capillary Viscometer	ASTM D 445
Gross Calorific Value	Calorimetric Bomb	ASTM D 4809
Density	Glass Hydrometer	ASTM D 1298
pH	pH meter	

All these methods and equipments is been analyzed and proven in the last 2 years, 2008 and is relevant for this present time.

CHAPTER 3

PROJECT METHODOLOGY

3.1 Materials

3.1.1 Bio Oil

Bio oil is a dark, viscous liquid with the same elemental composition of biomass. It is not actually "oil" in the traditional sense. Bio oil is made up of many different oxygenated organic compounds. To create bio-oil, biomass must be "flash pyrolyzed" – heated to high temperatures (500 to 550ºC) at residence time of 1.1 s with very high heating rate (10^3 to 10^5 ºC/s) and rapid quenching of vapors. There will be 2 samples of bio oil which are upper layer and lower layer. All experiments will be done on these 2 samples.

In this project, I will be using sample of bio oil produced from empty fruit bunches (EFB) that has 2 layer which are upper layer and bottom layer. All experiments will be repeated three times to have an accurate value of each property and will be done on both sample (upper and bottom layer). This bio oil was produced by Asiatic Centre for Genome Technology Sdn Bhd under Genting Group company and was produced in July 2009.

3.1.2 T.H.F. (Tetrahydrofuran)

T.H.F. will be used as solvent in doing all experiments to investigate the properties of bio oil. As bio oil is very viscous liquid, it is difficult to measure its viscosity. So, bio oil needs to be diluted with solvent without any reaction.

3.2 Methodology

3.2.1 Gas Chromatography-Mass Spectrometer

Generally, GC-MS functions using retention time of sample. We have to inject bio oil sample into the column (molecular sieve/ silica gel) using syringe and must be cleaned after each use. The molecules take different amounts of time to come out from the column, called retention time and mass spectrometer will capture and ionize the molecules separately. All the components will be analysed further to identify its component that affect the bio oil stability. Figure 3.1 below shows gas chromatography-mass spectrometer.

Figure 3.1: GC-MS

3.2.2 CHNS Analyzer

The sample must first be weighed and place the sample into analyzer. Analyzer will be initiated and gases (CO_2, H, H_2O, NO_x, SO_x) will be produced. The gases stream will be isolated according to type of gas and will quantitavely determined, usually using thermal conductivity detector. Figure 3.2 below shows CHNS analyzer.

Figure 3.2: CHNS Analyzer

3.2.3 Water Content Experiment

Water content in bio oil is determined using Karl Fischer titration (ASTM D-1744) Stromboli method with the HYDRANAL® Composite 5 Reagent. The sample will be placed in the sample vials and sealed with foil and rubber foil to avoid evaporation of the sample. The sample will be heated and the water evaporated will be absorbed by the molecular sieve and silica gel vapour through tube and the water content will be analysed. The value will be displayed at the monitor. Figure 3.3 below shows METTLER TOLEDO DL39 with Karl Fischer Coulometer.

Figure 3.3: METTLER TOLEDO DL39 with Karl Fischer Coulometer

3.2.4 Ash Content Experiment

Put sample on porcelain container. Sample is weighed and records the mass shown. After that, heat the sample in muffle furnace to 700ºC for 3 hours. Then, cool down the sample for a few hours. And the weigh after the burning is measured and recorded. The mass after burning is mass ash in sample.

$$W_{sample}-(W1-W2) = W_{ash}$$

Figure 3.4 in the next page shows furnace that was used in ash content experiment.

Figure 3.4: Furnace

3.2.5 Viscosity Experiment

Brookfield viscometer is being used to measure the kinematic viscosity in centipoises (cP). Set the temperature that we want the viscosity to be measured and set the spinning of the spindle in rpm. Wait until it reaches at the setting temperature (50ºC) and pipette bio oil onto the surface of the equipment. Wait until it finishes the spinning of the spindle. Take reading that been shown at the monitor. Figure 3.5 below shows Brookfield viscometer.

Figure 3.5: Brookfield viscometer

3.2.6 Gross Calorific Value Experiment

This experiment uses calorimetric bomb. Electrical energy is used to ignite the fuel. Weigh the sample first. Turn on the equipment and ensure bomb completely dry. Sample been added to cup and tighten the cover. Then, start the stirrer. Record the temperature readings until there is no change in temperature. The calorific value will be displayed at the monitor and been recorded. The gross calorific value is also known as high heating value. Figure 3.6 below shows bomb calorimeter.

Figure 3.6: Bomb Calorimeter

3.2.7 Density Experiment

Density experiment was been done using glassware apparatus such as beaker. The weigh of the beaker must be measured first. Sample was poured into the beaker for about 50 mL and weigh was recorded. And the density will be calculated simply by using formula below:

$$\rho_{\text{bio oil}}(\text{g/cm}^3) = (W_{\text{sample+beaker}} - W_{\text{beaker}})/50$$

3.2.8 pH Experiment

The pH meter is turned on first. Submerge the electrodes of pH meter into the sample and stir for a few seconds. After that, let the readings stabilize and record the results. Figure 3.7 below shows pH meter.

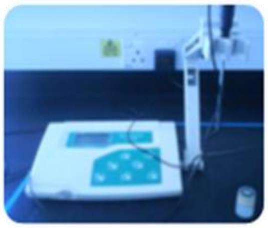
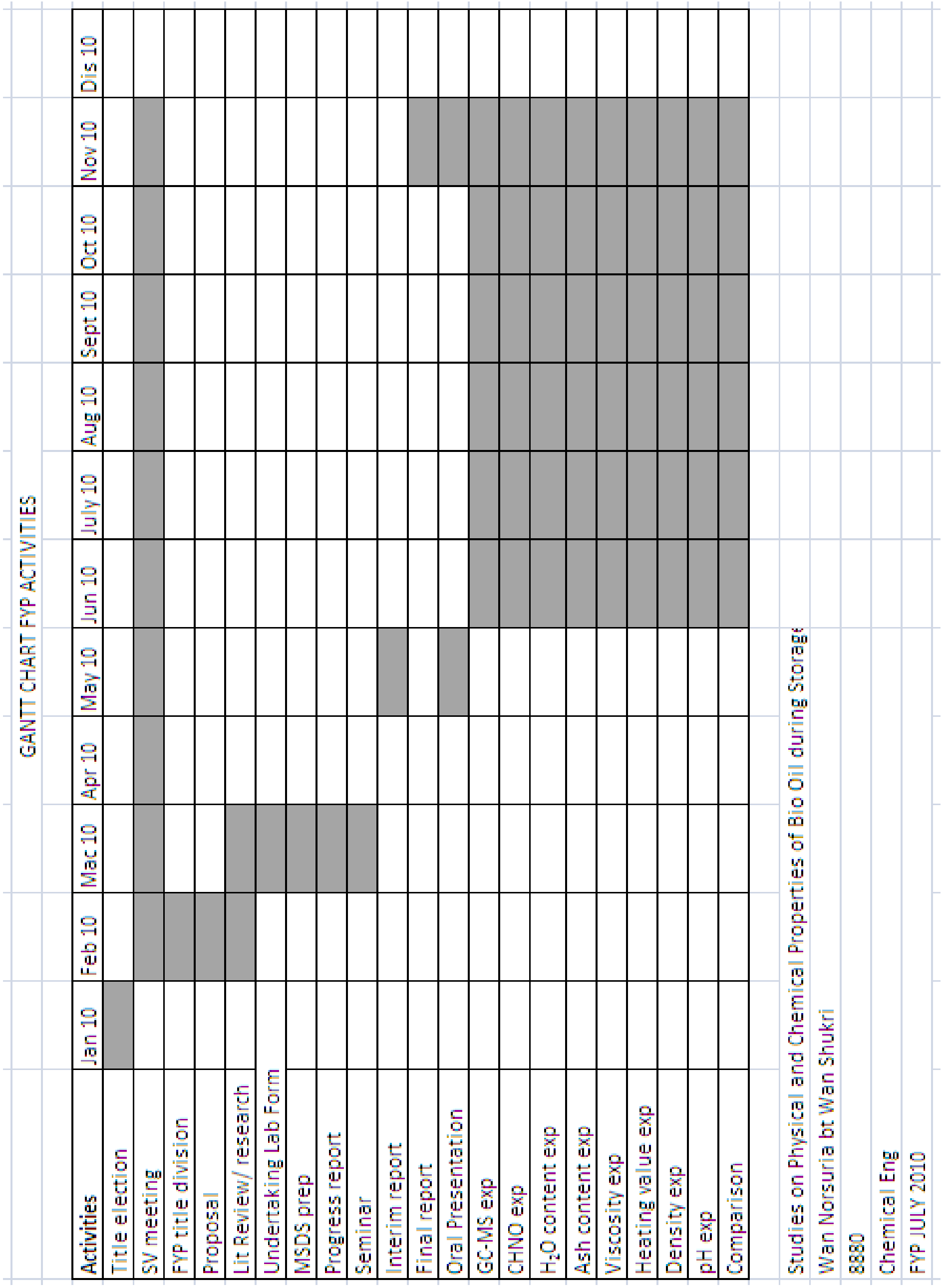


Figure 3.7: pH meter

3.3 Gantt Chart

Figure 3.8 below shows Gantt chart of this project.



GANTT CHART FYP ACTIVITIES

Activities	Jan 10	Feb 10	Mac 10	Apr 10	May 10	Jun 10	July 10	Aug 10	Sept 10	Oct 10	Nov 10	Dis 10
Title election	▨											
SV meeting		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	
FYP title division		▨										
Proposal		▨										
Lit Review/ research		▨	▨									
Undertaking Lab Form			▨									
MSDS prep			▨									
Progress report			▨									
Seminar			▨									
Interim report					▨							
Final report											▨	
Oral Presentation					▨						▨	
GC-MS exp						▨	▨	▨	▨	▨	▨	
CHNO exp						▨	▨	▨	▨	▨	▨	
H_2O content exp						▨	▨	▨	▨	▨	▨	
Ash content exp						▨	▨	▨	▨	▨	▨	
Viscosity exp						▨	▨	▨	▨	▨	▨	
Heating value exp						▨	▨	▨	▨	▨	▨	
Density exp						▨	▨	▨	▨	▨	▨	
pH exp						▨	▨	▨	▨	▨	▨	
Comparison						▨	▨	▨	▨	▨	▨	

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Figure 3.8: Gantt chart

3.4 Present Results

Table 3.1 below shows present result for bio oil properties investigation.

Table 3.1: Present result

PROPERTY	SAMPLE	METHODS
CHNS analyzer	C – 68.26% H – 8.02% N – 2.02% S – 0.03%	ASTM D 5373
Ash content	0.10 wt%	ASTM D 482
HHV	31.44 MJ kg^{-1}	ASTM D 5865
pH	3.6	pH meter
H_2O content	5.2%	ASTM D 4928

In this project, I will compare all the properties with this result and compare them with other article, with other bio oil from various feedstocks. And also, I have investigated other properties in this project such as gross calorific value and density that will be presented in result and discussion chapter.

CHAPTER 4

RESULTS AND DISCUSSION

All characterizations have been done and the results are presented below with graph to show the pattern of characterization during storage. Every characterization has been repeated for 3 times to ensure the reading taken is the precise one.

Doing characterization of bio oil is very difficult because it is complicated oxygenated liquid with high viscosity. In a simple way, the physical appearance of bio oil is very viscous, dark brown in colour with smoky odor and free flowing liquid depending on the feedstocks. Two sample of bio oil were used in this project consisted of heavy and light component from bio oil production.

4.1 Physical Appearance

Physically, bio oil or pyrolysis oil seems to be more viscous in time of storage. Handling becomes more difficult for sampling such as CHNS characterization. There are conglomerations formed as solid particles in bio oil increases during storage make bio oil emulsified. This is proven by increment ash content. The smoky odor of bio oil also becomes more intense once during storage.

4.2 Experimental Data

4.2.1 Density

Table 4.1 and figure 4.1 below show data for bio oil density result throughout February 2010 till October 2010.

Table 4.1: Density result

DATE	DENSITY (g/cm^3)	
	HEAVY	LIGHT
3 Feb 2010	1.0548	1.1943
1 Jun 2010	1.0584	1.1964
10 Aug 2010	1.0602	1.1972
3 Sept 2010	1.1098	1.1991
24 Sept 2010	1.1387	1.1995
1 Oct 2010	1.1560	1.1996
8 Oct 2010	1.1629	1.1998
15 Oct 2010	1.1631	1.2001
22 Oct 2010	1.1633	1.2002

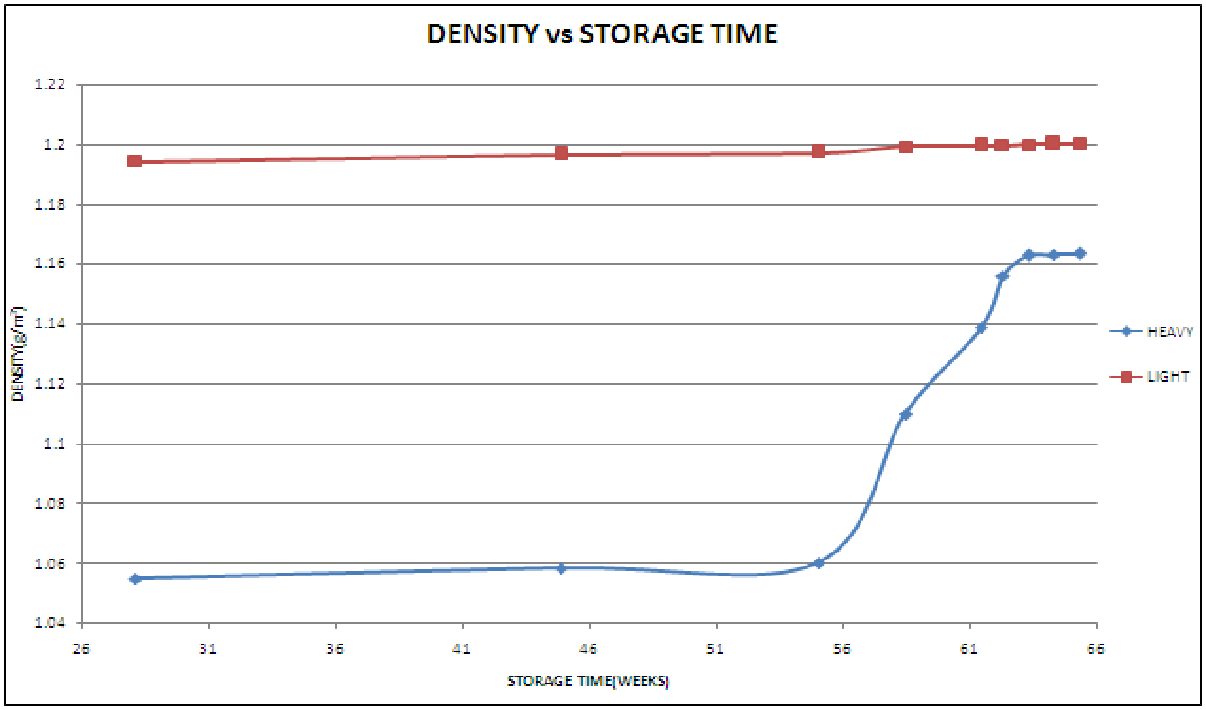

Figure 4.1: Density graph

Density is defined as mass over volume (g/cm^3). From the graph, we can see that over time, the density of both upper and lower layer keep increasing meaning mass of bio oil for constant volume increase. Density of bio oil is higher than density of petroleum fuel (0.8-1.0 g/cm^3). Density of bio oil increase due to some organic compounds in bio oil itself that is very reactive to form new component such as ester, ether and solid particles aggregation. The reactive compounds will interact and form larger molecules in bio oil during storage. And because of this, the density will keep increasing in time of storage.

4.2.2 pH

Table 4.2 below and figure 4.2 in the next page show data for bio oil pH result throughout February 2010 till October 2010.

Table 4.2: pH result

DATE	pH	
	HEAVY	LIGHT
6 Feb 2010	3.30	3.23
1 Jun 2010	3.027	2.75
3 Sept 2010	2.85	2.63
24 Sept 2010	2.83	2.60
1 Oct 2010	2.82	2.58
8 Oct 2010	2.79	2.57
15 Oct 2010	2.78	2.56
22 Oct 2010	2.76	2.54

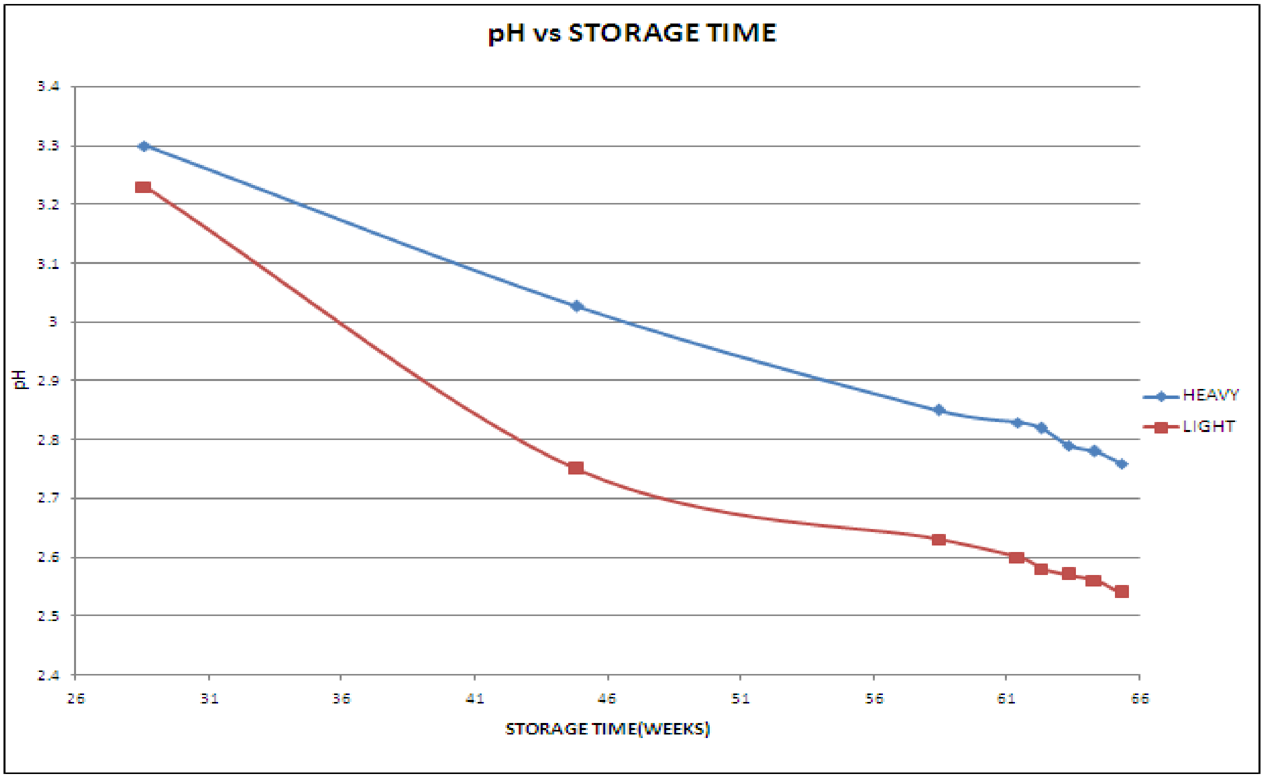

Figure 4.2: pH graph

Bio oil generally known for its acid content that is very high giving low pH reading. The increasing pH from time to time is due to the oxidation that happened in bio oil during ageing producing more and more carboxylic acid with reactive peroxide. From my studies, the pH of bio oil varies between 2 to 3.5. From the analysed result, the pH decreases in time of storage meaning the acid content in bio oil increases during storage. This is also due to reactive organic components in bio oil. The acidity of bio oil is due to high amount of carboxylic acid which are acetic acid and formic acid. This high corrosiveness of bio oil cause problems in storage and transportation part unless using stainless steel. Acidity of bio oil can be reduced in upgrading processes.

4.2.3 Water Content

Table 4.3 below shows data for bio oil water content throughout January 2010 till August 2010. Figure 4.3 displays water content result for heavy component while figure 4.4 displays water content result for light component.

Table 4.3: Water content result

DATE	Water Content (%)	
	HEAVY	LIGHT
8 Jan 2010	22.441	47.178
27 May 2010	22.830	47.183
13 Aug 2010	22.912	47.201

- **Heavy Component**

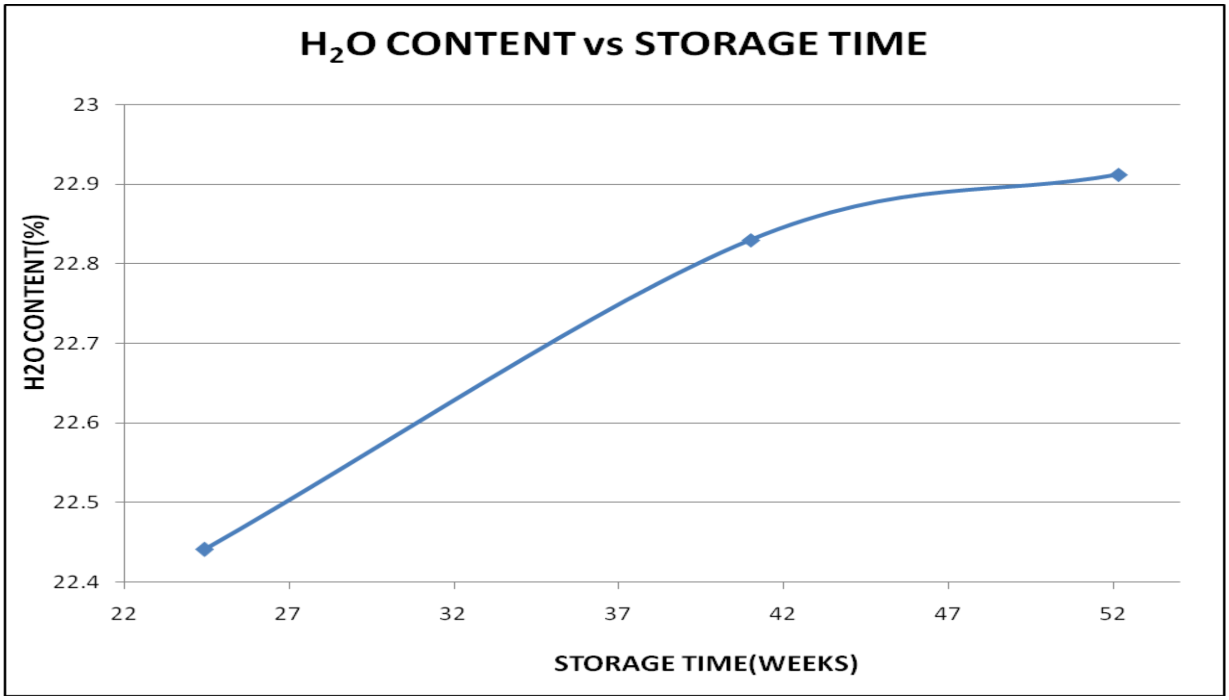

Figure 4.3: H_2O content graph for heavy component

- **Light Component**

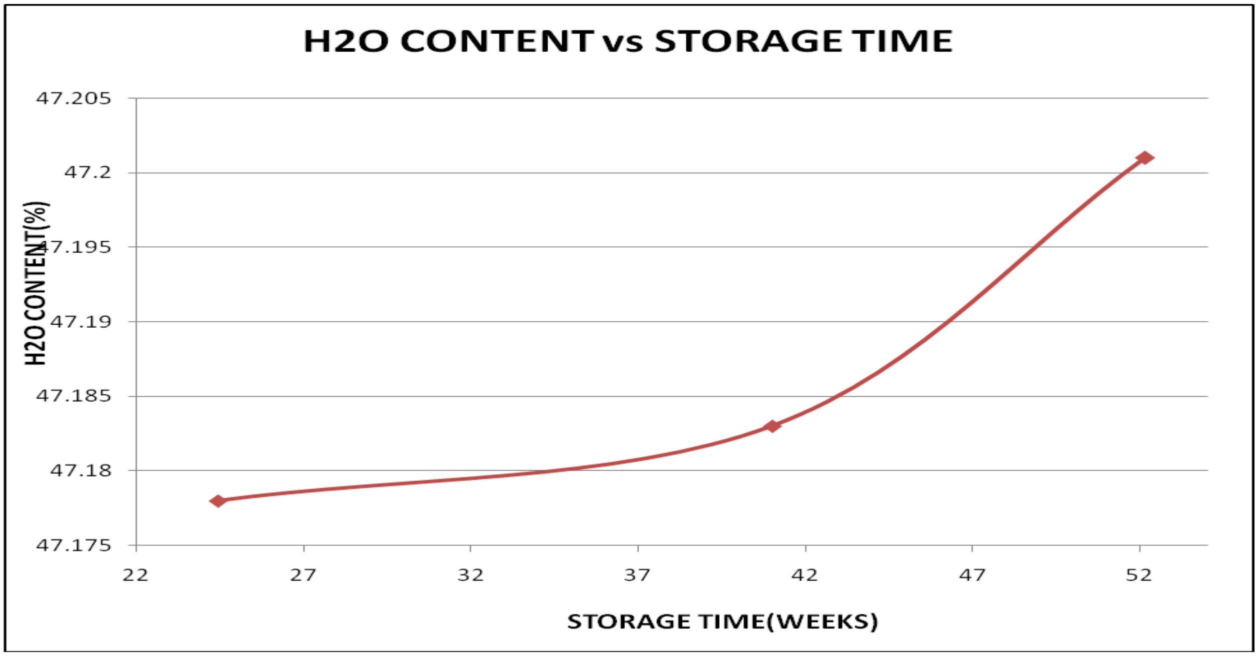

Figure 4.4: H_2O content graph for light component

When first produced, bio oil has very high content of water. The water come from moisture in feedstocks that bio oil been derives in pyrolysis process and also product from dehydration during pyrolysis process and storage. So, it keeps on increasing in time of storage. During storage, this pyrolysed oil will undergo reactions like esterifications in its components; carboxyl carbonyl and hydroxyl. Water is one byproduct from condensation reactions in bio oil. The increment of density, viscosity and water content during storage was due to condensation and polymerisation reactions. Polymerizations reaction will produce large molecules which have very poor mutual solubility with other components in bio oil. Water content has both advantage and disadvantage. It has advantage in improving its flow by reducing the viscosity but disadvantage in reducing the heating value of bio oil.

4.2.4 CHNS

Table 4.4 below shows data for bio oil water content throughout March 2010 till October 2010. Figure 4.5, 4.6, 4.7 and 4.8 display carbon, hydrogen, nitrogen and oxygen content result respectively for heavy and light component.

Table 4.4: CHNO result

DATE	CHNS (%)	
	HEAVY	LIGHT
9 March 2010	C – 65.37 H – 9.197 N – 0.571 O – 24.772	C – 50.72 H – 5.536 N – 1.704 O – 41.583
25 Aug 2010	C – 63.25 H – 8.401 N – 1.727 O – 25.637	C – 37.68 H – 4.641 N – 2.316 O – 42.389
20 Oct 2010	C – 60.25 H – 7.028 N – 2.183 O – 26.283	C – 35.19 H – 4.006 N – 2.989 O – 43.057

- **Carbon Content**

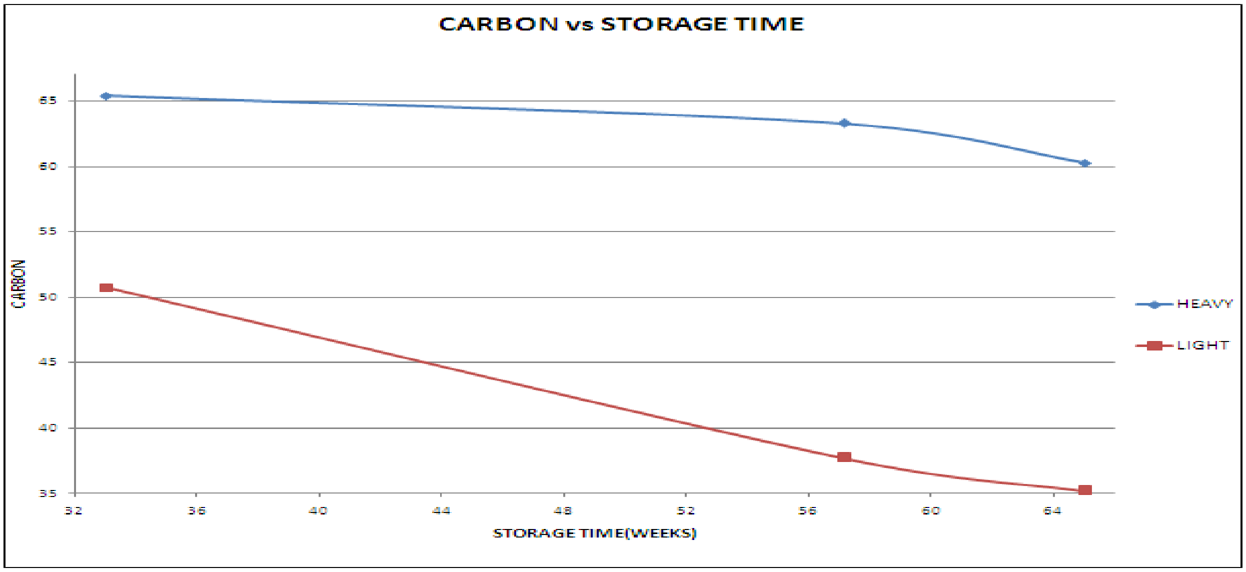

Figure 4.5: C content graph

Carbon content in bio oil decreases in time of storage. The decrement of carbon gives lower combustion energy advantage. But from graph, light component of bio oil shows very large decrement of carbon content. This will contribute to the low heating value of bio oil. In vice versa, the presence of long carbon chain lipids contributed to the high energy content of the bio-oil produced. The higher carbon content in heavy component compared to the light component may be due to the reaction that happened during the storage.

- **Hydrogen Content**

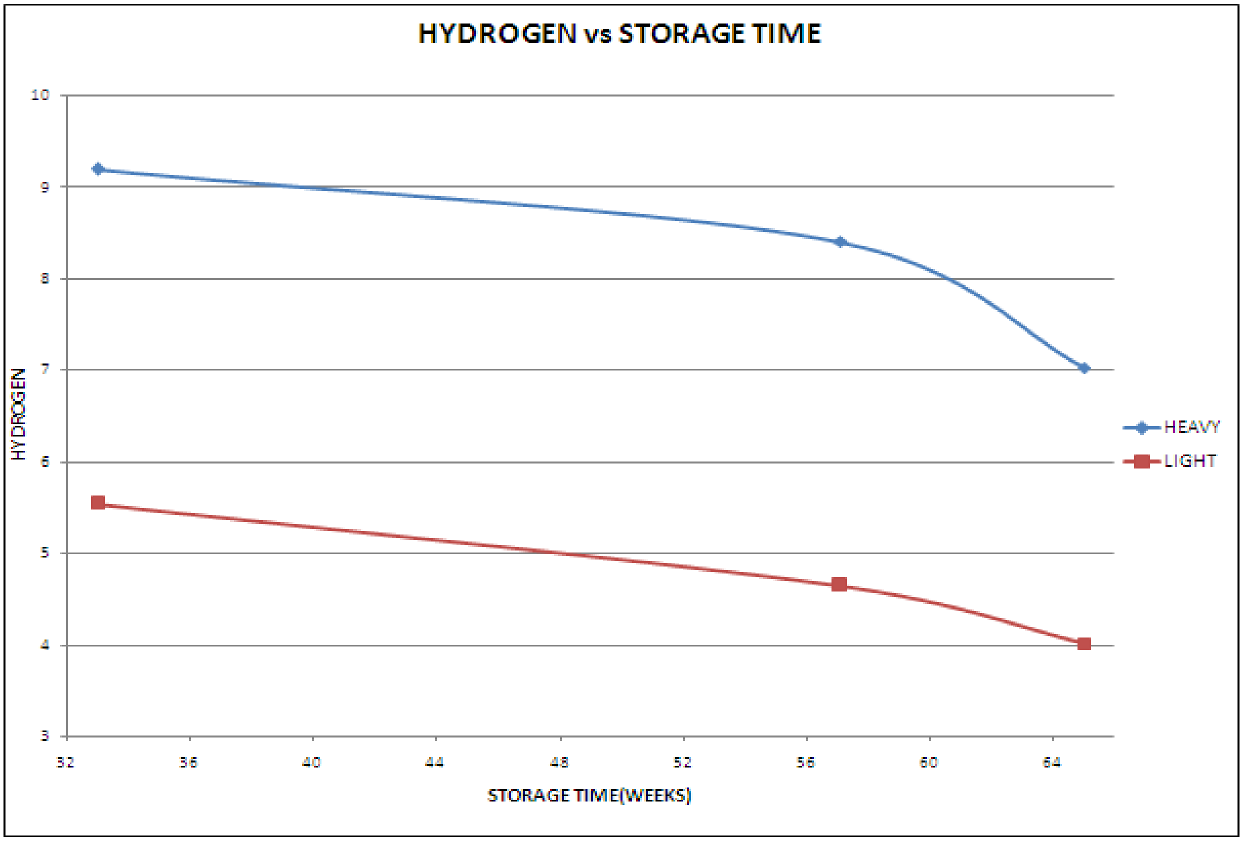

Figure 4.6: H content graph

Hydrogen content of bio oil in both components, heavy and light decreases in time of storage. This is because of large amount of hydrogen and oxygen react to form water that is partially dissolved in bio oil. This conversion to water is desirable because the oxygen content will decrease contribute to the high reading of C/O ratio that determine the energy content of bio oil.

- **Nitrogen Content**

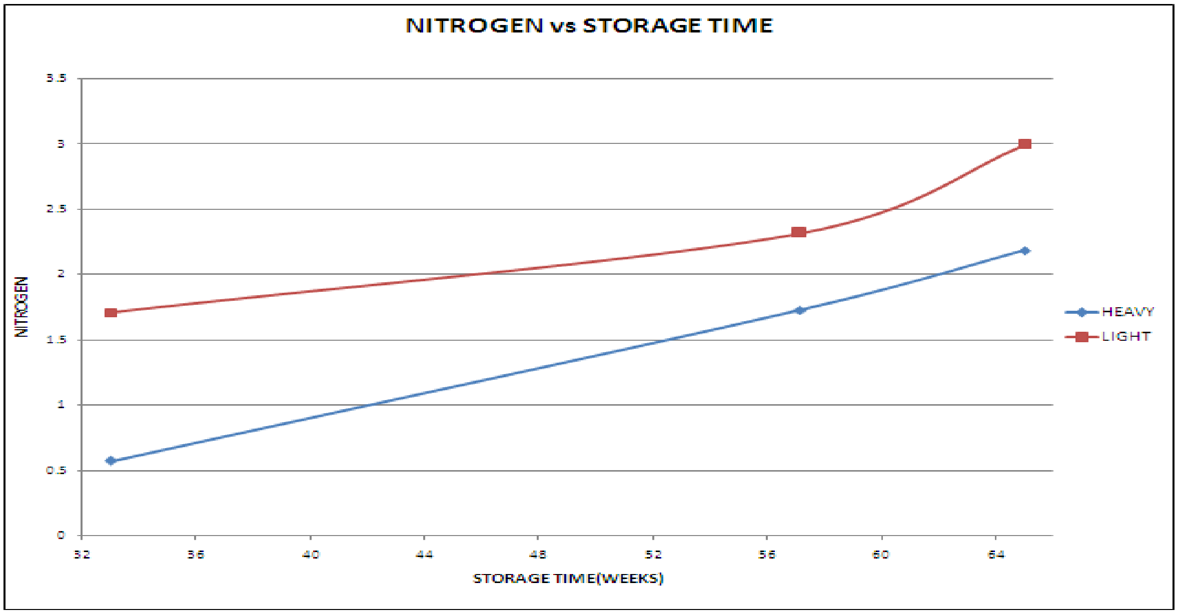

Figure 4.7: N content graph

Nitrogen content in both heavy and light component increases but value for heavy component is lower. This low nitrogen content in bio oil will reduce NO_x emission to the air. Due to this, bio oil is environmental friendly kind of oil.

- **Oxygen Content**

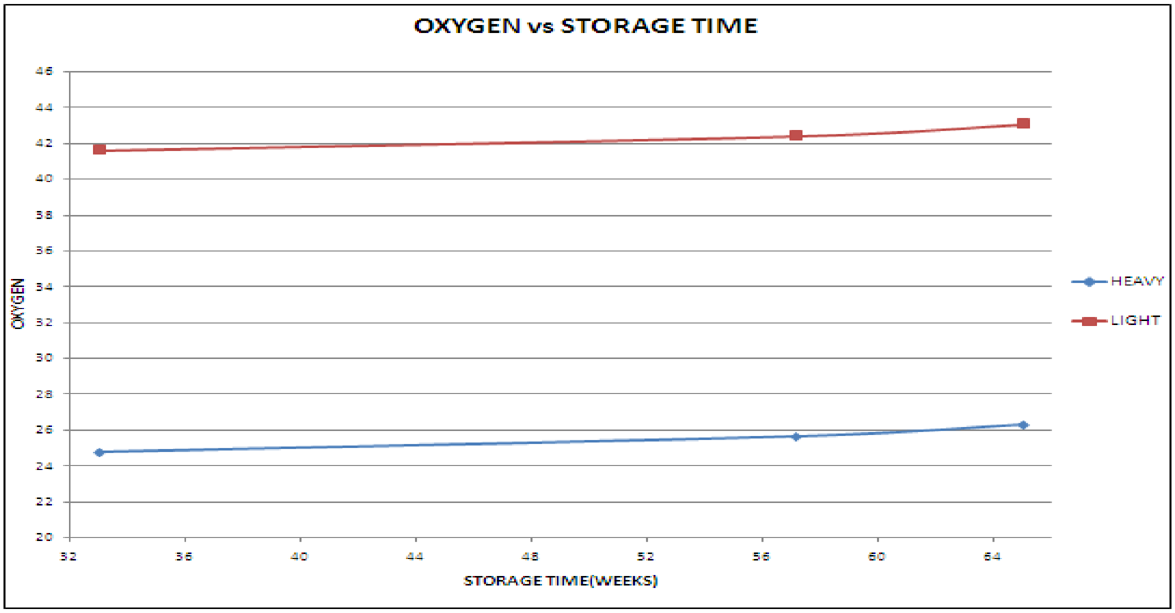

Figure 4.8: O content graph

The oxygen in bio-oils exists in a variety of functional groups such as hydroxyl, carboxyl, carbonyl and oxy groups. It is the presence of oxygen that is responsible for certain unfavourable properties of bio-oils such as low heating value and instability. Oxygen is present in most of the more than 300 compounds that have been identified in the oils. The distribution of these compounds mostly depends on the type of biomass used. The high oxygen content results in a low energy density (heating value) that is less than 50% of that for conventional fuel oils. Oxygen also is one important factor that contributes to the instability of bio oil. The oxygen content increment because of new compound generated by reaction in bio oil that consists of oxygen, precisely oxidation. High oxygen content will induce polymerization that increases the viscosity of bio oil.

4.2.5 Kinematic Viscosity

Table 4.5 and figure 4.9 below show data for bio oil viscosity result throughout August 2010 till October 2010.

Table 4.5: Viscosity result

DATE	Viscosity (cP)	
	HEAVY	LIGHT
24 Aug 2010	14.2	17.3
24 Sept 2010	15.8	18.4
1 Oct 2010	16.0	18.7

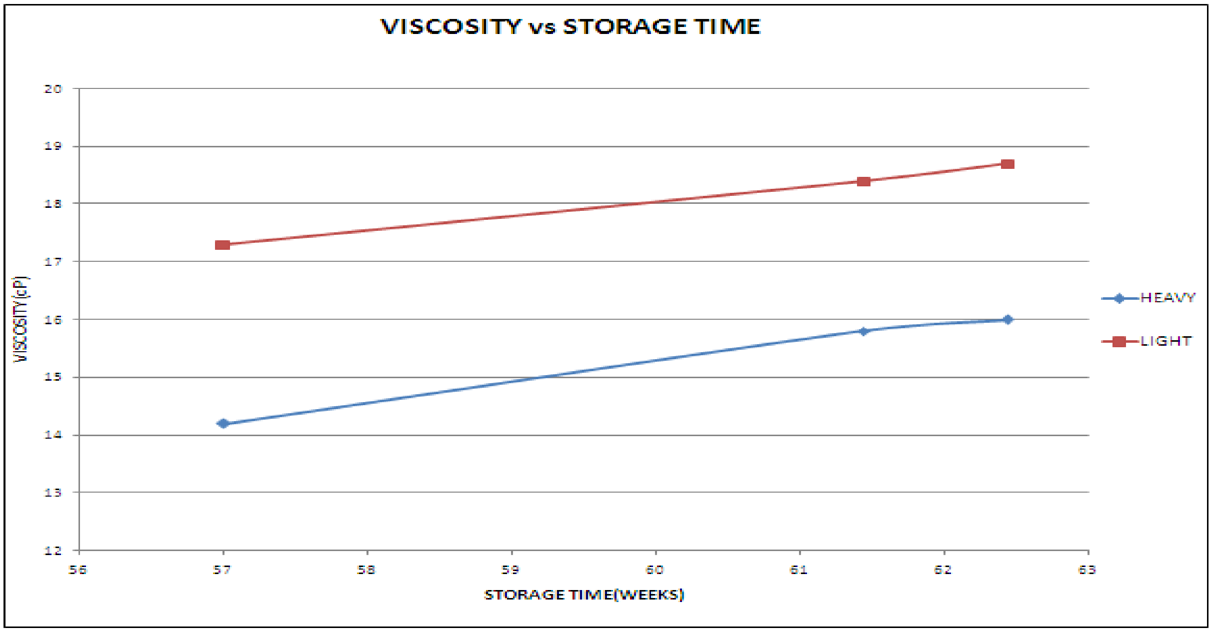

Figure 4.9: Viscosity graph

In time of storage, the viscosity of bio oil increase for both heavy and light components because of the polymerization that happened during ageing. The component of heterocyclic in bio oil makes it viscous and easily polymerized. Oxidation that happened also lead to polymerization. While thermal degradation that happened during storage generate partial decomposition of component that contribute to loss of volatiles that lead to high viscosity. Polymerization generates lignin-derived phenolic oligomers with large molecular weights in bio oil. The existence of these high MW compounds is one of the factors causing high viscosity. But it has been said that by increasing the temperature, the viscosity will be reduced because at low temperature, the high molecular weight component in bio oil tend to be in structured form. It can be concluded here that viscosity increment depends on the time of storage and measuring temperature.

4.2.6 Ash Content

Table 4.6 and figure 4.10 below show data for bio oil ash content result throughout April 2010 till October 2010.

Table 4.6: Ash content result

DATE	wt%	
	HEAVY	LIGHT
13 April 2010	0.053	0.311
2 Sept 2010	0.1327	0.5344
1 Oct 2010	0.1418	0.5502
21 Oct 2010	0.1493	0.5963

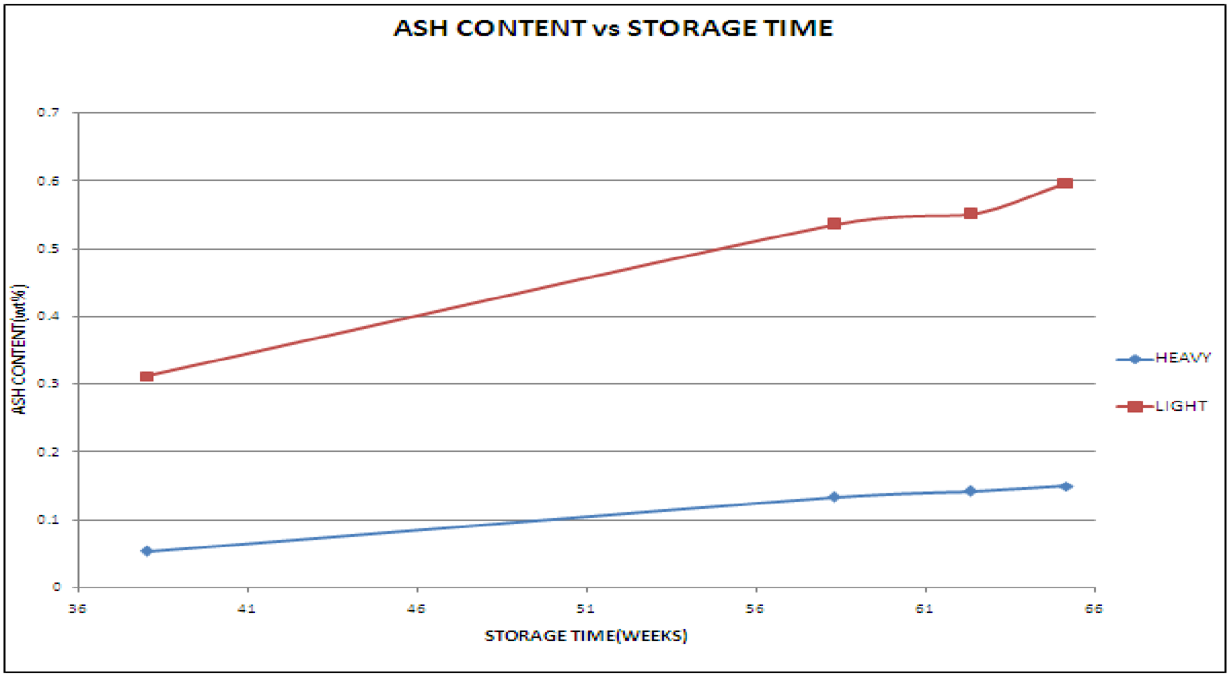

Figure 4.10: Ash content graph

Ash content in bio oil is derived from solid particles that existed in bio oil in early production. So, ash content depends a lot on the feedstocks or raw biomass material from bio oil derivation. The presence of solids and ashes is undesirable in bio oil. The ash content is lower for the heavy component, which contains a lesser amount of charcoal particles. In vice versa, light component has high content of ash content because light component has more solids particles than in heavy component that become residue after heating of bio oil. Ash content in bio oil that formed during combustion derived from inorganic compounds in bio oil. Agglomerations of solid particles in bio oil during ageing explain why the ash content in bio oil is increasing from time to time.

4.2.7 Gross Calorific Value

Table 4.7 below and figure 4.11 in the next page show data for bio oil high heating value (HHV) result throughout December 2009 till October 2010.

Table 4.7: Gross calorific value result

DATE	kJ/kg	
	HEAVY	LIGHT
24 December 2009	33,536.33	29,352
26 Aug 2010	29,476	24,330
1 Oct 2010	29,283	24,197

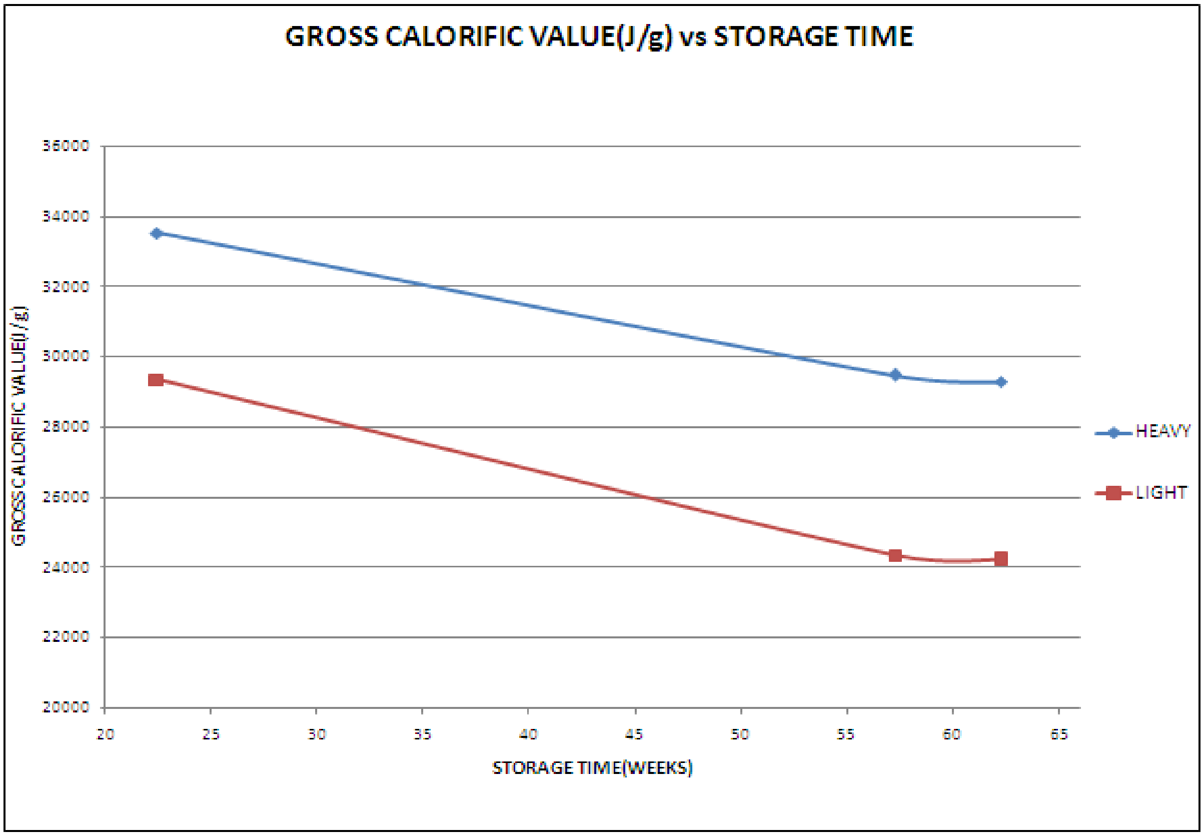

Figure 4.11: Gross calorific value graph

Gross calorific value is also known as high heating value. The heat produced by combusting a specific quantity and volume of fuel in an oxygen-bomb calorimeter under specific conditions. Heating value of bio oil decrease over time. The decrement is due to the increment of oxygen content in bio oil and the high water content that keep increasing time by time.

4.2.8 GCMS Analysis

Generally, components in bio oil consist of:

1) Phenol
2) 2-methyl-phenol
3) Decanoic acid, methyl ester
4) Decanoic acid

5) Pentanal
6) Tetradecanoic acid, methyl ester
7) Carboxylic acid
8) Hexanoic acid

Detail components of bio oil are attached in appendices.

GCMS (gas chromatography-mass spectrometer) analyzes the nature and type of organic compound in pyrolysis liquid product or bio oil. Generally, both heavy and light components have the same main compounds which are aldehyde (the most unstable), ketone, alcohol, acid, ester and many oxygenated compounds. But the area of each peak is depending on the reaction that happens in bio oil during storage. For an example, esterification that happened in bio oil during storage will produce more ester product and is reflected in the increase in ester area in GS-MS result. Same goes with the oxygenated compounds that become higher because of the oxidation that occured.

The main components in this Empty Fruit Bunches (EFB) bio oil are acids, phenols, ester, ketones and a few aromatics. These oxygenated compounds are attributable to hemicellulose and cellulose. Bio oil consists of cellulose, hemicellulose and lignin. Hemicellulose is linear polymers C_5 or C_6 compounds with lower degree of polymerization while cellulose is dehydrated glucose unit with degree of polymerization of 10 000. However, complete chemical characterization is impossible due to existence of pyrolytic lignin that derived from partial cracking of lignin molecules in bio oil. Lignin consists of random 3 dimensional structures of phenolic compounds. However, bio oil contains carboxylic acid (acetic acid and formic acid), carbonyl and an abundant amount of water.

4.3 Literature Comparison

Compared to the present results in chapter 3, the properties are more similar to heavy component as from the literature's reading also stated that heavy component's habit more to normal bio oil while light component has a lot of additives from the feedstocks. But the properties from this project is a bit off from the present results such as pH (from present result in chapter 3) is 3.4 while data gathering; chapter 4 found out that pH is 3.2. this is may be due to the research that started five months after the production process while the present result is taken right after the production.

The feedstocks is same which is EFB (empty fruit bunches) which is in this research is oil palm empty fruit bunches but the literature review did not state what type of EFB been used in the project. The differences also can be caused by the pyrolysis conditions involving temperature and pressure in the reactor. Further investigations can be done to compare the present results with the research's findings.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As the conclusion for this progress report, the objectives of this project has been accomplished to see bio oil stability during storage under room temperature. It can be seen from chapter 4 (result and discussion), the properties start to deteriorate from time to time. This will affect bio oil stability in trying to compare it with present fossil fuel. All characterizations had been done with correct steps. From the research, the chemical component in bio oil also has been identified. So, bio oil is not effective for long term storage. But from this stage, further improvement can be done such as reactive distillation in bio oil upgrading project. The second objective also been identified which is the component that can be removed is acid through esterification because bio oil has high amoun of carboxylic acid in it.

The recommendations that can be done to this project are to compare bio oil stability from EFB (empty fruit bunches) with bio oil originated other feedstocks as bio oil properties also dependable on feedstocks and pyrolysis conditions. Other bio oil properties also can be further studied during storage such as boiling point.

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APPENDICES

APPENDIX 1

1.1 GC-MS Analysis

1.1.1 Heavy Component

Molecular Formula	**Compound Name**	**Relative (%)**
$C_5H_8O_2$	Pentanal	0.50
$C_3H_6O_2$	Propanoic acid	0.87
$C_4H_8O_2$	1-hydroxy-2-butanone	0.16
$C_2H_4O_2$	Acetic acid	1.36
C_6H_6O	Phenol	11.53
$C_{16}H_{32}O_2$	Hexadecanoic-acid	0.92
$C_{12}H_{26}O$	2,6,8-Trimethyl-4-nonanol	0.21
$C_3H_6O_2$	Propanoic acid	0.93
$C_4H_6O_2$	Butyrolactone	0.04
$C_{17}H_{34}O_2$	Hexadecanoic acid, methyl ester	2.57
$C_{12}H_{24}O_2$	Dodecanoic acid	2.37
$C_3H_8O_2$	2-methoxyethan-1-ol	0.42
$C_8H_{10}O_3$	2,6-dimethoxyphenol	4.69
$C_4H_8O_2$	1,2-dimethoxyethene	0.7
$C_{14}H_{28}O_2$	Tetradecnoic acid	5.01
$C_5H_{10}O_2$	2-Furanmethanol	1.05
$C_{16}H_{30}O_2$	9-hexadecenoic acid	0.47
$C_7H_8O_2$	Phenol,2-methoxy-	3.05
C_7H_8O	Phenol,2-methyl-	1.54
$C_6H_8O_2$	1,2-cyclohexanedione	0.06
$C_{18}H_{36}O_2$	Octadecanoic acid	0.57
$C_{19}H_{34}O_2$	9,12-octadecadieonic acid, methyl ester	1.04
C_4H_6O	2,3-dihydrofuran	0.37
$C_{13}H_{26}O_2$	Dodecanoic acid	31.36
$C_{19}H_{38}O_4$	Hexadecanoic acid	1.06
$C_{19}H_{36}O_2$	9-octadecenoic acid, methyl ester	1.75
C13H26O2	Dodecanoic acid, methyl ester	5.82
C17H34O2	Heptadecanoic acid	2.07
C19H34O2	9,12-octadecadieonic acid, methyl ester	0.97
C10H20O2	Decanoic acid	1.09

$C_{11}H_{22}O_2$	Decanoic acid, methyl ester	0.83
$C_{15}H_{32}$	Pentadecane	1.19
$C_{13}H_{28}$	Tridecane	0.59
$C_{17}H_{34}$	Heptadecene	0.52
$C_{15}H_{30}$ O_2	tetradecnoic acid, methyl ester	2.59
	Other compounds(aromatics, nitrogen)	9.73

1.1.2 Light Component

Molecular Formula	**Compound Name**	**Relative (%)**
$C_4H_8O_2$	2-furanol, tetrahydro	0.03
$C_2H_4O_2$	Acetic acid	1.74
C_6H_6O	Phenol	10.94
$C_3H_6O_2$	2-propanone, 1 -hydroxy-	0.16
$C_4H_6O_2$	Acetic acid ethenyl ester	0.84
C5H10O2	2-Furanmethanol	0.47
C16H32O2	Hexadecanoic-acid	0.83
$C_3H_8O_2$	ethanol, 2-methoxy-	0.14
$C_4H_8O_2$	Formic acid, propyl ester	4.48
$C_6H_8O_2$	1,2-cyclopentanedione, 3-methyl-	0.23
$C_{16}H_{30}O_2$	9-hexadecanoic acid	3.79
c3h6O	acetone	2.85
$C_6H_6O_2$	1,2-Benzenediol	0.06
$C_4H_8O_2$	1-hydroxy-2-butanone	0.26
$C_8H_{10}O_3$	Phenol, 2,6-dimethoxy-	2.38
C4H8O3	Acetic acid, methyl ester	0.83
C5H12O	3-methyl-1-butanol	0.04
C13H26O	2-tridecanone	0.34
CH2O2	Formic acid	4.35
$C_7H_8O_2$	phenol,2-methoxy-	3.46
$C_3H_6O_2$	2-propanone, 1 -hydroxy-	0.35
C_7H_8O	Phenol,2-methyl-	0.57
C4H6O3	Butyrolactone	0.48
$C_5H_8O_3$	2-propanone, 1-(acetyloxy)-	0.25
C_7H_8O	Phenol,3-methyl-	0.39
$C_{15}H_{30}O_2$	pentadecanoic acid	0.86
C13H26O2	Dodecanoic acid, methyl ester	4.06
$C_{12}H_{24}O_2$	Dodecanoic acid	3.95
$C_{16}H_{32}O_2$	n-hexadecanoic acid	35.89
$C_{16}H_{30}O_2$	9-hexadecanoic acid	0.38
$C_3H_8O_2$	ethanol, 2-methoxy-	1.74
	Other compounds(aromatics, nitrogen)	12.86