Stabilization of Empty Fruit Bunch (EFB) Derived Bio-oil

by

Yiin Chung Loong

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

MAY 2013

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

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May 2013

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 contained herein have not been undertaken or done by unspecified sources or persons.

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(YIIN CHUNG LOONG)

ABSTRACT

Bio-oil is a promising alternative source of energy which can be produced from empty fruit bunch (EFB). Bio-oil comprises a mixture of highly oxygenated compounds, carboxylic acids and trace water. Bio-oil can be used as a substitute for conventional fuels after it is upgraded. However, bio-oil can react through many chemical reactions such as polymerization and this will lead to the increase in viscosity of bio-oil during storage. Thus, this research project will explore on the stabilization of empty fruit bunch derived bio-oil. The bio-oil that will be used in this research is produce from the catalytic pyrolysis of EFB. The optimum reaction condition used is catalytic pyrolysis of EFB using 5 wt% of H-Y catalyst at reaction temperature of 500 ℃ and nitrogen flow rate of 100 ml/min. This operating condition is able to obtain the maximum yield. There are 2 type of methods will be used in this research to improve the stability of the bio-oil: addition of anti-oxidants and addition of solvents. For the addition of anti-oxidants, three kinds of anti-oxidants which are propyl gallate (PG), tert-butyl hydroquinone (TBHQ), butylatedhydroxyanisole (BHA) and calcium chloride salts (CaCl2) are added to bio-oil in the amount of 1000 ppm. On the other hand, the second methods will use 10 wt% of solvents including acetone, ethanol 95 %, and ethyl acetate to increase the bio-oil's stability. All the test samples are subjected to accelerated aging involving exposure to high temperature of 80 ^{o}C for 7 days. The properties of samples which are chosen as the indicator of the aging are viscosity, water content and acidity. This progress report contains 6 chapters. Chapter 1 will discuss the introduction on the background, problem statement, objective and the scope of study for the project, relevancy of the project and feasibility of the project within the scope and time frame. A detailed literature review will be discussed in chapter 2. Besides, chapter 3 will focus on the research methodology and also the key milestones for the project in order to give a detail overview of the whole research project. Chapter 4 will be the results and discussion for the research project. Chapter 5 and 6 are the conclusion and references respectively.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my deepest gratitude to **AP. Dr. Suzana Yusup**, my Final Year Project (FYP) supervisor for her valuable guidance and advice when working on this project. During this period, her willingness to guide and motivate me had contributed tremendously to make this project smooth and a success. Besides, my deepest appreciation goes to the FYP coordinator, Dr. Nurhayati Mellon for providing sufficient information required in completing this project. My sincere thanks to the Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP) for offering me a great opportunity to undertake this project using the knowledge and skills learned in the university.

Apart from that, I would also like to take this opportunity to express my appreciation to **Kelvin Chan Yi Herng** and **Dang Khanh Vi**, Masters students assigned by AP. Dr. Suzana to assist me throughout the entire study. They put forth a great effort in helping me to understand the background of my project, obtaining the chemicals and materials needed for my experiments, and analyzing the findings of my study. They also give me their advices and knowledge based on their previous experience with Final year Project. Last but not least, I would like to thank all the **lab technicians** who have assisted me a lot in my lab work.

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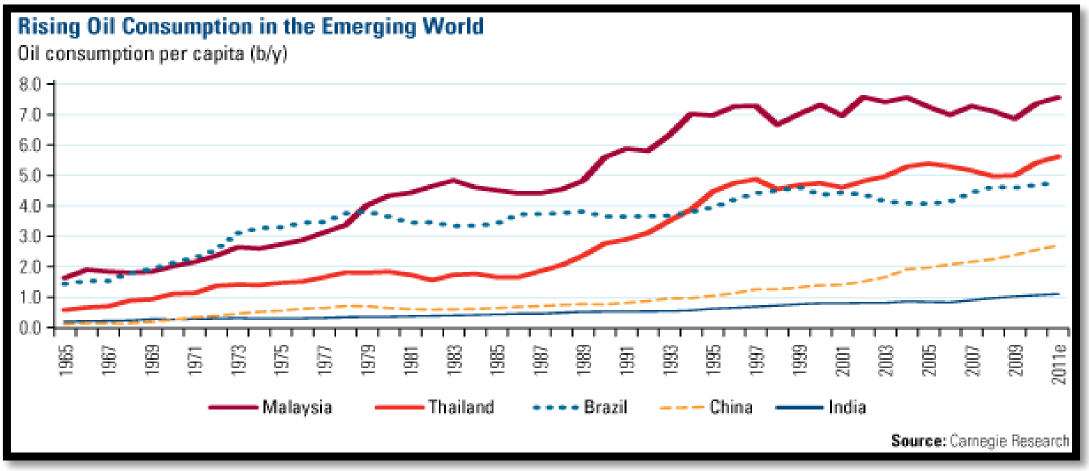
CHAPTER 1

PROJECT BACKGROUND

1.1 Background Study

The use of renewable energy sources is becoming increasingly important to achieve the changes, required to address the impacts of global warming (Heinzerling 2010). Figure 1 below shows the demand of fossil fuels in five countries which are Malaysia, Thailand, Brazil, China and India. Malaysia has the highest oil consumption per capita among the five countries. Hence, renewable fuels from biological sources such as biodiesel, bioethanol and pyrolysis liquid are becoming more crucial.



Source: Carnegie Research

Figure 1 Demand of fossil fuel

Biomass is the most common form of renewable energy and generates very low net greenhouse emissions. The energy from biomass can be obtained by various techniques, such as combustion or by upgrading it into a more valuable fuel, gas or oil. Biomass can also be transformed into a source of value-added products for the chemical industry by using a thermochemical method such as pyrolysis of bio-oil.

Furthermore, as pointed out by (Chang 2008), biomass utilization is carbon neutral as it does not emit additional carbon dioxide and carbon monoxide (greenhouse gases), NO_x and SO_x into the atmosphere, saving the usage of limited fossil fuels as well as reduce environmental pollution. Bio-oil is dark brown, free-flowing organic liquids that comprise highly oxygenated compounds. It contains compounds such as aldehydes, ketones, carboxylic acid, alcohol, phenolics and water. Presence of various reactive species in bio-oil can contribute to the unstability. The aging of bio-oil depends on the chemical composition of the bio-oil and the storage conditions. Temperature is the most important factor which accelerates the rate of aging. The aging reactions will result in undesirable physical properties which are increase in viscosity and water content. Hence, the stabilization of bio-oil as renewable energy is very critical in overcoming the global depletion of fossil fuels. The bio-oil used in this research is produce from the catalytic pyrolysis of Empty Fruit Bunch (EFB). (Heinzerling 2010)

1.2 Problem Statement

Upgraded bio-oil can be used as a substitute for conventional fuels. Most of the projects involved bio-oil requires that it retain these initial physical properties during storage. Unfortunately, the viscosity of some bio-oils will increase rapidly during storage. Thus, stabilization of EFB derived bio-oil is needed before proceed for further upgrading.

Problem Statement: What additives can be used to stabilize the EFB derived bio-oil and what is the optimum condition to study the accelerated aging of bio-oil and measure its properties?

1.3 Objective and Scope of Study

The objective of this project is to select the optimum condition to study the accelerated aging of bio-oil as well as to study the effects of addictive in stabilizing the bio-oil. The upgraded bio-oil should have higher stability than the original bio-oil such as lower value of viscosity, water content and acidity.

Table 1 shows that the bio-oils have the following undesired properties for fuel applications when compared to petroleum fuel oil: (1) high water content (2) high viscosity (3) high oxygen content (low heating value). These undesired properties have limited the range of bio-oil application. The differences in processing conditions and feedstock result in significant differences in the product yield and product composition of bio-oils. Due to the unique composition, bio-oil is highly oxygenated, acid and corrosive to common materials, thermally and chemically instable, as well as non-miscible with petroleum fuels. These poor fuel properties make bio-oil only possible to be used in boilers and furnaces, but hard to be directly used in diesel engines and gas turbines. To overcome these disadvantages, various physical or chemical methods have been proposed to upgrade bio-oil.

Table 1 Physical properties of bio-oil and petroleum fuel

Physical Property	**Value**		
	Bio-oil (Jatropha)	**Bio-oil (EFB)**	**Petroleum fuel**
Moisture content (wt%)	15-30	50	0.1
Heating value (MJ/kg)	16-19	10.43	40
Viscosity at 40^{o}C (cP)	40-100	45.47	18
Elemental composition (wt%)			
• Carbon	54-58	25.33	85
• Hydrogen	5.5-7.0	9.317	11
• Oxygen	35-40	64.59	1.0
• Nitrogen	0-0.2	0.32	0.3

As such, the scope of this project is to study the accelerated aging of EFB derived bio-oil at 80 ^{o}C in a sealed container for 1 week by:

1. Addition of solvents (10 wt%): acetone, ethanol 95 % and ethyl acetate.
2. Addition of anti-oxidants (1000 ppm): propyl gallate (PG), tert-butyl hydroquinone (TBHQ), butylatedhydroxyanisole (BHA) and calcium chloride salts (CaCl2).

and the aspects being studied are:

1. Effect of solvents and anti-oxidants on viscosity, water content and acidity of EFB derived bio-oil.
2. Percentage change in viscosity, water content and acidity of bio-oil with and without additives for 7 days.

1.4 Relevancy of the Project

The earth is expected to run short of its present sources of energy like petroleum, coal and charcoal. Though there may be shortage of energy, the need for energy will never go down; in fact, it's escalating day by day. In addition, most of the sources of energy nowadays are non-renewable. Today one of the best forms of renewable and alternative energy is bio-oil. Direct use of pyrolysis oil in prime movers has been proven possible in few short duration tests, but required significant modification to the engine in order to comply with stringent material compatibilities and requirements posed by the very specific chemical-physical characteristics of bio oil and to limit material erosion and corrosion physical and chemical bio-oil. Thus, several upgrading technologies have been tested at a laboratory scale.

Hence this project is mainly studying the method of adding antioxidants and solvents in order to stabilize the bio oil. Overall, bio-oils cannot be directly used as transportation fuels due to their high viscosity, high water and ash contents, low heating value, instability and high corrosiveness. Therefore, upgrading of bio-oil is needed to improve its properties for liquid fuel. Since there are still many researches are still carry on, hence this project has been relevant and there are lots of improvements and developments can be done.

1.5 Feasibility of the Project within the Scope and Time Frame

This project is feasible within the objective stated clearly and the scope specified as well as the timeframe since it is practical and realizable in terms of all aspects of its experimental setup, methodology to be used and the chemical substances to be used throughout the project. Before starting up with the project a lot of literature reviews had been done regarding on the background study of bio oil and upgrading technique of bio oil as well as the applications of bio oil in current modern days.

Based on the reviews done previously, the knowledge obtained can be applied in determining the appropriate upgrading techniques to be used in order to stabilize the bio oil before studying for its aging properties at 80 °C. In terms of scope of study, the project is feasible to be carried out in UTP as it has the required apparatus and equipment to run the pyrolysis reaction and stabilization. The main equipment such as the reactor (tube furnace reactor) and characterization equipment are available. Furthermore, EFB from the palm oil plantation and methanol as a solvent for cleaning the reactor and apparatus can be obtained as well. The scope of study chosen is also similar to other related researches done. So, it is relevant and can be used to compare directly with other literature readings.

Hence, this research project is feasible within the time frame and the scope of study. Strategic planning on the execution is needed for this research project to be completed on time and successfully.

CHAPTER 2

LITERATURE REVIEW

2.1 Bio-oil

Bio-oil is a dark brown, free flowing liquid organic liquids. It is comprised of highly oxygenated compounds with an unpleasant odour which is normally produced from a process called pyrolysis. Pyrolysis can generally be divided into two types; fast pyrolysis and slow pyrolysis. (Brown 2011) pointed out that these two pyrolysis reactions are different mainly in terms of heating rates and maximum reaction temperatures. Pyrolysis is a process of thermochemical decomposition of organic material in the absence of oxygen under a certain pressure and operating temperatures above 500°C (Abdullah 2008, Pattiya 2010).

Figure 2 Bio-oil

According to (Nilsen 2007), the main components of the aqueous phase are oxygenated organic compounds of lower molecular weight (such as phenols, cresols, benzenedioles, and their alkylated products), and mainly aromatics (such as benzene, toluene, indene and other polycyclic aromatic hydrocarbons) are found in the nonaqueous phase. However, as pointed out by (Iliopoulou 2012), raw bio-oil that has not been upgraded yet has several undesired characteristics; high water and oxygen content, corrosive, instable under storage and heating conditions, high viscosity, low calorific value and immiscible with petroleum fuels.

Bio-oil is a type of substitution for fossil fuel which can pump well, burn readily and ignite once it is atomized. Bio-oil requires more experimental researches and upgrading to improve its stability before it can be used to replace fossil fuel. Malaysia has the world’s second largest production of palm oil which covers about 59% of the world’s needs and 23% of empty fruit bunch (EFB) can be obtained from substantial fresh fruit bunch mass produced. From here it can be seen that empty fruit bunch can be utilized to be the feedstock for biomass pyrolysis. The reaction condition for the bio-oil used in this project are 5 weight percent (wt%) of H-Y catalyst at temperature of 500 ℃ and nitrogen flow rate of 100 ml/min. (Y.H. Chan 2013).

As a result of the instability, the bio-oil aging is occurring, causing the viscosity of the bio-oil to increase. This instability can actually be minimized or decreased either through the stabilization process after pyrolysis (through upgrading), or modification to the pyrolysis process to reduce the amount of oxygenated compound formed (catalytic pyrolysis or hydrotreating). However, according to (Yorgun 2008), catalytic pyrolysis is preferable because no H2 gas is required as in the case of hydrotreating and the atmospheric processing conditions offers processing and economic edges over hydrotreating.

Catalytic pyrolysis is a variant to the current pyrolysis process whereby it offers advantages over slow pyrolysis. As slow pyrolysis reaction requires at least several minutes, the reaction can be improved and enhanced by the introduction of catalyst. Since pyrolysis requires the breaking of carbon-carbon bonds, the introduction of catalyst is able to catalyze the reaction, facilitating the cracking reactions and de-oxygenation reaction, improving the quality of bio-oil produced compared to that of slow pyrolysis and it makes downstream upgrading processes less expensive (Gopakumar 2011). This process is able to remove oxygenated groups in bio-oil and improves the stability of bio-oil (Putun 2010). Introduction of catalyst in catalytic pyrolysis will decrease the amount of organic yield (bio-oil) and increase the amount of gas yield, water content and polyaromatic hydrocarbons (PAHs). This is explained by (French 2010) in his work, which pointed out that the oxygenated compounds in the bio-oil will undergo dehydration, decarboxylation, cracking, aromatization, alkylation, condensation and polymerization with deoxygenation simultaneously. Higher water content will reduce the higher heating value of the bio-oil (Crocker 2010).

Bio-oil can be used in various industries. The application of bio-oil is shown in Figure 3 below.

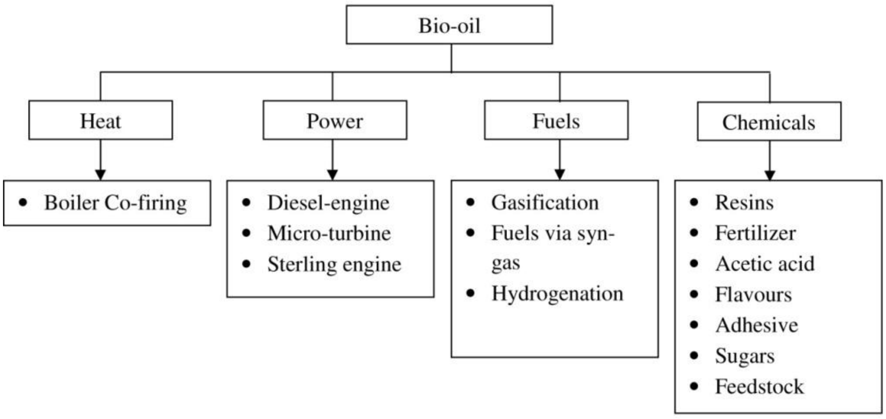


Figure 3 General overview of bio-oil's applications

2.2 Aging of bio-oil

Bio-oil is very unstable due to its reactive organic compounds. The aging of bio-oil depends on the chemical composition of the bio-oil and the storage conditions. Lignin compound will be formed in bio-oil after it is left for a few weeks or months. During storage the reactive components can interact to form larger molecules and altered its properties due to oxidation and thermal degradation.

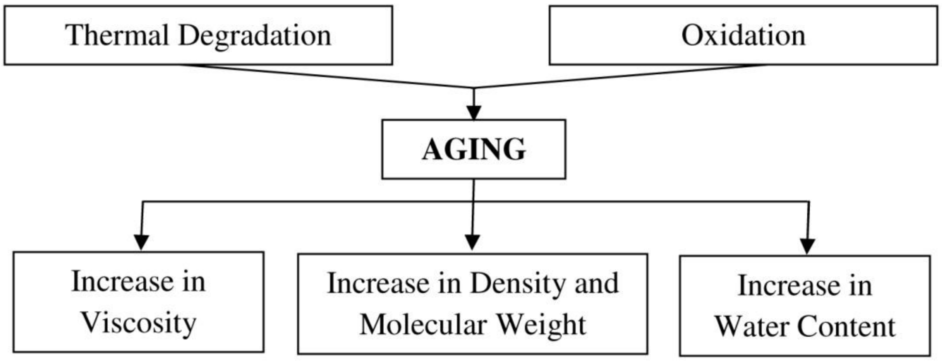


Figure 4 The factors and the effects of aging

Oxidation leads to polymerization resulting in the increase of viscosity. On the other hand, thermal degradation leads to partial decomposition of components and can result in loss of volatiles which further cause the bio-oil's viscosity to increase. The high-molecular-mass (HMM) fraction of water-insolubles which are lignin-derived material will be increased due to polymerization and condensation reactions of carbohydrate constituents, aldehydes and ketones. Increment of high-molecular-mass (HMM) lignin fraction will increase the density of bio-oil as well. This phenomenon is due to the reason that of molecular weight increases during storage results from etherification and esterification occurring between hydroxyl, carbonyl and carboxyl group components. Condensation reactions in bio-oil will result in the formation of water as byproduct and further reduces its heating value (L. Moens 2009). Besides, the most important factor driving the aging rate is temperature. Heating bio-oil to 60 ^{o}C or higher will promote internal reactions and polymerization that can be significant over a prolonged period (Corporation 2006).

Using a bio-oil made from oak at the National Renewable Energy Laboratory (NREL), the viscosity and weight average molecular weight both increased with time. Gel permeation chromatography which can be used in detecting the aromatic compounds showed that aging decreased the amount of lower molecular weight material (mw between 100 and 300) and increased the higher molecular weight material (mw between 300 and 10,000). The weight-average molecular weight of aromatic fraction increased from 530 to 990. Analysis for water content using Karl Fischer titration showed an increase in water content of 1.6% during aging at 60 ^{o}C and 90 ^{o}C. Besides, analysis by Fourier transform infrared spectroscopy (FTIR) of the bio-oils revealed an increase in water, an increase in carbonyls and ethers after aging. The carbonyls may have been the product of oxidation or from the hydrolysis if acetals to form aldehydes and alcohols. The formation of additional aldehyde hydrates or an equilibrium shift from acetals to hemiacetals may have kept the water content from increasing more (Diebold 1999).

On the other hand, analysis by gas chromatography with mass-spectrometric detection (GC/MS) of bio-oil made from poplar at NREL revealed that the levels of hydroxyacetaldehyde, propeal (acrolein), 2-methoxy-4-propenylphenol and 5-methylfurfural quickly decreased during aging in both neat bio-oil samples and methanol/oil samples (Diebold 1999). Therefore, antioxidants and solvents play an important role in maintaining the bio-oil's stability. Generally the antioxidants used are monohydroxy or polyhydroxy phenol compounds with various ring substitutions. These antioxidant compounds have low activation energy to donate hydrogen in order to affect the propagation of the free radical chain. This can help to delay the beginning of the aging or slow the rate of chemical reaction (M. Mittelbach 2003). Three commercial antioxidants that used for oxidation inhibitor in biodiesel based Jatropha oil were propyl gallate (PG), t-butyl hydroquinone (TBHQ) and butylatedhydroxyanisole (BHA) (D. Chaithongdee 2009). For another approach, organic solvents can also inhibit the chain of polymerization by converting the active units in the oligomer chain to inactive units. The solvents most probably react to form low molecular weight products. Table 2 below shows the summary of stabilization of bio-oil which indicates the operating of condition used for aging of bio-oil and the materials used to stabilize the bio-oil with respective effect. The parameters used in the red highlighted row are applied in this research project as it has the most suitable period and temperature for aging as well as the materials in stabilizing the EFB derived bio-oil.

Table 2 Summary of stabilization of bio-oil

Title	Material	Effects	Temperature	Storage time	Amount
Effect of antioxidants and additives on the oxidation stability of jatropha biodiesel (D. Chaithongdee 2009)	Anti-oxidants (PG, TBHQ, BHA) Additives (ZEP addictive, NITROX and L-power)	Anti-oxidants (oxidation stability increased with increases in the antioxidant concentration) Additives (did not improve the oxidation stability of Jatropha biodiesel)	30°C	20 weeks (examine every 2 weeks)	Anti-oxidants (0-750ppm) and additives (0-1000ppm)
Towards stabilization of bio-oil by addition of antioxidants and solvents (P. Udomsap 2011)	Anti-oxidants (PG, BHA, TBHQ) Solvents (acetone, biodiesel, ethanol, ethyl acetate and methanol)	Anti-oxidants (decreases the rate of the viscosity increase and reduce the acidity) Solvents (decreases the rate of the viscosity increase and increases the flash point for alcohol, acetone and ethyl acetate)	80°C	5 days (examine everyday)	Anti-oxidants (1000ppm) and solvents (10 wt%)

Additives to lower and stabilize the viscosity of pyrolysis oil during storage (J.P. Diebold 1997)	Ethyl acetate, methyl isobutyl ketone, acetone, methanol and ethanol	Lowered the initial viscosity at 40 ^{o}C by half and reduced the rate of aging	90^{o}C	96 hours (examine everyday)	10 wt%
Storage stability and aging effect of biodiesel blends treated with different antioxidants (Georgios Karavalakis 2011)	BHT, TBHQ, BHA, PG and PA	Butylated hydroxytoluene (BHT) and butylated hydroxyanisol (BHA) displayed a greater stabilizing potential in biodiesel blends. Propyl gallate (PG) and pyrogallol (PA) additives showed the strongest effectiveness in both the neat	Fully exposed to daylight	10 weeks (examine every 2 weeks)	1000ppm

Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase (M.E. Boucher 2000)	Methanol and pyrolytic aqueous phase	Methanol (reduces the viscosity, density, increases stability and slightly reduces the heating value) Pyrolytic aqueous phase (no significant effect on viscosity but beneficial for other properties)	80°C	5 days (examine everyday)	10 wt%
A rapid method for evaluation of the oxidation stability of castor oil FAME (Celio L. Cavalcante Jr. 2009)	DBPC, TBHQ, BHA and PG	BHA and PG shows an increase in oxidative resistance TBHQ and DBPC shows just moderate performance when compared to other antioxidants	120 ℃, 140 ℃ and 160 ℃	10 hours (examine every 2 hours)	3000-4000ppm

CHAPTER 3
METHODOLOGY

3.1 Research Methodology and Project Activities

Reading and reviewing materials is the most widely used methodology for this project. First of all, we need to understand the basic conceptual and fundamental of the project background before reading and reviewing research papers. All of these give a full insight in carry out the project. After extract the useful and important information from literature reviews, next step should be specifically listing all of the work areas in research and put them in order of priority. In conclusion, reading and reviewing is the main research methodology employed in this project. The knowledge and information obtained through reading and reviewing forms the main core of this project.

After a detailed literature review is done, the following project activities in this research are mainly involved experimental work. Experimental works can be conducted to investigate the optimum amount of anti-oxidants and solvents used to stabilize the bio-oil produced from EFB as well as to determine the most effective anti-oxidant and solvent. It is very important to estimate the time that will be needed to accomplish each research activity. Thus developing a Gantt chart by cross-referencing the work areas with the number of weeks does help to make sure the progress of project is kept on the right track.

3.2 Experimental Procedures/Approach

After reviewing on research papers it comes to the next procedure to set up the experiment. The preparation of experimental study is appropriate for a particular research problem usually will involve the consideration of the following:

(a) Collecting data

Having formulated the research problem, developed an experimental set up, constructed a research instrument and selected a sample, after that collect the data from which the process of drawing inferences and conclusions for project study.

(b) Processing and analysing data

Processing and analysing data involves a number of closely related operations which are performed with the purpose of summarizing the collected data and organizing these in a manner that they answer the research questions (objectives).

(c) Reporting the findings

Writing the report is the last, and for many, the most difficult step of the research process. The reports include what have been done, what have been discovered and what conclusions have been drawn from findings.

The figure below shows the general experimental procedures that will be implemented in this research project.

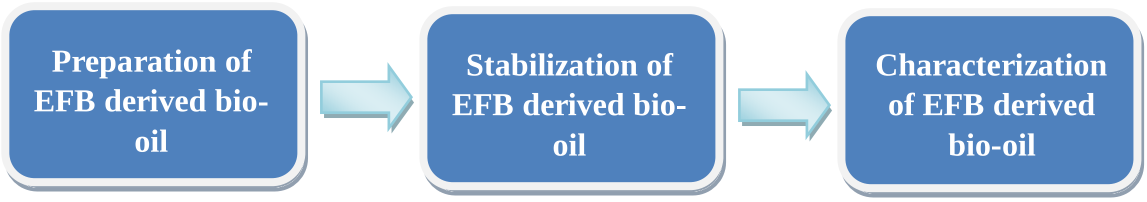


Figure 5 The schematic diagram depicting the general approach in this project

3.2.1 Raw Materials and Chemicals Needed

The raw materials and chemicals that are needed in conducting the experiments are listed as below:

i. Preparation of EFB derived bio-oil
    - Empty Fruit Bunch (EFB) - obtained from plant
    - Catalyst - H-Y zeolite
    - Methanol - cleaning purpose
    - Nitrogen flow - used in the reactor as inert gas flow

ii. Stabilization of EFB derived bio-oil

  - Anti-oxidants: propyl gallate (PG), tert-butyl hydroquinone (TBHQ), butylatedhydroxyanisole (BHA) and calcium chloride salts (CaCl2).
  - Solvents: acetone, ethanol 95 % and ethyl acetate.

3.2.2 Setup of Experiment

3.2.2.1 Preparation of EFB derived bio-oil

The reactor used for the preparation of EFB derived bio-oil will be a semi-batch reactor in UTP. The layout of the reactor is shown in the Figure 6 below:

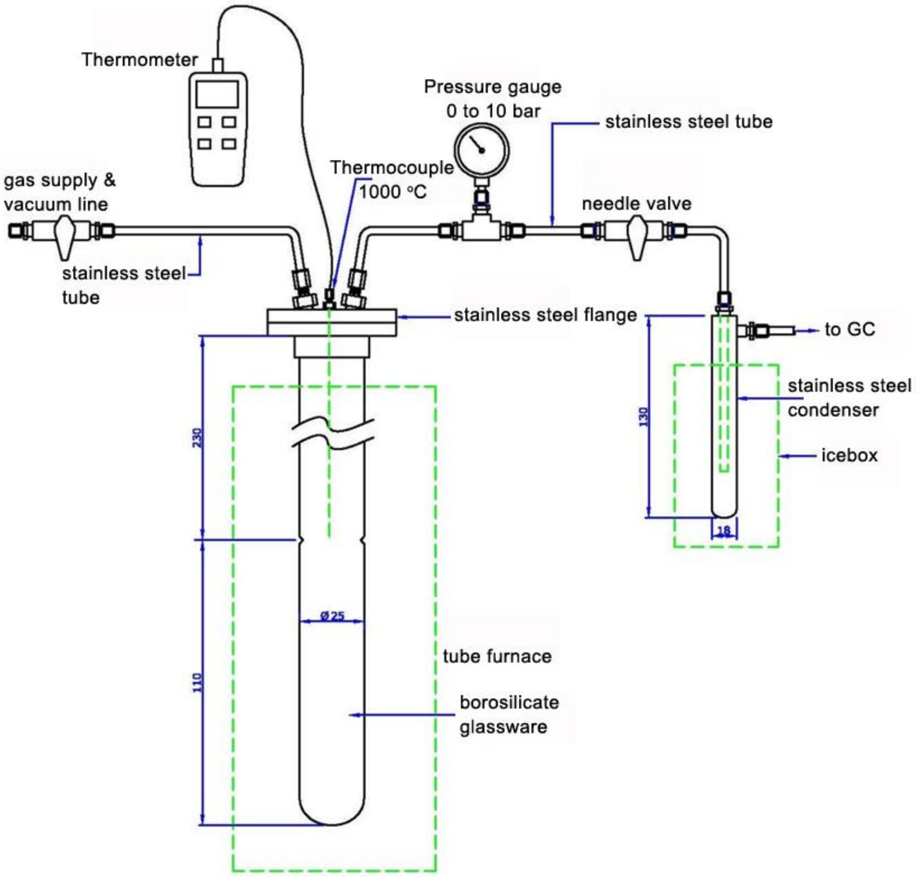


Figure 6 Semi-batch rector

First of all, the raw material EFB will be processed into particles of small size which is less than 500 µm. Then, they will be put into the reactor together with 5 weight percent (wt %) of H-Y catalyst. Next, nitrogen gas is allowed to flow through the reactor for a few minutes to drive out all the oxygen. After that, the temperature of the reaction (500 ^{o}C) and the flow rate of nitrogen gas (100 ml/min) are set. Lastly, the liquid will be collected in a condenser. (Diebold 1999, August 26)

3.2.2.2 Stabilization and Characterization of EFB derived bio-oil

(a) Aging of bio-oil at 80 ^{o}C in sealed containers for 1 week.

(b) Measure the value of viscosity, water content and acidity of bio-oil every day for 1 week.

(c) Repeat the procedure (a) and (b) with the addition of anti-oxidants (1000 ppm) and solvents (10 wt%) separately.

(d) Find the percentage change in the viscosity, water content and acidity of original and stabilized bio-oil for 7 consecutive days.

3.2.3 Variation of factors

As mentioned in Chapter 1, there are 2 subjects that are being investigated: effect of solvents and anti-oxidants on viscosity, water content and acidity of EFB derived bio-oil as well as the percentage change in viscosity and water content for 1 week.(Chang 2008)

3.3 Project Activities

The activities listed below are the project activities that need to be executed in order for this research project to meet its objectives:

Problem Statement and Objective

To identify the problem statement and purpose of having this research project

Literature Review

To gather the related and useful information from various sources such as journals and websites

Experimental

To identify the problems that need to be investigated and the experimental procedures which includes the chemicals required and the collection of results

Data Analysis and Interpretation

To analyze and intepret the results obtained follow by comparing the findings from literature review

Documentation and Reporting

To document and report the research project in detail as well as to discuss the recommendations which can produce better improvement

Conclusion

To conclude the findings obtained from experimental works and choose the most effective solution

3.4 Key Milestones

The key milestones are important agendas that need to be accomplished in time. Table 3 below shows the key milestones for the whole study. The ● represents the important milestones that need to be fulfilled on time.

Table 3 Key Milestones for Final Year Project (FYP I and FYP II)

No.		**1,2**	**3,4**	**5,6**	**7,8**	**9,10**	**11,12**	**13,14**	**15,16**	**17,18**	**19,20**	**21,22**	**23,24**	**25,26**	**27,28**
1	Confirmation of FYP Topic	🟩													
2	Literature Review		🟩	🟩											
3	Extended Proposal				●										
4	Rough Planning of Experiments				🟩	🟩									
5	Secure Raw Materials and Chemicals needed					●									
6	Detailed Planning of Experiments						🟩	🟩							
7	Run Experiments and Obtaining Results									🟩	🟩	🟩	🟩		
8	Analyze and Interpret the Results												🟩	🟩	
9	Documentation of the Whole Project and Presentation														●

3.5 Gantt Chart

The Gantt Charts for FYP I and II are outlined in Table 4 and 5 respectively.

Table 4 Gantt Chart for FYP I

No.		**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Selection of Project Title	🟦	🟦						Mid-semester Break							
2	Preliminary Research Work and Literature Review		🟦	🟦	🟦	🟦										
3	Submission of Extended Proposal Defence						●									
4	Proposal Defense									🟦	🟦					
5	Project Work continues											🟦	🟦	🟦		
6	Submission of Interim Draft Report														●	
7	Submission of Interim Report															●

🟦 Process
● Suggested milestone

Table 5 Gantt Chart for FYP II

No.		**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
1	Project Work Continues	🟨	🟨	🟨	🟨	🟨	🟨	🟨	Mid-semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									🟨	🟨	🟨	🟨	🟨			
4	Pre-SEDEX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (Soft Bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

🟨 Process

● Suggested milestone

3.6 Tools

The tools and equipment are very contributing in this project. The measuring of properties of bio-oil such as viscosity, acidity, water content and Gas chromatography-mass spectrometry (GC-MS) required the instruments in the laboratory.

3.6.1 Water content

Figure 7 Metrohm 870 Karl Fischer Titrino Plus

The water content of bio-oil samples were determined by using Metrohm 870 Karl Fischer Titrino Plus. The Metrohm 870 Karl Fischer Titrino Plus takes this into account: Two dosinos with their dosing units can be mounted directly onto reagent bottles that are located on the instrument. This means that dosing requires no additional bench space if no other reagents are to be added.

3.6.2 *Acidity*

Figure 8 EUTECH Instruments pH 510 pH/mV/ ℃ Meter

The acidity which is the pH value of bio-oil samples were measured by using EUTECH Instruments pH 510 pH/mV/°C Meter. It is an electronic device used for measuring the pH (acidity or alkalinity) of a liquid (though special probes are sometimes used to measure the pH of semi-solid substances). A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading.

3.6.3 *Viscosity*

Figure 9 Brookfield CAP 2000+ Viscometer

The viscosity of the bio-oil in this study is measured with Brookfield CAP 2000+ Viscometer. Brookfield's CAP-2000+ offers expanded temperature and viscosity ranges with variable speed capability. The CAP2000+ offers lower shear rates, making it suitable for many applications where small sample volume and good temperature control are necessary. The setting temperature for measuring the viscosity is 40 °C.

3.6.4 Gas chromatography-mass spectrometry (GC-MS)

Figure 10 GC 1: GCMS-QP2010 Plus

The GC/MS analyses were conducted on samples diluted (0.1g : 1.9g) in acetone using GCMS-QP2010 Plus, as shown in Figure 10. Gas Chromatography is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. The gas chromatography was used to determine the amount of each component present in the bio oil samples. This will help to analysis the reason affecting the other properties of bio oil, according to the present components available inside the samples.

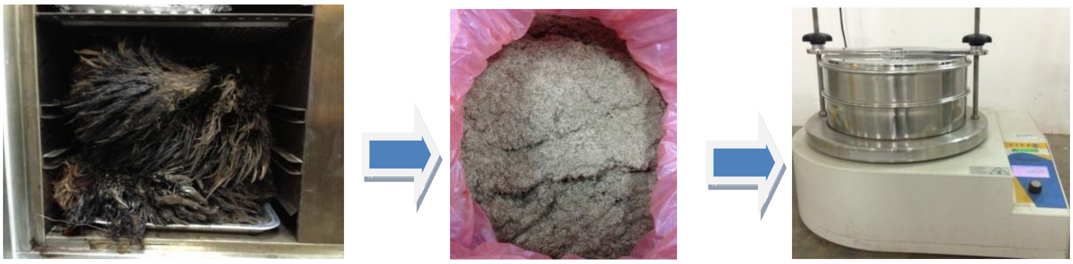
CHAPTER 4

RESULT AND DISCUSSION

4.1 Preparation of Empty Fruit Bunch (EFB) derived bio-oil

4.1.1 Empty Fruit Bunch (EFB) with particle size less than 500 μm

Fresh empty fruit bunches are taken from *Kilang Sawit FELCRA Berhad Nasaruddin, Bota, Perak, Malaysia*. They are then washed with water to remove the sand and dust particles. After that, they are dried again in the oven at 100 °C. The dried EFB is then grinded with FRITSCH Cutting Mill to below particle size of below 500 μm. The grinded EFB is sieved to obtain the desired particle size (< 500 μm). They are then dried in the oven at 100 °C for at least 24 hours before being used in the catalytic pyrolysis reaction. Figure 11 below shows the procedure of processing the EFB before it is used in the research project.



Drying washed EFB at 100^{o}C

Grinded EFB

Sieving EFB (< 500 μm)

Dried EFB with particle size of < 500 μm

Figure 11 Procedure of processing EFB

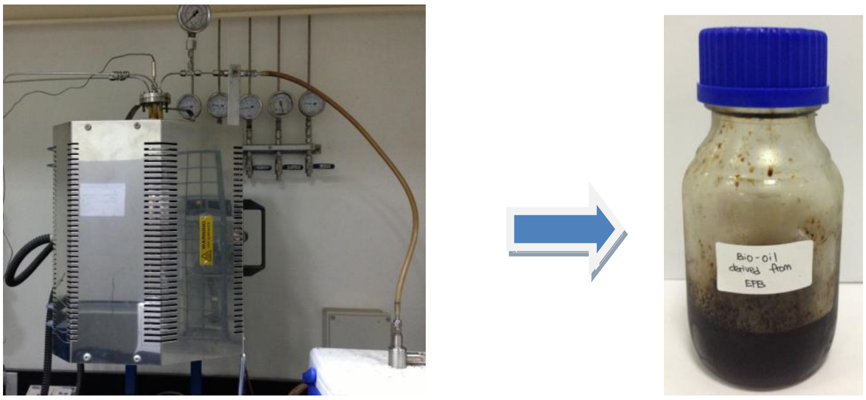
4.1.2 Catalytic Pyrolysis of EFB

In every run, about 15 gram of dried EFB, mixed well with zeolite catalyst, are loaded into the borosilicate glass tube, which is inserted inside the furnace. Besides, glass wool is used to prevent the reactant particles raised and blocked the gas inlet to the condenser. It will just allow the gas to pass through. Before the reaction is started, nitrogen gas is allowed to flow through the tube for a few minutes to remove all the oxygen.

After that, the desired temperature of the reaction, the furnace heating rate of 20 ℃/min and the flow rate of nitrogen gas are set. During the pyrolysis, the pyrolysis vapor produced is carried out by the nitrogen gas and pass through an ice bath condenser, where the condensable vapor is condensed to form bio-oil. The whole process needs around 35 minutes. The weight of the bio-oil produced is determined by measuring the difference between the weight of the condenser before and after the experiment. The liquid yield is calculated using the following equation:

$$Liquid\ Yield\ (wt\%) = \frac{Weight\ of\ bio - oil\ produced}{Weight\ of\ biomass}\ x\ 100\%$$

The bio-oil obtained from all the runs of experiment will be stored in a container and put into the refrigerator in order to slow down the rate of aging. Figure 12 below shows the process of catalytic pyrolysis of EFB.



Catalytic pyrolysis of EFB at 500 ^{o}C

EFB derived bio-oil

Figure 12 Catalytic pyrolysis of EFB

The estimated bio-oil required for the study of stabilization is around 29 runs of experiment. The weight percentage of liquid yield for every run is calculated and tabulated in the Table 6 below:

Table 6 Liquid yield (wt %) for catalytic pyrolysis of EFB

No. of Experiment	Weight of biomass (g)	Weight of bio-oil produced (g)	Liquid yield (wt %)
1	15.01	3.86	25.72
2	15.00	3.91	26.07
3	15.02	3.87	25.77
4	15.02	3.88	25.83
5	15.03	3.88	25.82
6	15.04	3.86	25.66
7	15.03	3.85	25.61
8	15.01	3.82	25.44
9	15.01	3.84	25.58
10	15.00	3.85	25.67
11	15.03	3.86	25.68
12	15.04	3.81	25.33
13	15.01	3.88	25.84
14	15.02	3.90	25.97
15	15.02	3.91	26.03
16	15.04	3.87	25.73
17	15.03	3.85	25.62
18	15.03	3.82	25.42
19	15.03	3.81	25.36
20	15.05	3.80	25.25
21	15.02	3.91	26.03
22	15.01	3.92	26.12
23	15.01	3.86	25.71
24	15.00	3.87	25.80
25	15.00	3.87	25.80
26	15.00	3.85	25.67
27	15.00	3.84	25.60
28	15.02	3.89	25.90
29	15.00	3.90	26.00
		Average Liquid Yield (wt %)	25.73

4.2 Stabilization and characterization of EFB derived bio-oil

High temperature can activate the internal chemical reactions, such as polymerization, esterification and transesterification which cause the increase in viscosity and acid value of the bio-oil. Hence, usage of anti-oxidants and solvents can help to maintain or even improve the stability of the bio-oil.

4.2.1 Addition of anti-oxidants (1000 ppm)

Based on the literature review, the most common temperature used for aging was 80 ^{o}C. Thus, the author had performed aging of EFB derived bio-oil at 80 ^{o}C. The value of viscosity, water content and acidity for the bio-oil with respective anti-oxidant will be measured. Figure 13 below shows the bio-oil with the addition of 1000 ppm of anti-oxidants which are propyl gallate, tert-butylhydroquinone and butylated hydroxyanisole.

Figure 13 Bio-oil with the addition of propyl gallate, tert-butylhydroquinone and butylated hydroxyanisole

On the other hand, the author is going to study the effect of commercial anti-oxidant which is calcium chloride salts (CaCl2) with the EFB derived bio-oil. This salt is extremely hygroscopic: it will absorb the moist out of the air and dissolve in the process. When all the solid salts have dissolved, the humidifier will not absorb any more moisture. The size of the salt is in pellets form when it is removed from the commercial product (thirsty hippo). The salt is grinded into powder form. Figure 14 below shows the bio-oil with the addition of 1000ppm of calcium chloride salt (CaCl2).

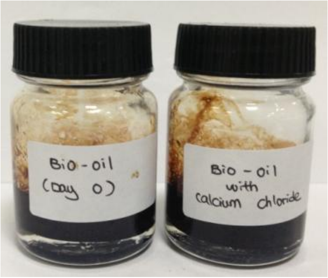


Figure 14 Bio-oil with the addition of calcium chloride salt (CaCl2)

The readings of viscosity, water content and acidity of pure bio-oil and bio-oil with antioxidants are tabulated in Table 7, Table 8 and Table 9 below respectively.

Table 7 Viscosity of pure bio-oil and bio-oil with antioxidants

DAY	Pure bio-oil (cP)	Bio-oil with TBHQ (cP)	Bio-oil with BHA (cP)	Bio-oil with PG (cP)	Bio-oil with CaCl2 (cP)
0	46.72	46.72	46.72	46.72	46.72
1	59.86	53.21	54.15	51.88	57.86
2	72.13	60.54	62.77	57.91	66.13
3	85.88	66.12	69.31	62.01	77.88
4	99.21	74.99	77.89	67.38	86.21
5	112.66	81.65	85.45	72.60	97.66
6	126.04	89.37	94.64	77.09	108.04
7	140.18	96.82	101.17	83.62	117.18

Table 8 Water content of pure bio-oil and bio-oil with antioxidants

DAY	Pure bio-oil (wt %)	Bio-oil with TBHQ (wt %)	Bio-oil with BHA (wt %)	Bio-oil with PG (wt %)	Bio-oil with CaCl2 (wt %)
0	50.0	50.0	50.0	50.0	50.0
1	50.2	48.6	49.2	48.1	49.5
2	50.5	47.2	48.3	46	48.8
3	50.9	45.7	47.3	44.2	47.2
4	51.2	44.4	46.4	42.3	46.7
5	51.5	43	45.5	40.6	46.1
6	51.9	41.9	44.4	38.9	45.7
7	52.3	41.1	43.3	37.2	45.3

Table 9 Acidity of pure bio-oil and bio-oil with antioxidants

DAY	Pure bio-oil (pH)	Bio-oil with TBHQ (pH)	Bio-oil with BHA (pH)	Bio-oil with PG (pH)	Bio-oil with CaCl2 (pH)
0	2.69	2.69	2.69	2.69	2.69
1	2.63	2.75	2.72	2.79	2.60
2	2.58	2.81	2.74	2.90	2.52
3	2.53	2.88	2.77	3.10	2.44
4	2.47	2.92	2.81	3.18	2.35
5	2.42	2.98	2.84	3.26	2.21
6	2.38	3.05	2.88	3.35	2.10
7	2.33	3.11	2.91	3.44	2.02

The percentages change in viscosity, water content of bio-oil and change in acidity of bio-oil with and without anti-oxidants, which were subjected to accelerated aging are presented in Figure 15, Figure 16 and Figure 17 below respectively.

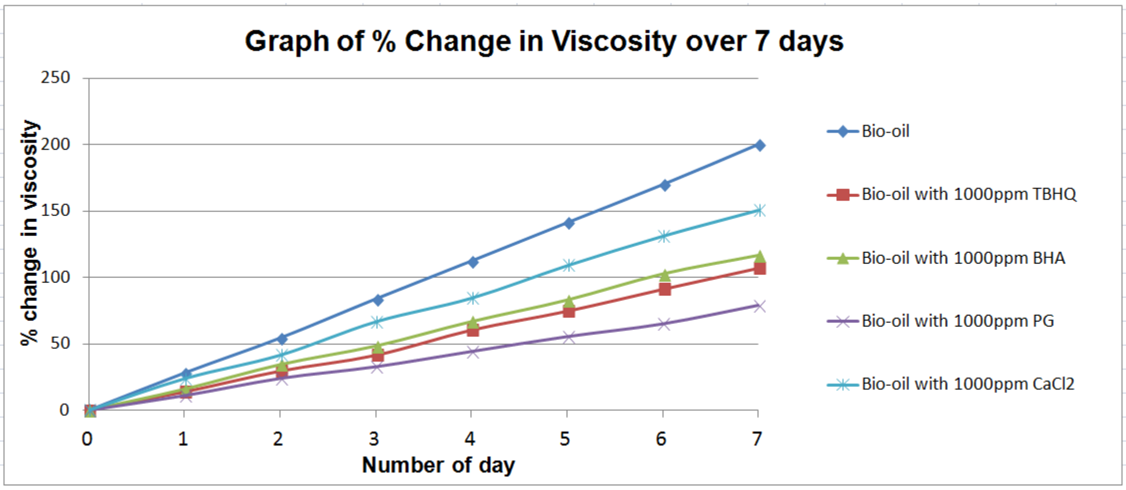


Figure 15 Graph of percentage change in viscosity of bio-oil with and without anti-oxidants

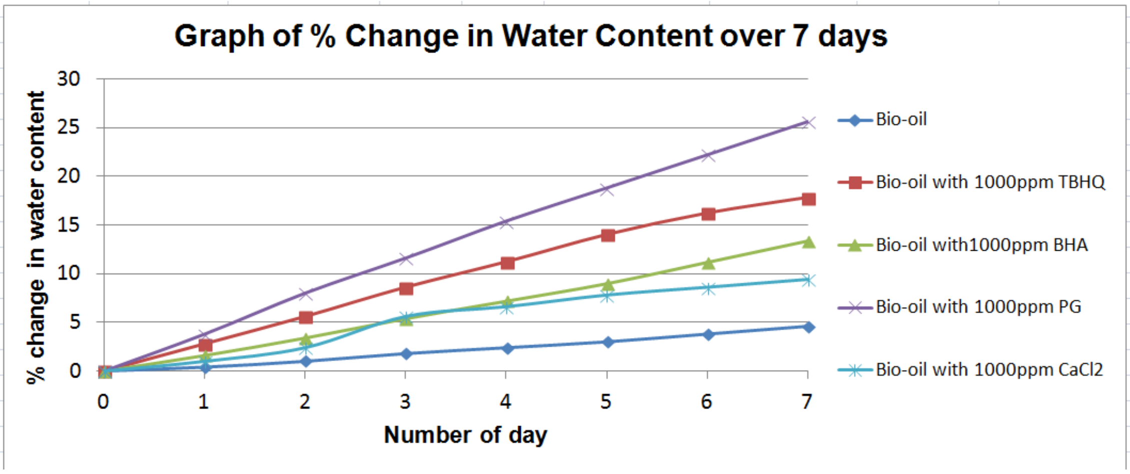


Figure 16 Graph of percentage change in water content of bio-oil with and without anti-oxidants

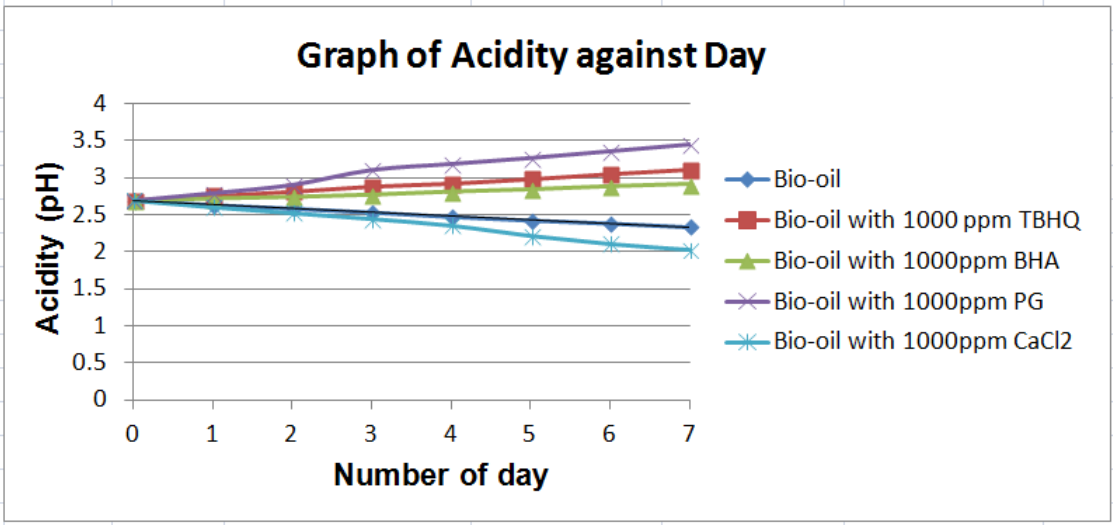


Figure 17 Graph of change in acidity of bio-oil with and without anti-oxidants

The accelerated aging of bio-oil can bring negative effects to the properties of bio-oil such as viscosity, water content and acidity. From the results obtained, the viscosity of pure bio-oil increased with the viscosity change of 200.04 % after 7 days. This phenomenon is due to the reason that the reactive organic compounds in the bio-oil interacted to form larger molecules or undergone polymerization during the aging. Storage of bio-oil at higher temperature will lead to faster polymerization. Meanwhile, the rate of increase of viscosity values of the bio-oil with anti-oxidants is lower than the pure bio-oil. Based on Figure 11, the percentages change of viscosity of bio-oil with PG, TBHQ, BHA and CaCl2 are 78.98 %, 107.23 %, 116.55 % and 150.81 % respectively after 7 days of aging at 80 ^{o}C.

Besides, the water content of pure bio-oil increased with the water content change of 4.6 % after 7 days. Addition of anti-oxidants helps to increase the rate of reduction of water content. According to Figure 12, after 7 days, the percentages change of water content of bio-oil with PG, TBHQ, BHA and CaCl2 are 25.60 %, 17.80 %, 13.40 % and 9.4 % respectively. In addition, all the anti-oxidants also manage to reduce the acidity of bio-oil except CaCl2. Based on Figure 13, the pH value of pure bio-oil is 2.33 after 7 days of aging whereas the pH value of bio-oil with PG, TBHQ, BHA and CaCl2 3.44, 3.11, 2.91 and 2.02 respectively. Thus, the effectiveness of antioxidants increase in the following order: CaCl2, BHA, TBHQ and PG. Bio-oil with PG and CaCl2 were undergone Gas chromatography–mass spectrometry (GC-MS) analysis and will be further discussed in section 4.3.

4.2.2 Addition of solvents (10 wt%)

In separate samples, 10 wt% of ethanol 95 %, acetone and ethyl acetate are added to the EFB derived bio-oil. All samples are subjected to accelerated aging for 1 week in the oven at 80 ^{o}C. The value of viscosity, water content and acidity for the bio-oil with respective solvents will be measured. Figure 18 below shows the bio-oil with the addition of solvents which are ethanol 95 %, acetone and ethyl acetate.

Figure 18 Bio-oil with the addition of ethanol 95 %, acetone and ethyl acetate

The readings of viscosity and water content pure bio-oil and bio-oil with antioxidants are tabulated in Table 10 and Table 11 below respectively

Table 10 Viscosity of pure bio-oil and bio-oil with solvents

DAY	Pure bio-oil (cP)	Bio-oil with ethyl acetate (cP)	Bio-oil with acetone (cP)	Bio-oil with ethanol 95 % (cP)
0	46.72	46.72	46.72	46.72
1	59.86	50.21	51.05	48.88
2	72.13	54.32	56.47	50.91
3	85.88	59.19	61.21	52.01
4	99.21	64.01	67.19	55.38
5	112.66	68.63	72.45	58.60
6	126.04	72.88	78.66	61.09
7	140.18	76.90	83.67	64.62

Table 11 Water content of pure bio-oil and bio-oil with solvents

DAY	Pure bio-oil (wt %)	Bio-oil with ethyl acetate (wt %)	Bio-oil with acetone (wt %)	Bio-oil with ethanol 95 % (wt %)
0	50.0	53.7	52.8	53.5
1	49.8	53.2	52.2	53.2
2	49.5	53.0	51.6	53.1
3	49.1	52.9	51.2	53.2
4	48.8	52.5	50.7	53.3
5	48.5	52.2	50.2	53.1
6	48.1	51.8	49.6	53.0
7	47.7	51.5	49.3	53.1

The chosen chemical solvents which are ethanol 95 %, acetone and ethyl acetate can mix homogeneously with the bio-oil. The initial viscosity values of bio-oil with solvents are lower than the pure bio-oil due to the dilution. The percentages change in viscosity and water content of bio-oil with and without solvents, which were subjected to accelerated aging are presented in Figure 19 and Figure 20 below respectively.

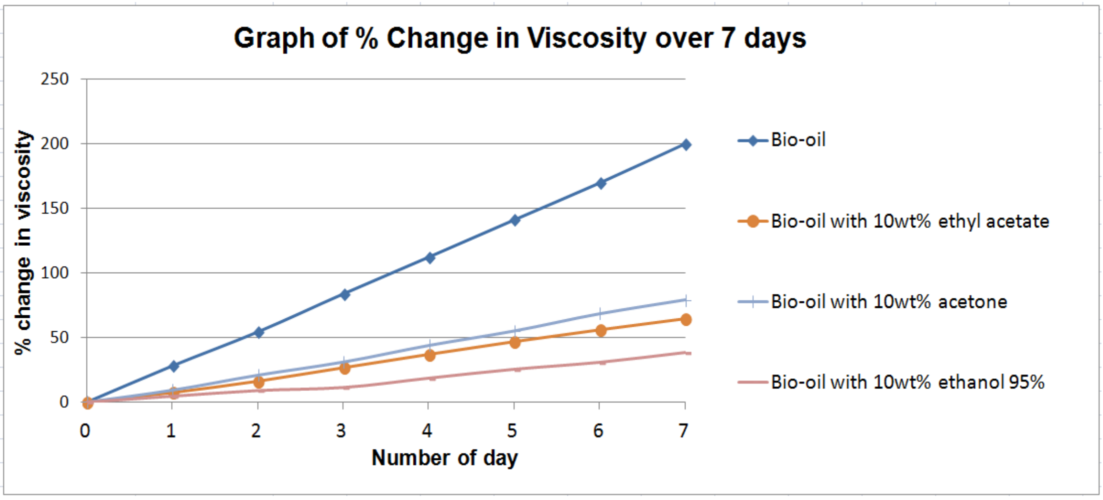


Figure 19 Graph of percentage change in viscosity of bio-oil with and without solvents

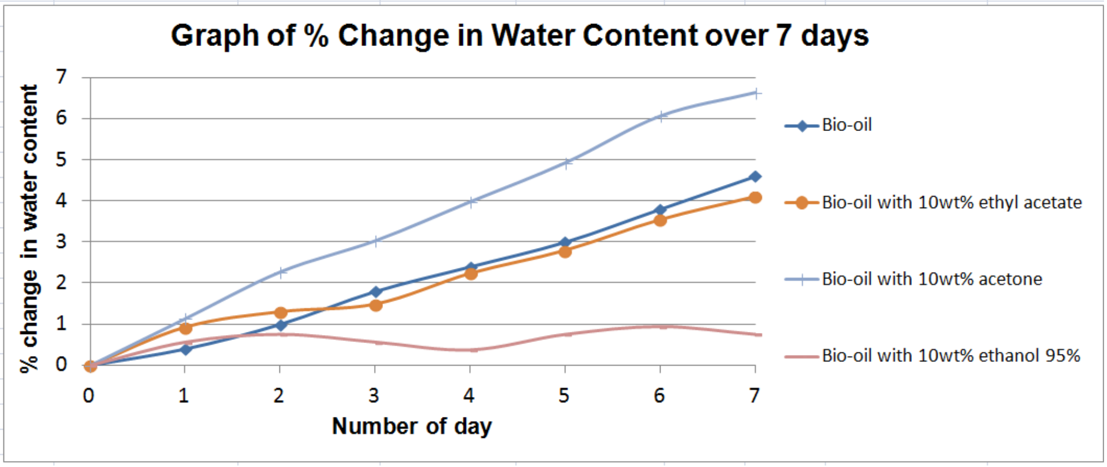


Figure 20 Graph of percentage change in viscosity of bio-oil with and without solvents

Figure 19 shows that after the accelerated aging at 80 ^{o}C for 7 days, the percentage change in viscosity of bio-oil with solvents are increased slightly compared to the pure bio-oil. This indicates that the solvents are able to increase the stability of bio-oil. The percentages change of viscosity of bio-oil with ethyl acetate, acetone and ethanol 95 % are 64.60 %, 79.09 % and 38.31 % respectively.

Besides, the water content of bio-oil was reduced by the addition of solvents. Based on Figure 20, the percentages change of water content of bio-oil with ethyl acetate, acetone and ethanol 95 % are 4.10 %, 6.63 % and 0.75 % respectively. Hence, the effectiveness of solvent increase in the following order: ethyl acetate, acetone and ethanol 95 %. For the solvent-bio-oil blends, no phase separation was observed after 7 days of accelerated aging. It shows that addition of ethanol 95 % to the pure bio-oil inhibited phase separation. This is particularly important to bio-oil storage at high temperatures. Bio-oil with ethanol 95 % was chosen for Gas chromatography–mass spectrometry (GC-MS) analysis and will be further discussed in section 4.3.

4.3 Gas chromatography–mass spectrometry (GC-MS) analysis

The comparison of compounds in pure bio-oil and bio-oil with PG, pure bio-oil and bio-oil with ethanol 95 %, pure bio-oil and bio-oil with calcium chloride salts are tabulated in Table 12, Table 13 and Table 14 below respectively.

Table 12 Comparison of compounds in pure bio-oil and bio-oil with PG

Peak No.	Retention time (min)	Compound name	(a) Pure bio-oil	(b) Bio-oil with PG
1	1.703, 1.702	Methyl Alcohol	✓	✓
2	1.919,1.918	Acetone	✓	✓
3	2.048, 2.043	Acetic acid, methyl ester	✓	✓
4	2.097	Formic acid	✓	×
5	2.232	1-Propanol	×	✓
6	2.351	3-Pentyn-1-ol	×	✓
7	2.367	Acetic acid, hydroxy-	✓	×
8	2.399	Acetic acid ethenyl ester	✓	×
9	2.448	Propanal, 2-methyl-	×	✓
10	2.778, 2.718	Acetic acid	✓	✓
11	2.994	Crotonic acid	✓	×
12	3.139, 3.134	2-Propanone, 1-hydroxy-	✓	✓
13	3.404	Methyl Isobutyl Ketone	✓	×
14	3.491	Acetic acid, hydroxy-, methyl ester	✓	×
15	3.620, 3.604	1,2-Propanediol, 3-methoxy-	✓	✓
16	3.772, 3.690	Propanoic acid	✓	✓
17	3.923, 3.950	Propanoic acid, 2-hydroxy-,	✓	✓
18	4.047, 4.052	2-Furanmethanol, tetrahydro-, acetate	✓	✓
19	4.128, 4.112	Pyridine	✓	✓
20	4.209	Propanoic acid, 2-methyl-	×	✓
21	4.295, 4.290	1-Hydroxy-2-butanone	✓	✓
22	4.555, 4.555	3-Hexene, (Z)-	✓	✓
23	4.652	Benserazide	✓	×
24	4.663	3-Pentanol, 2-methyl-	×	✓
25	4.717	Isocrotonic acid	✓	×
26	4.749	Muramic acid	×	✓
27	4.771	Acetamide	✓	×
28	4.846	3-Furaldehyde	✓	×
29	4.895	Oxalic acid	×	✓
30	4.911, 4.938	Pyridine, 2-methyl-	✓	✓
31	4.987, 4.992	Butanoic acid	✓	✓
32	5.041, 5.057	2H-Pyran-2-one	✓	✓
33	5.176	Butanoic acid	×	✓
34	5.241, 5.357	1,2-Ethanediol, monoacetate	✓	✓

35	5.289, 5.300	2-Furanmethanol	✓	✓
36	5.403, 5.403	2-Propanone, 1-(acetyloxy)-	✓	✓
37	5.441, 5.446	Pyridinium, 1-amino-4-methyl-	✓	✓
38	5.624, 5.630	L-Mannose, 6-deoxy-	✓	✓
39	5.711, 5.711	4-Hydroxy-3-hexanone	✓	✓
40	5.830, 5.829	2-Cyclopenten-1-one	✓	✓
41	5.873	Ethanone, 1-(2-furanyl)-	×	✓
42	5.938	Butanoic acid, 5.932	✓	×
43	5.981	1-Methyl-1-vinyl-1-silacyclobutane	×	✓
44	6.046, 6.046	2-Cyclopenten-1-one, 2-hydroxy-	✓	✓
45	6.138, 6.137	Cyclohexane	✓	✓
46	6.175, 6.191	2-Pentene, 4,4-dimethyl-	✓	✓
47	6.289, 6.267	2-[N-Aziridylmethyl]glutaronitrile	✓	✓
48	6.343	2-Butanone, 3,3-dimethyl-	✓	×
49	6.440, 6.445	2-Cyclopenten-1-one, 3-methyl-	✓	✓
50	6.489	2-Penten-4-yn-1-ol	×	✓
51	6.543	3-Buten-1-ol, 3-methyl-2-methylene	✓	×
52	6.586, 6.586	Phenol	✓	✓
53	6.753	1-Pentanol, 2-ethyl-4-methyl-	×	✓
54	6.791	2-Furanmethanol, tetrahydro-, acetate	✓	×
55	6.948	Methoxyacetic acid, octyl ester	✓	×
56	7.013, 7.007	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	✓	✓
57	7.099, 7.094	Cyclooctene	✓	✓
58	7.142	Cyclobutanemethano	×	✓
59	7.207	3-Hexanone, 4-methyl-	✓	×
60	7.240, 7.234	Cyclopropanecarboxylic acid	✓	✓
61	7.385, 7.391	Trifluoroacetic acid	✓	✓
62	7.542, 7.542	Phenol, 2-methoxy-	✓	✓
63	7.596	Pyrrolidine	✓	×
64	7.683, 7.682	Propanamide, N-methyl-2-amino-	✓	✓
65	7.742	1H-Pyrrole-2-carboxaldehyde	✓	×
66	7.796, 7.790	Cyclohexane	✓	✓
67	7.882, 7.882	2,3-Dimethyl-undec-1-en-3-ol	✓	✓
68	7.969, 7.969	1,3-Cyclohexanedione	✓	✓
69	8.012, 8.006	Ethyl 2-cyanocrotonate	✓	✓
70	8.109, 8.098	Pyrrolidine	✓	✓

71	8.169	Benzoic acid	✓	✓
72	8.174	Phenol	×	✓
73	8.309, 8.306	1-.beta.-d-Ribofuranosyl-3-[5-tetraazolyl]-1,2,4-triazole	✓	✓
74	8.336	2,5-Heptadien-4-one, 2,6-dimethyl-	×	✓
75	8.374, 8.374	Phenol, 2-methoxy-4-methyl-	✓	✓
76	8.423, 8.417	Pentanoic acid	✓	✓
77	8.628, 8.628	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	✓	✓
78	8.736, 8.736	1,6;3,4-Dianhydro-2-O-acetyl-	✓	✓
79	8.785, 8,784	1,1-Dodecanediol, diacetate	✓	✓
80	8.855, 8.855	2H-Pyran-2-one	✓	✓
81	8.930, 8.930	1,2-Benzenediol	✓	✓
82	9.011, 9.006	N-(1-Cyanopropenyl)formamide	✓	✓
83	9.136, 9.135	Benzenemethanol	✓	✓
84	9.222, 9.211	endo-2,3-O-Ethylidene-.beta.-d-erythrofuranose	✓	✓
85	9.287	4-Hydroxy-3-methylacetophenone	✓	×
86	9.325, 9.325	t-butyl ether of 2-ethylhexanol	✓	✓
87	9.390	13,13-Dimethyl-3,6,9-trioxa-13-silatetradecan-1-ol	✓	×
88	9.535, 9.530	Phenol, 2,6-dimethoxy-	✓	✓
89	9.633	2-Propenoic acid	✓	×
90	9.746, 9.741	Heptane, 3-bromo-	✓	✓
91	9.816	Cyclopentanone, dimethylhydrazone	×	✓
92	9.919, 9.919	Benzaldehyde, 3-hydroxy-4-methoxy-	✓	✓
93	10.032, 10.027	1,4-Benzenediol, 2,6-dimethyl-	✓	✓
94	10.151, 10.151	1,2,4-Trimethoxybenzene	✓	✓
95	10.216, 10.210	Phenol, 2-methoxy-4-(1-propenyl)-	✓	✓
96	10.259, 10.259	Methylparaben	✓	✓
97	10.394	Pyrimidine	×	✓
98	10.475, 10.470	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	✓	✓
99	10.583, 10.583	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	✓	✓
100	10.637, 10.637	Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)-	✓	✓
101	10.718, 10.713	Acetamide, 2-(4-hydroxy-3-	✓	✓

		methoxyphenyl)-		
102	10.908, 10.907	2-Amino-1-(3,4-dimethoxyphenyl)ethanone	✓	✓
103	11.107, 11.102	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	✓	✓
104	11.145	Benzene, 1,1'-propylidenebis-	✗	✓
105	11.410, 11.404	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	✓	✓
106	11.507, 11.502	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	✓	✓
107	11.712, 11.712	2,4(3H,5H)-Thiazoledione	✓	✓
108	11.907, 11.901	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	✓	✓
109	12.074, 12.074	Benzene, 1,1'-butylidenebis-	✓	✓
110	12.393, 12.393	4H-1,3,2-Dioxaborin	✓	✓
111	12.582	Pyrrolidine	✓	✗
112	12.755	3,4-Dihydroxy-5-methoxybenzaldehyde	✗	✓
113	13.133, 13.133	Octanoic acid	✓	✓
114	13.608	Propyl Gallate	✗	✓
115	13.614	Octadecane, 2,6-dimethyl-	✓	✗
116	14.073	Hexadecanamide	✓	✗
117	14.543	Dimethyl tetradecanedioate	✓	✗
118	14.878	9-Octadecenamide, (Z)-	✓	✗
119	15.299	13-Octadecenal, (Z)-	✓	✗
120	15.386	Hexadecanedioic acid	✓	✗

Table 13 Comparison of compounds in pure bio-oil and bio-oil with ethanol 95 %

Peak No.	Retention time (min)	Compound name	(a) Pure bio-oil	(b) Bio-oil with ethanol 95 %
1	1.703, 1.703	Methyl Alcohol	✓	✓
2	1.821	Ethanol	✗	✓
3	1.919,1.930	Acetone	✓	✓
4	2.048, 2.048	Acetic acid, methyl ester	✓	✓
5	2.097, 2.097	Formic acid	✓	✓
6	2.367	Acetic acid, hydroxy-	✓	✗
7	2.399	Acetic acid ethenyl ester	✓	✗
8	2.778, 2.772	Acetic acid	✓	✓
9	2.994	Crotonic acid	✓	✗
10	3.139, 3.145	2-Propanone, 1-hydroxy-	✓	✓

11	3.404	Methyl Isobutyl Ketone	✓	×
12	3.491	Acetic acid, hydroxy-, methyl ester	✓	×
13	3.620, 3.610	1,2-Propanediol, 3-methoxy-	✓	✓
14	3.772, 3.750	Propanoic acid	✓	✓
15	3.923	Propanoic acid, 2-hydroxy-	✓	×
16	3.944	2-Hexen-4-yn	×	✓
17	4.047, 4.047	2-Furanmethanol, tetrahydro-, acetate	✓	✓
18	4.128, 4.112	Pyridine	✓	✓
19	4.220	Propanoic acid, 2-methyl-	×	✓
20	4.295, 4.296	1-Hydroxy-2-butanone	✓	✓
21	4.555, 4.560	3-Hexene, (Z)-	✓	✓
22	4.652	Benserazide	✓	×
23	4.663	1,2-Butanediol	×	✓
24	4.717	Isocrotonic acid	✓	×
25	4.755	Acetic acid	×	✓
26	4.771	Acetamide	✓	×
27	4.846	3-Furaldehyde	✓	×
28	4.901	3-Pentanone, 2,4-dimethyl-	×	✓
29	4.911, 4.938	Pyridine, 2-methyl-	✓	✓
30	4.987, 4.992	Butanoic acid	✓	✓
31	5.041, 5.057	2H-Pyran-2-one	✓	✓
32	5.187	Hexanoic acid, 6-bromo-	×	✓
33	5.241, 5.246	1,2-Ethanediol, monoacetate	✓	✓
34	5.289, 5.300	2-Furanmethanol	✓	✓
35	5.403, 5.403	2-Propanone, 1-(acetyloxy)-	✓	✓
36	5.441, 5.446	Pyridinium, 1-amino-4-methyl-	✓	✓
37	5.624, 5.630	L-Mannose, 6-deoxy-	✓	✓
38	5.711, 5.711	4-Hydroxy-3-hexanone	✓	✓
39	5.830, 5.830	2-Cyclopenten-1-one	✓	✓
40	5.873	Ethanone, 1-(2-furanyl)-	×	✓
41	5.938	Butanoic acid, 5.932	✓	×
42	6.046, 6.046	2-Cyclopenten-1-one, 2-hydroxy-	✓	✓
43	6.138, 6.138	Cyclohexane	✓	✓
44	6.175	2-Pentene, 4,4-dimethyl-	✓	×
45	6.186	Propanoic acid	×	✓
46	6.289, 6.289	2-[N-Aziridylmethyl]glutaronitrile	✓	✓
47	6.343, 6.375	2-Butanone, 3,3-dimethyl-	✓	✓
48	6.440, 6.446	2-Cyclopenten-1-one, 3-methyl-	✓	✓
49	6.543	3-Buten-1-ol, 3-methyl-2-methylene	✓	×
50	6.586, 6.586	Phenol	✓	✓
51	6.791, 6.786	2-Furanmethanol, tetrahydro-, acetate	✓	✓
52	6.948, 6.948	Methoxyacetic acid, octyl ester	✓	✓
53	7.013, 7.007	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	✓	✓

54	7.099, 7.099	Cyclooctene	✓	✓
55	7.142	Diazene, bis(1,1-dimethylethyl)-	×	✓
56	7.207	3-Hexanone, 4-methyl-	✓	×
57	7.240, 7.240	Cyclopropanecarboxylic acid	✓	✓
58	7.385, 7.396	Trifluoroacetic acid	✓	✓
59	7.542, 7.542	Phenol, 2-methoxy-	✓	✓
60	7.596, 7.591	Pyrrolidine	✓	✓
61	7.683, 7.688	Propanamide, N-methyl-2-amino-	✓	✓
62	7.742, 7.747	1H-Pyrrole-2-carboxaldehyde	✓	✓
63	7.796, 7.796	Cyclohexane	✓	✓
64	7.882, 7.888	2,3-Dimethyl-undec-1-en-3-ol	✓	✓
65	7.969, 7.969	1,3-Cyclohexanedione	✓	✓
66	8.012, 8.012	Ethyl 2-cyanocrotonate	✓	✓
67	8.109, 8.104	Pyrrolidine	✓	✓
68	8.169	Benzoic acid	✓	×
69	8.174	Phenol, 2-ethyl-	×	✓
70	8.309, 8.306	1-.beta.-d-Ribofuranosyl-3-[5-tetraazolyl]-1,2,4-triazole	✓	✓
71	8.336	3,4-Pentadienal	×	✓
72	8.374, 8.374	Phenol, 2-methoxy-4-methyl-	✓	✓
73	8.423, 8.428	Pentanoic acid	✓	✓
74	8.628, 8.628	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	✓	✓
75	8.736, 8.736	1,6;3,4-Dianhydro-2-O-acetyl-	✓	✓
76	8.785, 8,785	1,1-Dodecanediol, diacetate	✓	✓
77	8.855, 8.855	2H-Pyran-2-one	✓	✓
78	8.930, 8.930	1,2-Benzenediol	✓	✓
79	9.011, 9.011	N-(1-Cyanopropenyl)formamide	✓	✓
80	9.136, 9.136	Benzenemethanol	✓	✓
81	9.222, 9.217	endo-2,3-O-Ethylidene-.beta.-d-erythrofuranose	✓	✓
82	9.287	4-Hydroxy-3-methylacetophenone	✓	×
83	9.325, 9.325	t-butyl ether of 2-ethylhexanol	✓	✓
84	9.390, 9.384	13,13-Dimethyl-3,6,9-trioxa-13-silatetradecan-1-ol	✓	✓
85	9.535, 9.536	Phenol, 2,6-dimethoxy-	✓	✓
86	9.633, 9.633	2-Propenoic acid	✓	✓
87	9.746, 9.746	Heptane, 3-bromo-	✓	✓
88	9.827	3-[(Cyclohexyl-methyl-amino)-methyl]-3H-benzooxazol-2-one	×	✓
89	9.919, 9.919	Benzaldehyde, 3-hydroxy-4-methoxy-	✓	✓
90	10.032, 10.032	1,4-Benzenediol, 2,6-dimethyl-	✓	✓
91	10.151, 10.151	1,2,4-Trimethoxybenzene	✓	✓
92	10.216, 10.211	Phenol, 2-methoxy-4-(1-propenyl)-	✓	✓
93	10.259, 10.259	Methylparaben	✓	✓
94	10.389	Cyclopentane, chloro-	×	✓
95	10.475, 10.470	Ethanone, 1-(4-hydroxy-3-	✓	✓

		methoxy5phenyl)-		
96	10.583, 10.589	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	✓	✓
97	10.637, 10.637	Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)-	✓	✓
98	10.718, 10.719	Acetamide, 2-(4-hydroxy-3-methoxyphenyl)-	✓	✓
99	10.908, 10.913	2-Amino-1-(3,4-dimethoxyphenyl)ethanone	✓	✓
100	11.107, 11.107	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	✓	✓
101	11.410, 11.405	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	✓	✓
102	11.507, 11.507	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	✓	✓
103	11.712, 11.713	2,4(3H,5H)-Thiazoledione	✓	✓
104	11.907, 11.902	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	✓	✓
105	12.074, 12.074	Benzene, 1,1'-butylidenebis-	✓	✓
106	12.172	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-	×	✓
107	12.393, 12.393	4H-1,3,2-Dioxaborin	✓	✓
108	12.582, 12.588	Pyrrolidine	✓	✓
109	13.133, 13.133	Octanoic acid	✓	✓
110	13.614	Octadecane, 2,6-dimethyl-	✓	×
111	14.073	Hexadecanamide	✓	×
112	14.543	Dimethyl tetradecanedioate	✓	×
113	14.878	9-Octadecenamide, (Z)-	✓	×
114	15.299	13-Octadecenal, (Z)-	✓	×
115	15.386	Hexadecanedioic acid	✓	×

Table 14 Comparison of compounds in pure bio-oil and bio-oil with CaCl2

Peak No.	Retention time (min)	Compound name	(a) Pure bio-oil	(b) Bio-oil with CaCl2
1	1.703, 1.697	Methyl Alcohol	✓	✓
2	1.838	Ethanol	×	✓
3	1.919,1.919	Acetone	✓	✓
4	2.048, 2.043	Acetic acid, methyl ester	✓	✓
5	2.097, 2.097	Formic acid	✓	✓
6	2.367	Acetic acid, hydroxy-	✓	×
7	2.399	Acetic acid ethenyl ester	✓	×
8	2.778, 2.761	Acetic acid	✓	✓
9	2.994	Crotonic acid	✓	×
10	3.139, 3.139	2-Propanone, 1-hydroxy-	✓	✓
11	3.404	Methyl Isobutyl Ketone	✓	×

12	3.491	Acetic acid, hydroxy-, methyl ester	✓	×
13	3.620, 3.609	1,2-Propanediol, 3-methoxy-	✓	✓
14	3.772, 3.685	Propanoic acid	✓	✓
15	3.923	Propanoic acid, 2-hydroxy-	✓	×
16	3.944	Pyrazine	×	✓
17	4.047, 4.052	2-Furanmethanol, tetrahydro-, acetate	✓	✓
18	4.128, 4.128	Pyridine	✓	✓
19	4.209	Propanoic acid, 2-methyl-	×	✓
20	4.295, 4.295	1-Hydroxy-2-butanone	✓	✓
21	4.555, 4.555	3-Hexene, (Z)-	✓	✓
22	4.652	Benserazide	✓	×
23	4.657	Propanoic acid, 2-hydroxy-2-methyl	×	✓
24	4.717	Isocrotonic acid	✓	×
25	4.749	Propane, 2-ethoxy-	×	✓
26	4.755	Acetic acid	×	✓
27	4.771	Acetamide	✓	×
28	4.846	3-Furaldehyde	✓	×
29	4.900	Propanoyl chloride, 2-methyl-	×	✓
30	4.911, 4.949	Pyridine, 2-methyl-	✓	✓
31	4.987	Butanoic acid	✓	×
32	4.998	Propanoic acid, 2-hydroxy-2-methyl	×	✓
33	5.041, 5.057	2H-Pyran-2-one	✓	✓
34	5.171	Butanoic acid	×	✓
35	5.241, 5.257	1,2-Ethanediol, monoacetate	✓	✓
36	5.289, 5.300	2-Furanmethanol	✓	✓
37	5.403, 5.408	2-Propanone, 1-(acetyloxy)-	✓	✓
38	5.441	Pyridinium, 1-amino-4-methyl-	✓	×
39	5.484	Pyridine, 3-methyl-	×	✓
40	5.538	1,3-Butadiene	×	✓
41	5.624, 5.635	L-Mannose, 6-deoxy-	✓	✓
42	5.711, 5.711	4-Hydroxy-3-hexanone	✓	✓
43	5.830, 5.824	2-Cyclopenten-1-one	✓	✓
44	5.873	Ethanone, 1-(2-furanyl)-	×	✓
45	5.938, 5.932	Butanoic acid, 5.932	✓	✓
46	6.046, 6.046	2-Cyclopenten-1-one, 2-hydroxy-	✓	✓
47	6.138, 6.137	Cyclohexane	✓	✓
48	6.186	Propanoic acid	×	✓
49	6.289, 6.273	2-[N-Aziridylmethyl]glutaronitrile	✓	✓
50	6.343, 6.348	2-Butanone, 3,3-dimethyl-	✓	✓
51	6.440, 6.445	2-Cyclopenten-1-one, 3-methyl-	✓	✓
52	6.543	3-Buten-1-ol, 3-methyl-2-methylene	✓	×
53	6.586, 6.580	Phenol	✓	✓
54	6.688	2-Furancarboxylic acid, 2-	×	✓

		ethylcyclohexyl ester		
55	6.791, 6.786	2-Furanmethanol, tetrahydro-, acetate	✓	✓
56	6.948	Methoxyacetic acid, octyl ester	✓	×
57	7.013, 7.002	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	✓	✓
58	7.099, 7.094	Cyclooctene	✓	✓
59	7.207	3-Hexanone, 4-methyl-	✓	×
60	7.234	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	×	✓
61	7.240	Cyclopropanecarboxylic acid	✓	×
62	7.283	2(3H)-Furanone, dihydro-3-methyl-	×	✓
63	7.358	Butanoic acid, 2-propenyl ester	×	✓
64	7.385	Trifluoroacetic acid	✓	×
65	7.412	Benzene, 1-fluoro-4-methoxy-	×	✓
66	7.542, 7.542	Phenol, 2-methoxy-	✓	✓
67	7.596, 7.591	Pyrrolidine	✓	✓
68	7.683, 7.661	Propanamide, N-methyl-2-amino-	✓	✓
69	7.720	Acetic acid, 2-(2-furoylhydrazono)	×	✓
70	7.742	1H-Pyrrole-2-carboxaldehyde	✓	×
71	7.796, 7.785	Cyclohexane	✓	✓
72	7.877	4-Methyl-4-(tetrahydropyran-2-yl)oxypentane-2,3-dione	×	✓
73	7.882	2,3-Dimethyl-undec-1-en-3-ol	✓	×
74	7.969, 7.963	1,3-Cyclohexanedione	✓	✓
75	8.012, 8.001	Ethyl 2-cyanocrotonate	✓	✓
76	8.109, 8.093	Pyrrolidine	✓	✓
77	8.169, 8.169	Benzoic acid	✓	✓
78	8.260	Pentane, 2-methyl-	×	✓
79	8.309	1-.beta.-d-Ribofuranosyl-3-[5-tetraazolyl]-1,2,4-triazole	✓	×
80	8.336	Pentanoic acid	×	✓
81	8.374, 8.374	Phenol, 2-methoxy-4-methyl-	✓	✓
82	8.423	Pentanoic acid	✓	×
83	8.628, 8.617	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	✓	✓
84	8.660	Sulfurous acid, butyl isohexyl ester	×	✓
85	8.736	1,6;3,4-Dianhydro-2-O-acetyl-	✓	×
86	8.785, 8,784	1,1-Dodecanediol, diacetate	✓	✓
87	8.855, 8.855	2H-Pyran-2-one	✓	✓
88	8.930, 8.925	1,2-Benzenediol	✓	✓
89	9.011, 9.001	N-(1-Cyanopropenyl)formamide	✓	✓
90	9.136, 9.130	Benzenemethanol	✓	✓
91	9.222, 9.217	endo-2,3-O-Ethylidene-.beta.-d-erythrofuranose	✓	✓
92	9.287	4-Hydroxy-3-methylacetophenone	✓	×

93	9.325, 9.319	t-butyl ether of 2-ethylhexanol	✓	
94	9.390	13,13-Dimethyl-3,6,9-trioxa-13-silatetradecan-1-ol	✓	×
95	9.535, 9.530	Phenol, 2,6-dimethoxy-	✓	✓
96	9.633, 9.633	2-Propenoic acid	✓	✓
97	9.746, 9.741	Heptane, 3-bromo-	✓	✓
98	9.881	Ethanone, 1-(2-hydroxyphenyl)-	×	✓
99	9.919	Benzaldehyde, 3-hydroxy-4-methoxy-	✓	×
100	9.984	2-Cyclohexen-1-one	×	✓
101	10.032, 10.027	1,4-Benzenediol, 2,6-dimethyl-	✓	✓
102	10.151, 10.151	1,2,4-Trimethoxybenzene	✓	✓
103	10.216, 10.216	Phenol, 2-methoxy-4-(1-propenyl)-	✓	✓
104	10.259, 10.259	Methylparaben	✓	✓
105	10.432	1-Trifluoroacetoxy-2-methylpentane	×	✓
106	10.475, 10.470	Ethanone, 1-(4-hydroxy-3-methoxy5phenyl)-	✓	✓
107	10.583	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	✓	×
108	10.637, 10.637	Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)-	✓	✓
109	10.718, 10.713	Acetamide, 2-(4-hydroxy-3-methoxyphenyl)-	✓	✓
110	10.908, 10.907	2-Amino-1-(3,4-dimethoxyphenyl)ethanone	✓	✓
111	11.059	1,2-Dimethoxy-4-n-propylbenzene	×	✓
112	11.107, 11.102	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	✓	✓
113	11.199	Pyridinium, 1-[(ethoxycarbonyl)amino]-, hydroxide, inner salt	×	✓
114	11.410	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	✓	×
115	11.507, 11.577	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	✓	✓
116	11.712, 11.712	2,4(3H,5H)-Thiazoledione	✓	✓
117	11.907, 11.901	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	✓	✓
118	12.026	Benzene, 1,4-difluoro-2,3-dimethyl	×	✓
119	12.074, 12.074	Benzene, 1,1'-butylidenebis-	✓	✓
120	12.393, 12.393	4H-1,3,2-Dioxaborin	✓	✓
121	12.582	Pyrrolidine	✓	×
122	12.787	Dixanthogen	×	✓
123	13.133, 13.133	Octanoic acid	✓	✓
124	13.614	Octadecane, 2,6-dimethyl-	✓	×

125	14.073	Hexadecanamide	✓	×
126	14.543	Dimethyl tetradecanedioate	✓	×
127	14.624	N,N'-[trans-1,4-Cyclohexylene]-bis[s-2-aminoethyl thiosulfuric acid]	×	✓
128	14.878	9-Octadecenamide, (Z)-	✓	×
129	15.299	13-Octadecenal, (Z)-	✓	×
130	15.386	Hexadecanedioic acid	✓	×

After accelerated aging of pure bio-oil at 80 ^{o}C, the bio-oil revealed an increase in water content, acidity and viscosity. Molecular building reactions occurred to give rise to larger molecules and led to the increment of viscosity. The formation of additional aldehyde hydrates or an equilibrium shift from acetals to hemiacetals result in the water content from increasing more as well as the molecule decomposing reactions will lead to increased acids. Hence, selected solvents and antioxidants are used to maintain the stability of bio-oil during storage or expose to higher temperature. The yellow highlighted components in Table 12, Table 13 and Table 14 shows that the antioxidants and solvents used to stabilize the bio-oil are not consumed and remained in the bio-oil. This proves that the additives may be able removed from the bio-oil after the process of stabilization in order to produce pure and stabilized bio-oil.

Based on Table 12, propyl gallate limits the access of air to the bio-oil which can help to minimize the possibility of forming peroxides that catalyze olefinic polymerization. However, due to the disappearance of olefinic compounds in bio-oil, bio-oil apparently do not contain enough free-radical trap molecules for stabilization. Hence, the phenolics formed will be used as free-radical traps and stopped the chain reaction of polymerization. Many phenolics are good free-radical traps and can be used to prevent olefins from the polymerizing effect of free-radicals. In addition, the decrease in carbonyls and ethers may result in decreases of water content during aging. Furthermore, all the antioxidants reduced molecule decomposing reactions which led to lower acidity after aging except calcium chloride salts (CaCl2). This phenomenon may be due to the presence of propanoyl chloride (blue highlighted) in bio-oil which has the acidic property as shown in Table 14.

Last but not least, from Table 13, it indicates that solvent can terminate the chain of oligomers, breaking polymer chains to lower-molecular-weight products and converting the reactants to inactive forms. In context, ethanol 95 % can react with the reactive sites in the oligomers that were termination polymerization. Likewise, polymeric esters were transesterified with alcohol to form a lower-molecular-weight methyl ester. Besides, aldehyde groups can also be converted to acetals which reduce the availability for polymerization. Addition of ethanol 95 % to bio-oil also inhibited phase separation.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, it is unstable to store bio-oil for a long period of time due to its complex compositions. Heating bio-oil to 60 ^{o}C or more will activate the internal chemical reactions such as polymerization, esterification and transesterification which lead to increase in viscosity, water content and acidity. Besides, condensation reactions in bio-oil will result in the formation of water as byproduct and further reduces its heating value. In this research project, based on the literature review, the optimum condition used by the author to study the accelerated aging of bio-oil is 80 ^{o}C for 7 days. These conditions enable the effectiveness of additives used to stabilize the bio-oil becomes more obvious.

The additives used in this research project to stabilize the bio-oil derived from empty fruit bunch (EFB) are 1000 ppm of antioxidants (propyl gallate (PG), tert-butyl hydroquinone (TBHQ), butylatedhydroxyanisole (BHA) and calcium chloride salts (CaCl2)) and 10 wt% of solvents (ethanol 95 %, acetone and ethyl acetate). All the chosen antioxidants and solvents are able to improve the stability of bio-oil in term of viscosity and water content during aging. Furthermore, all the aforementioned antioxidants help to reduce the acidity of bio-oil as well except CaCl2. From this study, the effectiveness of antioxidants increases in the following order: CaCl2, BHA, TBHQ and PG. On the other hand, the effectiveness of solvents increases in the following order: acetone, ethyl acetate and ethanol 95 %. The pure bio-oil, bio-oil with PG, bio-oil with ethanol 95 % and bio-oil with CaCl2 are chosen for GC-MS analysis.

Based on the results from GC-MS analysis, it shows that antioxidant compounds have low activation energy to donate hydrogen in order to affect the propagation of the free radical chain. This can help to delay the beginning of the aging or slow the rate of chemical reaction. All the antioxidants manage to reduce the acidity of bio-oil after aging except CaCl2 due to the formation of propanoyl chloride after mixing with bio-oil. Besides, organic solvents can also inhibit the chain of polymerization by converting the active units in the oligomer chain to inactive units. The solvents most probably react to form low molecular weight products which resulted in lower viscosity. In addition, both antioxidants and solvents able to reduce the water content in bio-oil due to the decrement of aldehyde hydrates. Addition of ethanol 95 % also inhibited phase separation.

5.2 Recommendations

As the research of stabilization is indefinitely wide, various future works can be done to further expand and continue the research in various aspects of stabilization. In order to commercialize the stabilization of bio-oil a in a big scale, the idea of stabilization of empty fruit bunch (EFB) derived bio-oil need to be promoted to the people. As such, the researches in the laboratory scale are being carried out actively in order to explore the possible and best ways to stabilize bio-oil. Some of the recommendations that can be expanded in the future are:

a) Study the effects of additives in other properties of bio-oil such as heating value, density, elemental analysis, Fourier transform infrared spectroscopy (FTIR) analysis and etc.
b) Explore the possibility of using other methods to stabilize the EFB derived bio-oil such as fractionation, emulsification and mild hydrogenation.

CHAPTER 6
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