

**PHENOL FROM PALM BIO-OIL
VIA SALT EXTRACTION**

By

HAZWAN ARIF BIN MD YUSOF @ GHANI (10670)

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

SEPT 2011

**Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan
Malaysia**

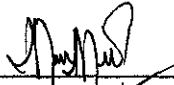
CERTIFICATION OF APPROVAL
PHENOL FROM PALM BIO-OIL
VIA SALT EXTRACTION

By

Hazwan Arif Bin Md Yusof @ Ghani

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

Approved by,

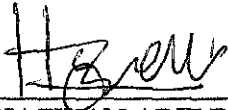


(Dr. Murni Melati Ahmad)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2011

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.



HAZWAN ARIF BIN MD YUSOF @ GHANI

ABSTRACT

Renewable source of energy and chemicals is highly sought after nowadays with the alarming global concerns on the price insecurity, source depletion and environmental impact of the fossil fuel usage. Biomass becomes the source of interest to obtain energy and products that are environmental friendly with net zero carbon footprints, especially for Malaysia that has to manage abundant agricultural wastes. Malaysian palm biomass i.e. kernel shell, empty fruit bunch and trunk can be processed using a thermal treatment called pyrolysis to produce bio-oil, a complex mixture of phenolic compounds, acetic acid and aldehyds. In this study, phenol is going to be extracted using liquid-liquid extraction method. Addition small amount of salt at ambient condition in different of cations and anions including $ZnSO_4$, $MgSO_4$, Na_2SO_4 , K_2SO_4 , $ZnCl_2$, $MgCl_2$, $NaCl$ and KCl ; into bio-oil would form two phases of bio-oil which is light phase and dark phase. The results of this separation were analyzed by using GC-FID. It found that polar compound will concentrated in light phase while the non-polar compound including phenol concentrated in dark phase. Different types of salt and salts concentration will give different value of phenol in dark phase.

ACKNOWLEDGMENT

First and foremost, I would like to express my gratitude to God for making the Final Year Project (FYP) II a successful and beneficial for me. A token of appreciation also goes to my supervisor, Dr. Murni Melati Ahmad for her knowledge, idea, and guidance and advises throughout the progress of completing this project.

Thanks to Mr. Azwan Fitri Zainal Abidin for sharing ideas and knowledge as well as his support throughout this project. Thanks to AP Dr. Suzana Yusop for letting me use the facilities at Block P Bio-Hydrogen.

I am also would like to take this opportunity to express very sincere thanks to Dr. Lukman B. Ismail, coordinator of Final Year Project. Without his management and coordination, the flow of this project might not be as expected.

Finally, I would like to express deepest appreciation to those involved directly and indirectly in the completion of this research project. With the full cooperation from these people, I have successfully achieved the objective of this project.

Table of Contents

Abstract	i
Acknowledgment	ii
Chapter 1 Introduction	1
1.1 Background	1
1.1.1 Pyrolysis Oil.....	1
1.1.2 Phenol.....	4
1.2 Problem Statement	6
1.2.1 Problem Identification.....	6
1.2.2 Significant of the Project.....	7
1.3 Objective	7
1.4 Scope of the Study	7
1.5 Relevancy of the Project	9
1.6 Feasibility of the Project	9
Chapter 2 Literature Review	10
2.1 Current and Past Technology in Phenol Extraction from Pyrolysis Oil	10
2.2 Analysis on Past Project about Method to Extract Phenol from Pyrolysis Oil.....	12
2.3 Analysis on Current Bio-Oil Separation Process	14
Chapter 3 Methodology.....	16
3.1 Description of Methodology	16
3.2 Flow Charts of Research Activities	17
3.3 Tool, Equipment and Material	18
3.4 Pyrolysis of Empty Fruit Bunch.....	19
3.5 Pyrolysis of Palm Kernel Shell	20

3.6 Physical Properties Characterization and Equipment	21
3.7 Screening of Suitable Salt as Extractant	22
Two types of anions and four types of cations are chosen for this screening process. It presents eight types of salt. The details are as follow:	22
3.7.1 Experiment Procedure.....	22
3.8 GC-FID ANALYSIS.....	23
Chapter 4 RESULT AND DISCUSSION.....	24
4.1 Bio-oil Production.....	24
4.2 Bio-oil characterization.....	25
4.3 Phase separation.....	27
4.3.1 Screening process.....	27
4.3.2 GC-FID Analysis for two phases of bio-oil.....	27
4.3.3 FID-GC analysis to Dark layer of two different salts	29
4.3.4 Effect of Salts Concentration	30
Chapter 5 conclusion.....	33
Chapter 6 reference	34
Chapter 7 Appendix	37
7.1 Phenol Properties	37
7.2 Fluidized Bed Reactor Calibration.....	37
7.2.1 Trial 1	37
7.2.2 Trial 2.....	38
7.2.3 Trial 3	38
7.3 Gantt Charts of Research Activities.....	39
7.4 Key Milestone	40

LIST OF TABLES

Table 1 Physical properties of pyrolysis oil.....	2
Table 2 Identification of chemical compounds in pyrolytic oil by GC/MS.....	4
Table 3 Analysis on Past Project about Method to Extract Phenol from Pyrolysis Oil.....	12
Table 4 Analysis on current bio-oil separation process	14
Table 5 Physical properties characterization and equipment.....	21
Table 6 Types of Salt	22
Table 7 Properties of bio-oil	25
Table 8 Intensity for different concentration of salt	31
Table 9 Feeder Speed: 0.7-0.8 rpm	37
Table 10 Feeder Speed: 3.4 – 4.1 rpm	38
Table 11 Feeder Speed: 6.1 – 6.7 rpm	38

LIST OF FIGURES

Figure 1 Research Activities.....	17
Figure 2 FID-GC	18
Figure 3 Pyrolysis Process using Fluidized Bed Reactor.....	19
Figure 4 Microwave Pyrolyzer.....	20
Figure 5 Phase Separation Procedure.....	22
Figure 6 Bio-oil from Fluidized Bed Reactor	24
Figure 7 FID-GC result for PKS bio-oil	26
Figure 8 After addition of various types of salt	27
Figure 9 Light phases of bio-oil after adding 40% concentration of MgSO ₄	28
Figure 10 Dark phases of bio-oil after adding 40% concentration of MgSO ₄	28
Figure 11. Dark phases of bio-oil after adding 40% concentration of Na ₂ SO ₄	29
Figure 12. Bio-oil with different MgSO ₄ salt in increasing concentration	30
Figure 13 FID-GC result for dark phases of bio-oil after adding 40% concentration of MgSO ₄	31

Figure 14. FID-GC result for dark phases of bio-oil after adding 100% concentration of MgSO ₄	31
Figure 15 Gantt Chart.....	39
Figure 16 Key Milestone.....	40

CHAPTER 1 INTRODUCTION

1.1 Background

Malaysia as the largest producer of palm oil in the world generates a significant amount of oil palm wastes. The existence of more than 3 million hectares of oil palm plantations in Malaysia that produced approximately 90 million metric ton of renewable biomass per year in the form of trunks, fronds, shells, palm press fiber and the empty fruit bunch, is appealing for feasibility studies on producing high-value products and energy from biomass (MPOB, 2009).

The increasing of petroleum prices, concerns over security of supply and concerns about climate change are major driver in investigating biomass as alternative to replace the reliance on petroleum product as energy sources. Moreover, Kelly-Yong et al. (2007) have reported the feasibility of utilizing palm oil wastes as renewable energy source, specifically on the production of bio-oil, bio-gasoline, syngas and hydrogen.

A specific work reported by Abdullah et al. (2007) investigated pyrolysis technology to produce bio-oil from oil palm fruit bunches. This thermal decomposition process breaks down biomass into a mixture of condensable liquids, char and gases using moderate temperature without oxygen (Bridgwater, 2000; Czernik and Bridgwater, 2004; Mohan et al. (2006).

1.1.1 Pyrolysis Oil

Pyrolysis may be described as the thermal degradation of materials in the complete absence of inadequate presence of oxygen (Mohan et al. 2006). The liquid product from pyrolysis is compromised of highly-oxygenated compounds (Czernik and Bridgwater, 2004; Abdullah et al. 2007; Azizan et al, 2009) and is in the form of dark

brown, free-flowing oil. This bio-oil contains almost 25 wt% water. Guaiacols, pyrones, acetic acid, formic acid, and other carboxylic acids (Mohan et al, 2006) and the other major groups of compounds including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics (Piskorz et al., 1988).

The liquid yields and properties of the pyrolysis oil vary depending on the biomass used (Czernik and Bridgwater, 2004; Abdullah et al., 2007; Azizan et al, 2009; Ringer et al, 2006; Oasama and Meir, 2005; Oasama and Peacocke, 2001). The high oxygen content makes the bio-oil having different properties and between compared to hydrocarbon fuels (Oasama and Czernik, 1999). In fact, bio-oil is immiscible with liquid hydrocarbon due to high polarity and hydrophilic nature. Furthermore, based on the Bridgwater (2003), bio-oil has time dependent behavior; properties such as viscosity, volatility, phase separation and decomposition of gums change with time. These changes may be due to aldol condensations between some compound in bio-oil such as aldehydes, ketones and others, to form larger molecules during storage and handling. The stability and ageing behavior are found to highly dependent on temperature (Czernik and Bridgwater, 2004).

Table 1 Physical properties of pyrolysis oil

Physical properties	Goh et al. Pyrolytic Oil Study 2000	M.N Islam et al. Study 1999
Calorific value (MJ/kg) ASTM D240	9.9	22.1
Density (kg/m ³) ASTM D 5004	1.1083	1.2
Viscosity (at 50oC) (cSt) astm d 445	2.06	14.63
Ph	2.42	2.7
Flash Point (oC) ASTM D 93	50	54
Pour point (oC) ASTM D 97	-22	-10
Distillation (oC) ASTM D 86 IBP (initial boiling point)		
10%	99	94
30%	100	100

50%	100	120
70%	101	155
75%	170	182
80%	-	190
90%	238	-
	-	-
Decomposed at	238	190

Table 1 shows the physical properties of the pyrolysis oil on a study conducted by M.S Goh et al. (2006). These were compared to M.N.Islam et al.'s study (1999). In this study, the energy content in terms of higher heating value of the pyrolysis oil was low, 9.9 MJ/kg, due to the presence of high percentage of moisture and oxygenated components. The density of pyrolysis oil was 1.1083 g/cm³, it was relatively low. The kinematic viscosity of pyrolysis oil at 50oC was 2.06 cSt. The pyrolysis oil produced can be estimated have higher water contents. The pH of pyrolysis liquids is low (pH 2.42). The pH was affected mainly by high amounts of volatile acids, mainly acetic and formic acids. The pour point was lower for the present study than M.N.Islam et.al's study. For the pyrolysis liquids analyzed the low viscosity was an indication of a low pour point. The flash point was 50oC. This is due to a high amount of low boiling volatile compounds in pyrolysis oil.

Many studies investigated the feasibility of bio-oil upgrading via common processes applicable for fossil oil (Mahfud, 2007; Huber et al, 2006; Vijaya, 2001). Gutierrez proposed a feasibility study on co-processing upgraded bio-oil in a standard refinery plant. However, due to the oxygenated compounds in the bio-oil that makes it acidic, the equipment must be made of stainless steel even if the catalyst use is similar. Furthermore, steam reforming of such a mixture is very difficult, expensive and energy intensive due to extensive coke formation and catalyst deactivation (Rioche et al., 2005; Czernik et al., 2002)

1.1.2 Phenol

Kawser et al. (2000) have reported about potential of phenol derived from pyrolysis oil as substitute for petroleum-based phenol. Phenol is an organic compound with the chemical formula C_6H_5OH . Phenol is considered as an important chemical with divergent applications. For example, it can be used to manufacture molding products for automotive parts, household appliances, electrical components; in bonding and adhesive resins for laminating, plywood, protective coating, insulation materials, abrasive coating; in foundry industries for sand moulds and cores, Phenol has been commercially synthesized from petroleum resources; however, the production of petroleum-based phenol is quite expensive (Kawser et al., 2000).

SRI Consulting has reported that global production and consumption of phenol in 2010 were almost 8.5 million metric tons. Global capacity utilization was 83% in 2010, down from 79% in 2009. Phenol consumption in 2010 is estimated to have increased by 7% from 2009; it is expected to average growth of 4.5% per year from 2010 to 2015. Until 25 March 2011, phenol prices were assessed as USD1.920-1.950/tonne. As the global demand on phenol increased and cost on producing phenol from petroleum derived also increases, there is a need to find alternative to find phenol from non-petroleum product.

Table 2 Identification of chemical compounds in pyrolytic oil by GC/MS

Chemical compounds	Area percent, %
Phenol	36.186
2 methoxy phenol	4.58
2,6-dimethoxy phenol	4.565
2-methoxy -4 methyl phenol	2.399
4-ethyl -2 methoxy phenol	2.211
3-[(trimethylsilyloxy]-phenol	1.964
2-methoxy -4(1-propenyl) phenol	1.484
2,6-dimethoxy-4-(2-propenyl)phenol	1.39
2 - methyl phenol (o-cresol)	0.518
4- methyl phenol (p-cresol)	0.485
2- methoxy -4-propyl phenol	0.26

Total of Phenol and its derivatives	56.042
Triphenylphosphine oxide	12.971
4-hydroxy benzoic acid	6.106
4 -hydroxy -methyl ester benzoic acid	2.039
3-hydroxy-4 methoxy benzoic acid	1.906
2-methyl -ethyl ester propenoic acid	0.436
2 hydroxy-3-methyl-2 cyclopentenone	1.361
3-ethyl-2-hydroxy-2-cyclopentenone	0.256
4-hydroxy -3-methoxy benzaldehyde	0.963
4-hydroxy-3,5-dimethoxy benzaldehyde	0.427
1,4-dimethoxy -2,6-dimethyl benzene	0.418
Others	17.075
TOTAL	100

Goh et al. (2006) reported pyrolysis oil from oil palm shell was rich in phenolic compounds. Table 3 shows the results of GC/MS analysis of pyrolysis oil from oil palm shell. From the results, it shows that the pyrolysis oil contents high fraction of phenolic compounds, up to 56.042 area %. The other compounds in pyrolysis oil from oil palm shell comprised benzoic acids, ketones (cyclopentenone), aldehydes (benzaldehyde) and benzene.

As phenol is considered as an important chemical with divergent applications, this study will propose optimal extraction system for phenol from pyrolysis oil by identify the suitable extractant and optimal conditions that gives high yield of phenol based on pyrolysis oil feedstock, extractant concentration and pH.

1.2 Problem Statement

1.2.1 Problem Identification

Bio-oil cannot be used in an engine due to its low heating value, high viscosity, chemical instability, incomplete volatility and solid sediment. Many methods for upgrading bio-oil to a usable liquid fuel, such as emulsification, hydrotreating and catalytic cracking have been studied and need to be further improved (Changyan et al, 2010).

As the bio-oil is not immiscible with liquids hydrocarbons, the integration process with fossil oil is difficult, expensive and energy intensive. By using environmental friendly, inexpensive and renewable extractant, the focus of processing bio-oil can be re-shifted to recover the high-value added components bio-oil.

There are about 300 compounds of bio-oil. A number of chemicals can be extracted which includes phenols for resin and adhesive industry, acetic acid for the production of derivatives like vinyl acetate monomer, volatile organic acids in formation of de-icers, levoglucosan, hydroxyacetaldehyde and some additives for pharmaceutical, fiber and fertilizer industries and even flavoring agents in food products (Czernik and Bridgwater, 2004; Chum et al, 1989; www.btgworld.com). The selection of which chemicals to be extracted is depend on lower technological barrier, high price of compound and high demand for the compound.

Current recovery technique to extract high-value phenols involves reactive liquid-liquid reaction, steam distillation and liquid phase chromatography that are either involving methods or extractant that are expensive, energy intensive, sensitive and not environmental friendly.

Furthermore, instead of using an energy intensive method such as catalytic conversion to upgrade the bio-oil into gasoline, diesel, hydrogen or other product, exploration can be performed on common extractants and environmental-friendly low cost technique to extract the high-value of phenol. It is also aimed that the usage of these extractant and method will allow increased yield of recovery. The extractant used must be cheap or cost competitive, renewable and recyclable. The stabilized chemicals can then be processed together with chemicals from crude fossils oil into the end products via catalytic conversion.

1.2.2 Significant of the Project

Through this project, we aims to investigate and identify to extract high-valued phenol from pyrolysis oil by using cheap, competitive, renewable and recyclable extractant

1.3 Objective

This study embarks on the following objectives:

1. To pyrolyze two types of palm wastes available in Malaysia i.e. kernel shell and empty fruit bunch into bio-oil.
2. To characterize and measure phenol amounts in the bio-oil from palm kernel shell
3. To screen and identify the suitable common salts to form two phase system in order to enhance the recovery of phenol from bio-oil.
4. To observe the effect of concentration of salt on-two phase formation.

1.4 Scope of the Study

The main focus of this work is to produce bio-oil from palm waste which is Plam Kernel Shell (PKS) by using Fluidized Bed Reactor. Then, then project is continued with

screening process by using eight types of salt that have different cations and anions to do phase separation of bio-oil. The salts are:

- i. NaCl
- ii. KCl
- iii. MgCl₂
- iv. ZnCl₂
- v. Na₂SO₄
- vi. K₂SO₄
- vii. MgSO₄
- viii. ZnSO₄

Afterwards, the top and bottom of the bio-oil after phase separation will be analyzed by using GC-FID equipment to prove the existence of phenol whether in the dark phase or in the light phase.

1.5 Relevancy of the Project

Phenol has been commercially synthesized from petroleum resources; however, the production of petroleum-based phenol is quite expensive. To decrease reliance on the petroleum product, phenols derived from oil palm shell have been looked at as a potential substitute for petroleum-based phenol

1.6 Feasibility of the Project

In the first semester, this project is covered the literature review for the current method and types of extractant that have been used to extract phenolic compounds from pyrolysis oil. The formulation of methodology that will be used also determined to choose the right extractant to extract phenolic compounds from pyrolysis oil based on several criteria which is cheap, competitive, renewable and recyclable extractant and also environmental-friendly low cost technique.

The second semester will cover the experimental work to investigate the right extractant that gives highest yield of specified purity of phenol in two phase of bio-oil.

CHAPTER 2 LITERATURE REVIEW

The literature review is done on current and past technology in extracting phenol from pyrolysis. Literature review also provides information on type of solvent, temperature, pressure and Ph of solvent during the extraction process.

2.1 Current and Past Technology in Phenol Extraction from Pyrolysis Oil

Generally, bio-oil can be phase separated into an aqueous fraction and organic fraction via water addition. These fractions can be further extracted to obtain phenol with varying yields, depending on the source of bio-oil.

There are several technologies have been explored to separate the phenolic compounds from complex mixtures of bio-oil. There are liquid-liquid extraction (Amen-Chen et al., 1997), steam distillation (Murwanashyaka et al., 2001) and liquid phase chromatography (Zhang, 1990).

A review on the feasibility of using solvent fractionation to separate the valuable compounds in bio-oil has been done by Mohan et al. (2006). This review includes fractionation of syringol from cashew nut shell oil using hexane, ethyl acetate, chloroform and methanol (Ds et al., 2004), National Renewable Energy Laboratory (NREL) solvent method using ethyl acetate, NaHCO_3 , H_3PO_4 and NaCl (Chum et al., 1989) and the other types proposed by Shinrer et al., (1964) using ether, HCL and NaOH, Christian et al. (2005) using ethyl acetate and Oasama and co-workers (2003) using diethyl ether and Dichloromethane.

Mariamni et al. (2007) reported the extraction of phenol from pyrolysis oil using Ethyl acetate and sodium bicarbonate. The liquid-liquid extraction of phenol from bio-oil also can be done by using sodium bicarbonate, sodium hydroxide and sulfuric acid (Goh et al., 2006).

Affendi et al. (2007) also cover the review of separation of phenol from pyrolysis oil. This review includes the extraction of phenol by using NaOH, methylene chloride and sulphuric acid that proposed by Gallivan et al. (1980). Another review also includes the separation of reactive phenols using ethyl acetate and sodium bicarbonate (Chum et al., 1989, 1992, 1993).

In another work, Abedi et al. (2001) investigated a few design of one-stage and multi-stage extraction system using water and solvents to separate high-value compounds in bio-oil and upgrade the left-over fraction into hydrogen. Qin et al. (2009) reported that addition of salt solution such as LiCl, CaCl₂, K₂CO₃, (NH₄)SO₄ and Fe(NO₃) could provide initial separation for complex mixture bio-oil. Their study found out that the upper layers exhibited mostly water soluble compounds and acetic acid while the bottom layer contained high lignin pyrolysis compounds.

Given the suitable extractant, high value of chemicals which is phenol can be extracted at room temperature with minimal cost. Therefore, the main focus of this work is to develop a systematic liquid-liquid extraction method based on environmental-friendly, recyclable and common extractant(s) to optimally recover the high value products from the aqueous and organic phases of the bio-oil obtained from pyrolysis of Malaysia biomass.

2.2 Analysis on Past Project about Method to Extract Phenol from Pyrolysis Oil

Table 3 Analysis on Past Project about Method to Extract Phenol from Pyrolysis Oil

References	Feed	Process	Performance Indicator	Note
Gallivan et. Al (1980)	Bark, Sawdusk, Tree Tops & Limbs	Liquid-liquid extraction method by using Methylene Chloride as extractant at temperature 21°C	<ul style="list-style-type: none"> • 33% 	-
Chum et. al (1993)	Sawdusk & Bark	Liquid-liquid extraction process by using Ethyl Acetate & NaHCO ₃ as extractant	<ul style="list-style-type: none"> • 30%(Sawdusk) • 50%(Bark) 	-
Kelley et. al (1997)	Ground softwood	Liquid-liquid extraction by using ethyl acetate as solvent at Ph 7	<ul style="list-style-type: none"> • 35% 	-
Md-Kawser et. al (2000)	Oil Palm Shell	Liquid-liquid extraction by using standard solvent at Ph 3.1 and 5% of aqueous solution at Ph 8.9	<ul style="list-style-type: none"> • 24.2% 	-
Roy et. al (2000)	Softwood bark	Fractional condensation process at 65-750°C and 15-20kPa then continued with Liquid separation process at 15°C	<ul style="list-style-type: none"> • 70% 	<ul style="list-style-type: none"> • This method produced highest yield of phenol but required high temperature in the process
Goh et. al (2006)	Oil Palm Shell	Liquid-liquid extraction process using three types of extractant.	<ul style="list-style-type: none"> • 56.042% 	<ul style="list-style-type: none"> • Complete recovery of phenol can be

		NaHCO ₃ (Ph 8.7) NaOH (Ph 14) & H ₂ SO ₄ (Ph 6)		achieved at Ph 13 – 14 using alkaline solution
Amen-Chen	Eucalyptus Wood Tar	Extraction begin with dissolving oil into ethyl acetate before continue with adding alkaline solution. Then phenol were generated by acidification using H ₂ SO ₄	-	<ul style="list-style-type: none"> • Adding ethyl acetate will decrease the oil density • Phenol were better extracted from aqueous phase at Ph below 7

2.3 Analysis on Current Bio-Oil Separation Process

Table 4 Analysis on current bio-oil separation process

References	Feed	Process	Note
Qin et al. (2009)	Rice Husk	<ul style="list-style-type: none"> Phase separation process by adding salt solution (Lithium Chloride & Potassium Carbonate) Extraction using diethylether & dicholomethane 	<ul style="list-style-type: none"> Most of phenolic compound is found at bottom phase
Changyan et al. (2010)	Corn Stover	<ul style="list-style-type: none"> Separate the oil into two phase using water at 40°C Addition of inorganic salt during separation Extracting the top phase with mix solvent containing petane & furans (1:1) under vacumm 	<ul style="list-style-type: none"> Top phase containing alkenes & low molecular lignin Inorganic salt will increase the yield of light oil from 6% to 22% ZnCl₂ promote higher yield of light oil compare to NaCl & CaCl₂ ZnCl have strongest salting out effect Phenols presented in the light oil are about 46% The two-step fractionation procedure is an effective method to separate bio-oil into light oil, heavy oil, and chemicals. The light oil, with no combustion residue and a much lower temperature of evaporation and combustion, is a good alternative fuel for engines.
Rui-Lu et al. (2010)	Rice Husk	<ul style="list-style-type: none"> The fine particles were removed using a 0.45 mm membrane Water was removed by adding sufficient amount of anhydrous sodium sulfate Bio-oil was fractioned using solvent- 	<ul style="list-style-type: none"> Most of bio-oil compound dissolved in methanol compared to other

		or solid-extraction techniques with various polarities, e.g., methanol, ethyl acetate and acetone	
--	--	---	--

CHAPTER 3 METHODOLOGY

3.1 Description of Methodology

Stage 1: Bio-oil production

- Bio-oil is produced from palm wastes types Empty Fruit Bunch (EFB) using Fluidized Bed Reactor.
- Bio-oil is produced from palm wastes types Palm Kernel Shell (PKS) using Microwave Pyrolyzer

Stage 2: Characterization of Bio-oil and Phenol

- To analyze the chemical composition of the feedstock of bio-oil with FID-GC and determine the composition of phenol using FID-GC.
- To analyze the water content measured by Karl-Fisher meter.
- To analyze other physical properties – pH, viscosity, HHV, elemental analysis etc. – using appropriate measurement methods.

Stage 3: Screening of suitable salt as extractant

- To choose the suitable extractant to form two-phase separation of bio-oil.

Stage 4: Phenol Measurement

- To detect and measure phenol in both phases and identify partition preference

3.2 Flow Charts of Research Activities

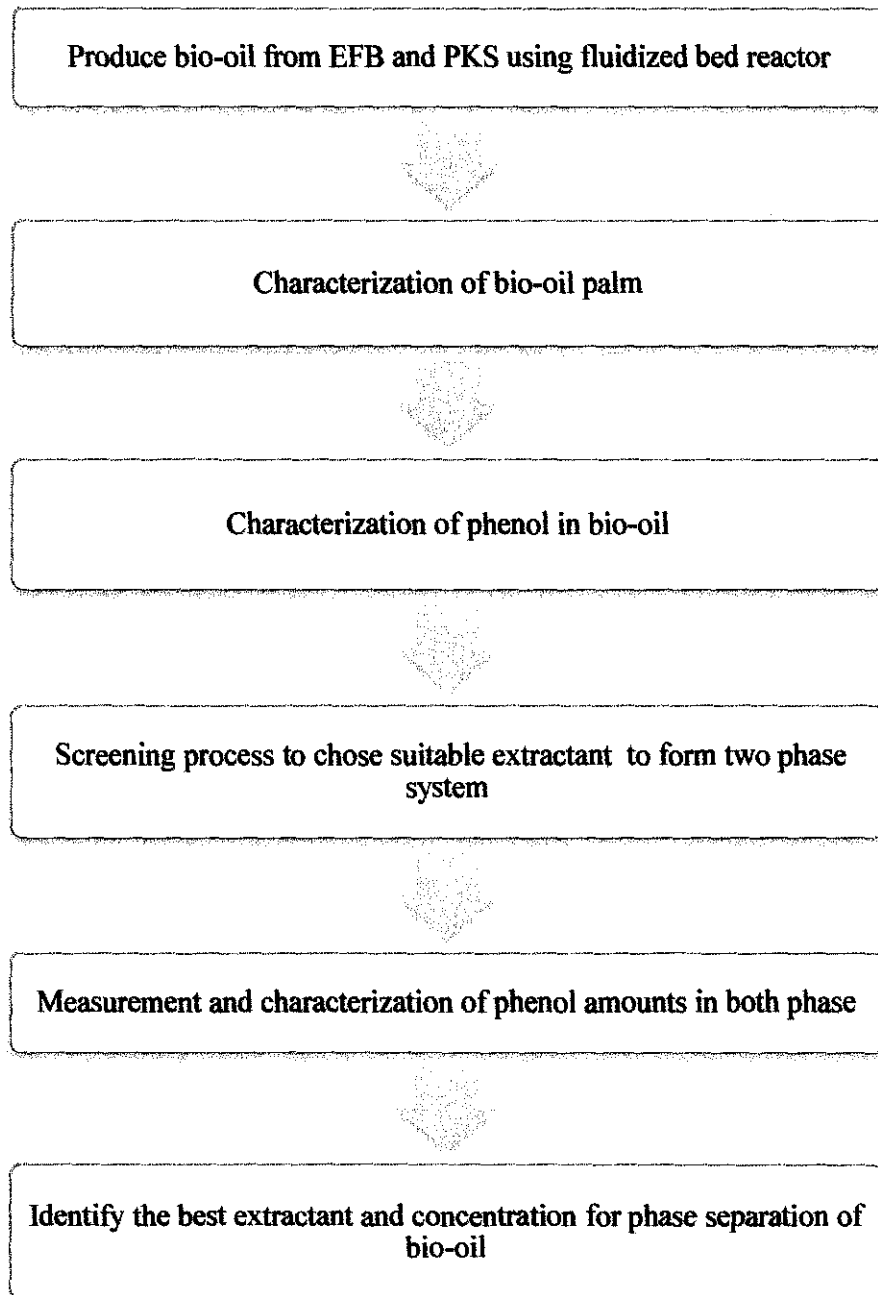


Figure 1 Research Activities

3.3 Tool, Equipment and Material

- Flame Ionization Detector – Gas Chromatography (FID-GC)



Figure 2 GC-FID

- Karl-Fisher Meter
- FTIR
- CHNS
- Viscometer
- Biomass oil from empty fruit brunch and kernel shell
- Fluidized Bed Reactor

3.4 Pyrolysis of Empty Fruit Bunch

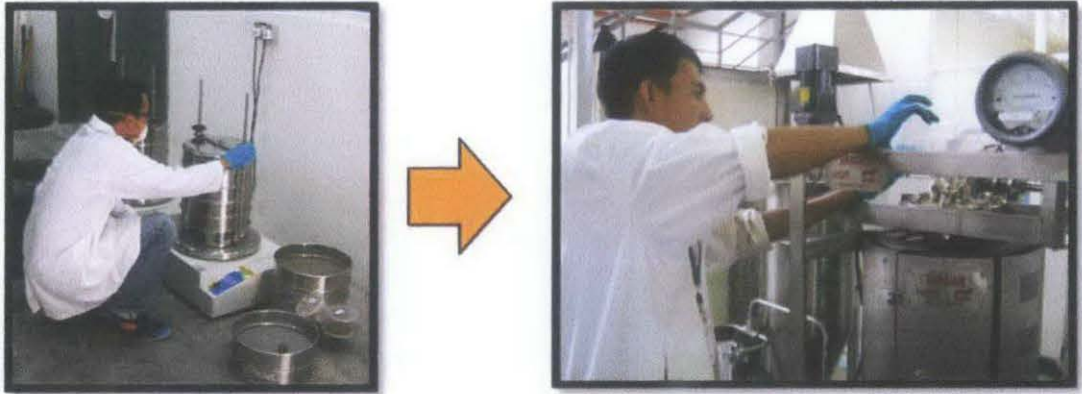


Figure 3 Pyrolysis Process using Fluidized Bed Reactor

Palm wastes types Empty Fruit Bunch was dried first before it were cut by using chopper to separate it into small pieces. Then the EFB was grinded using grinder, before it was sieved into five particles size which is 700 μm and above, 500 μm to 700 μm , 350 μm to 500 μm , 200 μm to 350 μm , and below 200 μm . It was then dried in an oven for 24 hours at 100°C.

The next step is to produce bio-oil using Fluidized Bed Reactor. The reactor is heated until the temperature reach 500°C. Then, 1.5kg of EFB with particles sizes 350 μm to 500 μm was feed into Hooper. From Hooper, the palm waste was feed into reactor at speed rate 3.4 rpm to 4.1 rpm. The carrier gas used for this process is Nitrogen.

During the process, the bio-oil produced was cooled at two condensers that have two different temperatures which is 25°C and 10°C. The other condenser used Glycol to cool the gas from the process at -10°C.

3.5 Pyrolysis of Palm Kernel Shell

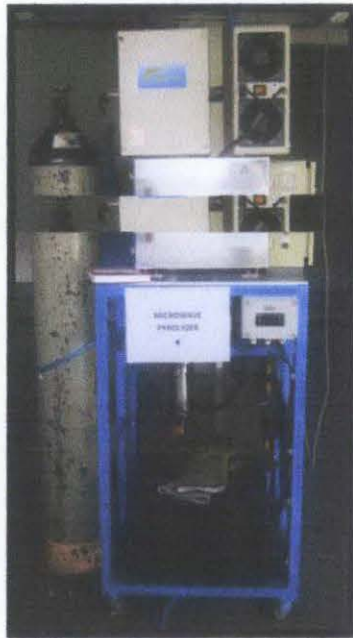


Figure 4 Microwave Pyrolyzer

Because yield of bio-oil from Fluidized Bed Reactor is not enough for this study, other alternative had to be found. Another bio-oil from PKS was produced using Microwave Pyrolyzer with assistant from Centre for Biofuel & Biochemical Research (CBBR) Department, UTP. The PKS size for this production is 1-2 μ m and the machine operates at heating power 2kWatt.

3.6 Physical Properties Characterization and Equipment

The physical properties for bio-oil produced are measured by using the standard and equipment that listed in the table below.

Table 5 Physical properties characterization and equipment

Physical Properties	Standard / Method	Equipment
Water Content	ASTM E 203-96 / Karl Fisher Titration	Karl-Fisher Meter
Ash Content	E7 / Burn off method	-
Viscosity	ASTM D 445	Viscometer
pH number	-	pH meter
Higher Heating Value (HHV)	1720 DIN 51900	Parr adiabatic bomb & Parr Calorimeter Controller
Element Composition	-	CHNS

3.7 Screening of Suitable Salt as Extractant

Two types of anions and four types of cations are chosen for this screening process. It presents eight types of salt. The details are as follow:

Table 6 Types of Salt

Anion	Cation	Salt
Cl ⁻	Na ⁺	NaCl
Cl ⁻	K ⁺	KCl
Cl ⁻	Mg ⁺²	MgCl ₂
Cl ⁻	Zn ⁺²	ZnCl ₂
SO ₄ ⁻²	Na ⁺	Na ₂ SO ₄
SO ₄ ⁻²	K ⁺	K ₂ SO ₄
SO ₄ ⁻²	Mg ⁺²	MgSO ₄
SO ₄ ⁻²	Zn ⁺²	ZnSO ₄

3.7.1 Experiment Procedure



Figure 5 Phase Separation Procedure

1 ml of bio-oil type PKS was added into a bottle. Then, 2 ml of chosen salt was mixed with the bio-oil in the bottle. These two simple steps are repeated for all the salt as stated in the Table 6. Then, all the samples were keeping for 24 hours in ambient temperature.

After that, the upper layer and the bottom layer were separated through pouring out from the tube. This method can be done due to large difference in viscosity of two phases.

Then, two phases were characterized.

3.8 GC-FID ANALYSIS

The composition of bio-oil and phase separation of bio-oil was analyzed using GC-FID type Shimadzu, Model GC-2014. The separation was made using BPX-5 capillary column (30m x 0.25mm) with film thickness 0.25 μ m. The operating conditions of GC-FID were as follow: temperature of splitter; 280°C, temperature of column; 35°C and temperature of detector; 280°C. The analysis time for each run was 32.75 minutes and carrier the carrier gas is Nitrogen.

CHAPTER 4 RESULT AND DISCUSSION

4.1 Bio-oil Production

Only small amount of pyrolysis oil were produced after the process. It occurred due to some problems during producing bio-oil from Fluidized Bed Reactor. Biomass was stuck in Hooper and cannot be feed into reactor. It happens because of the stirrer in the failed to stir biomass in the Hooper

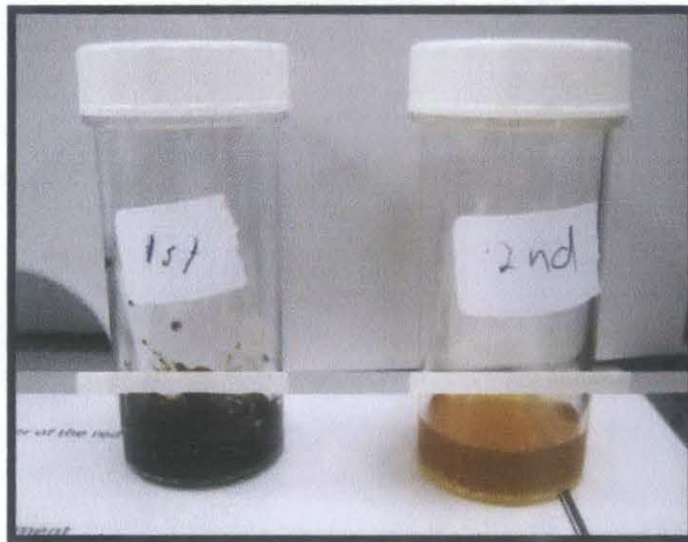


Figure 6 Bio-oil from Fluidized Bed Reactor

Another alternative was found. Bio-oil from PKS was produced using Microwave Pyrolyzer with assistant from Centre for Biofuel & Biochemical Research (CBBR) Department, UTP. The PKS size for this production is 1-2 μ m and the machine operates at heating power 2kWatt.

4.2 Bio-oil characterization

Table 7 Properties of bio-oil

Properties	Value
Ash Content	0.73%
Water Content	42 wt%
Calorific Value	-
CHNS value	C=13.24, H=1.836, N=0.61775, S=0.0265
pH value	2.503

The ash content for this bio-oil is very low which only 0.73%. The calorific value for this bio-oil cannot be measured by using Bomb Calorimeter due to low heating value and high oxygen content. This statement is supported by CHNS value that showed this bio-oil contains low value of carbon. When the value of Carbon is low, the calorific value also is very low. It also cannot be measured due to high water content which is 42 wt%.

By using pH meter, the pH value is measured. It shows that this bio-oil is acidic. It is because bio-oil contains acidic compounds such as acetic acid. This statement is proved by result from GC-FID as below:

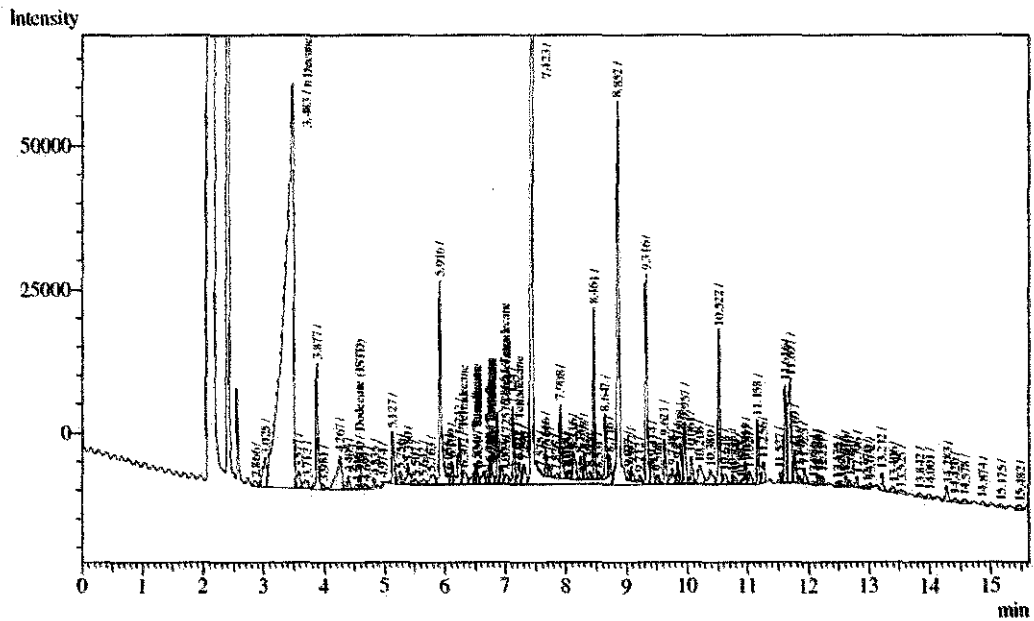


Figure 7 GC-FID results for PKS bio-oil

Based on the Figure 7, retention time at 3.483 is representing the peaks for acetic acid. The area percentage for this peak is 26% that proved that acetic acid is one of the main components of this bio-oil. This is the reason why the pH of this bio-oil is quite acidic.

Meanwhile the retention time at 7.423 is representing the peak for phenol. At this peak, the area percentage for this area is 316,205 that proved that the concentration of phenol is high in this bio-oil. This is the main force for this project to continue in order to extract phenol from bio-oil.

4.3 Phase separation

4.3.1 Screening process

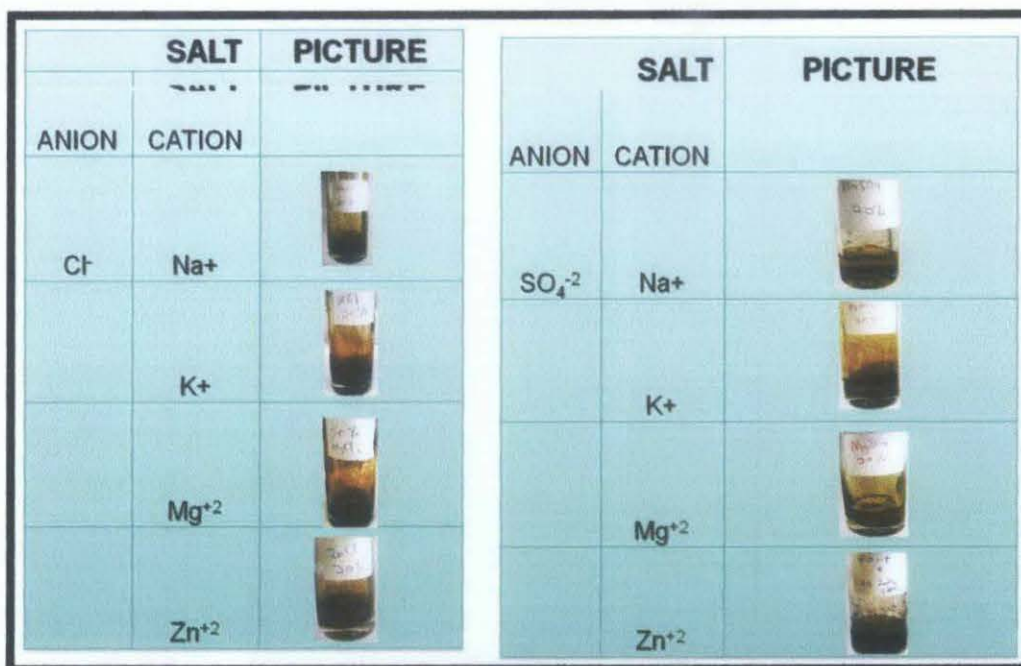


Figure 8 After addition of various types of salt

After bio-oil was mixed with salts concentration, it separated into two phases which is light phase and dark phase. Based on the physical observation, it is clearly showed anion sulfate give more distinct portioning toward the bio-oil. It is in line with the statement made by Robert (1996) that claims anion sulfate is more effective compared to chloride in term of salting out effect. For cations, it shows Zn and K are the least effective compared to Mg and Na.

4.3.2 GC-FID Analysis for two phases of bio-oil

Based on before observation, the analysis is continued by analyzing bio-oil that mixed with salts concentration of MgSO₄ and NaSO₄. This analysis is conducted by using FID-GC. The results are as follow:

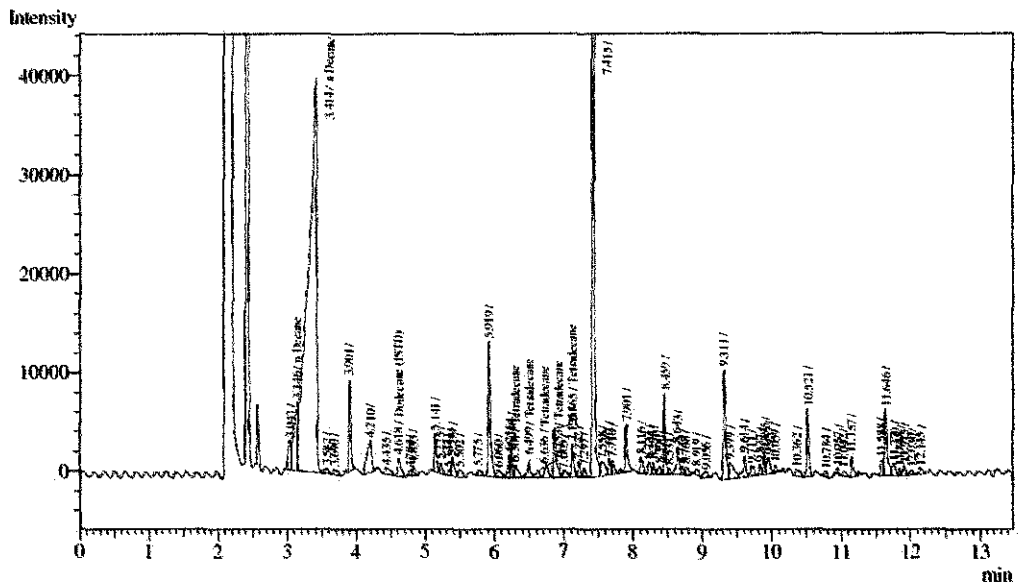


Figure 9 Light phases of bio-oil after adding 40% concentration of MgSO₄

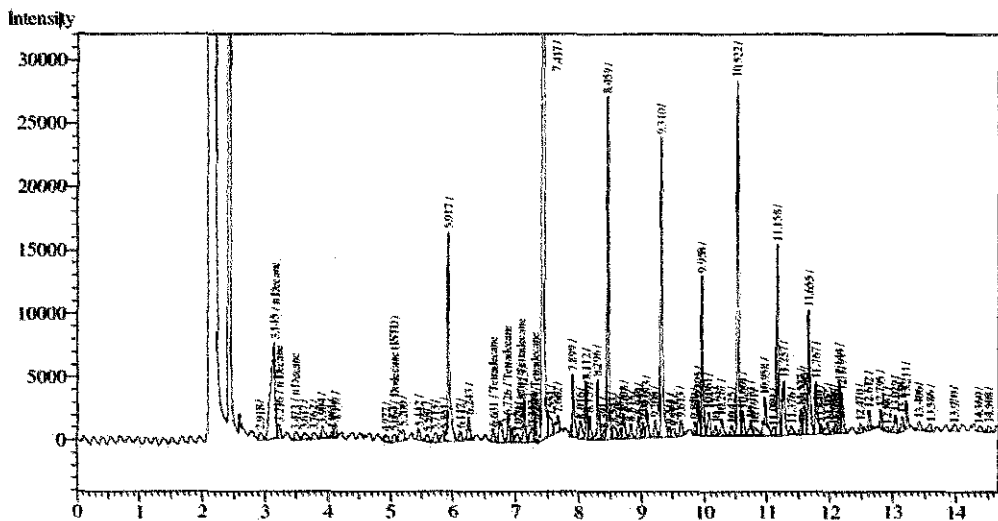


Figure 10 Dark phases of bio-oil after adding 40% concentration of MgSO₄

Comparing the result for light phases and dark phases of bio-oil after adding 40% salt concentration of MgSO₄, it shows that concentration of phenol is higher in dark phases compared to the light phases. In dark phases, the percentage for peak area of phenol is 38% which are higher than light phases which are only 21%. The peaks from

figure above also shows that acetic acid is higher in the light phases compare to the dark phases. It can be seen at retention time 3.414 for light phases and 3.145 for dark phases.

This happen because phenol is non-polar compound while acetic acid is polar compound. When salt is added into bio-oil, it will decrease the solubility of non-polar molecules in the bio-oil. It also will break the weak equilibrium of the bio-oil system. It will make the compounds in bio-oil separated into two phases according to their polarity.

4.3.3 FID-GC analysis to Dark layer of two different salts

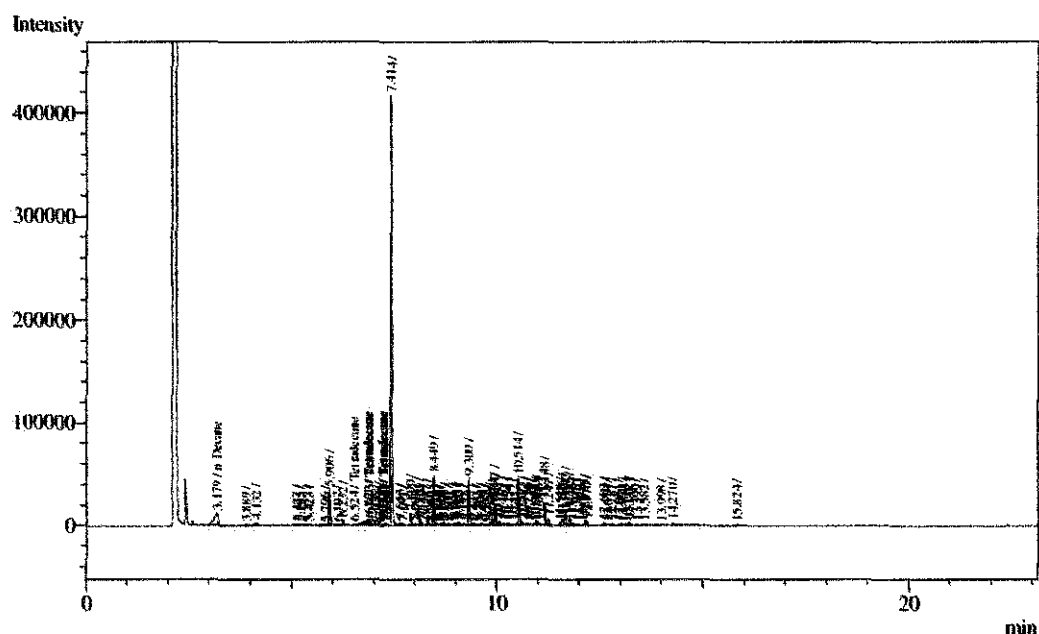


Figure 11 Dark phases of bio-oil after adding 40% concentration of Na₂SO₄

Comparing the dark phases of bio-oil after adding 40% concentration of Na₂SO₄ and MgSO₄, it shows that Na₂SO₄ gives higher value of phenol after phase separation. Based on the area percentage of phenol for both graph, the value of phenol after separation process using 40% of Na₂SO₄ is 45.73%. This value is greater than value from bio-oil that mixed with 40% of MgSO₄ which is only 38%.

The values for dark phases of bio-oil with 40% concentration of Na_2SO_4 also were compared with value of dark phases of bio oil with 100% concentration of MgSO_4 . Based on the result, the 100% concentration of MgSO_4 gives 45.72% area of phenol. Comparing to the 40% of Na_2SO_4 which is 45.73%, it can be say that Na_2SO_4 is greater than MgSO_4 in term of salting out effect in order to separate phenol from bio-oil although it have lower concentration of salt solution. It is in line with the statement made by Robert (1996) that claim Na^+ more effective compared to Mg^{2+} in term of salting out effect

4.3.4 Effect of Salts Concentration

This study also focuses on effect of salts concentration to the phase separation of bio-oil. Six samples of bio-oil that mixed with different concentration of MgSO_4 which is 20%, 30%, 40%, 60%, 80% and 100%.



Figure 12 Bio-oil with different MgSO_4 salt in increasing concentration

Based on the figure above, it clearly shows that the higher concentration give more distinct separation toward the bio-oil. This figure indicates as the concentration is increased, the bio-oil separation can be easily distinguished. In other words, the upper layer and bottom layer can be easily recognized and separated. This statement is supported by Qin-Hua et al. (2009) that mention, bio-oil is well separated as the concentration of the salt added increases.

Because of that, two samples of dark phases of bio-oil that mixed with $MgSO_4$ were analyzed using FID-GC to know the concentration of phenol in each dark phase. The results are as follow:

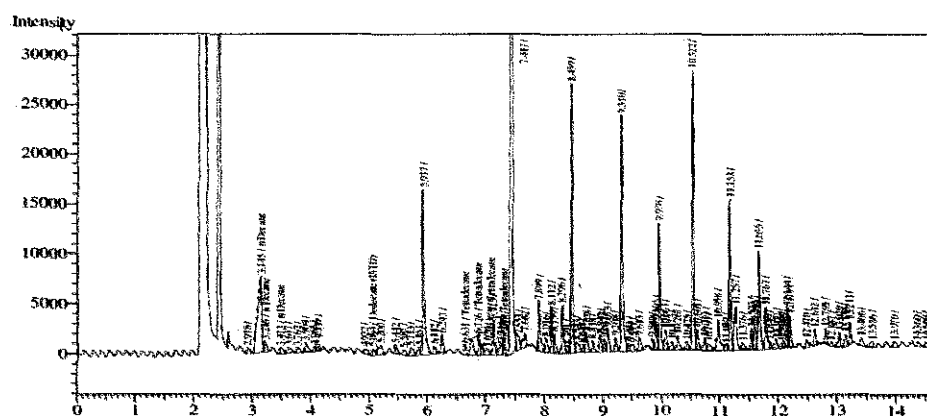


Figure 13 GC-FID results for dark phases of bio-oil after adding 40% concentration of $MgSO_4$

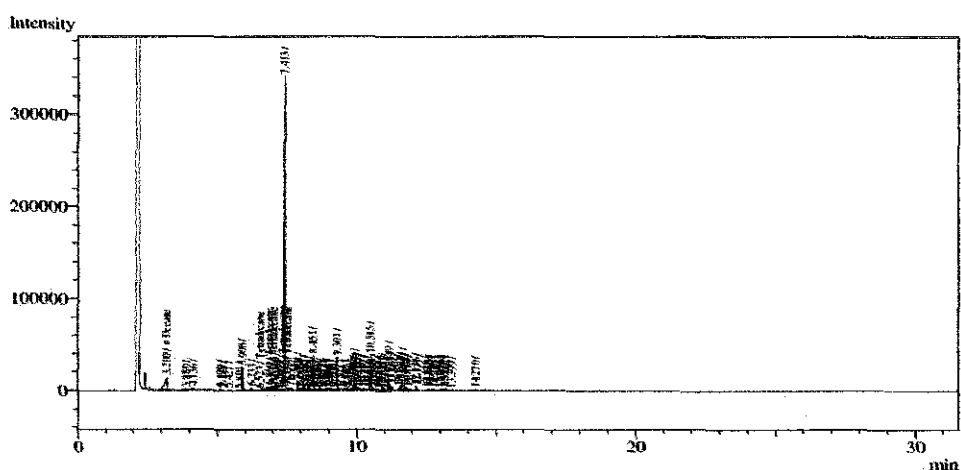


Figure 14 GC-FID results for dark phases of bio-oil after adding 100% concentration of $MgSO_4$

Table 8 Area percentage for different concentration of salt

Concentration of Salt	Area percentage
40% of $MgSO_4$	38%
100% of $MgSO_4$	45.72%

Based on the table above, as the concentration increases, the amount of phenol in the dark phase also increases. This is due to increasing of concentration of salt that can give more salting out effect to bio-oil in order to separate non-polar and polar compound. As the result, more non-polar compound will go to the dark side if concentration of salt increases. It means that more value of phenol compound can be recovered from bio-oil.

CHAPTER 5 CONCLUSION

The major conclusion of this study is that extraction of phenol from palm wastes bio-oil can be started by addition of salt solution. The addition of salt solution into bio-oil with ratio 2:1 can quickly result in phase separation which is into dark phase and light phase. Dark phases contain non-polar compounds that majority is from phenol compounds. While light phase contain polar compound which is compound that soluble in water. This statement already proved in the Result and Discussion section when acetic acid compound is found more in the light phases.

It also can be concluded that anion sulfate is more effective compared to chloride in term of salting out effect. For cations, Na^+ is greater than Mg^{2+} in terms of salting out effect by comparing the concentration of phenol in dark phases. Last, as the concentration of salt increases, the amount of phenol that separated from bio-oil also increases.

As conclusion, phenol can be recovered from bio-oil by adding concentration of Na_2SO_4 into bio-oil. To increase the value of phenol recovered from bio-oil, the concentration of salts should be increases.

Further research is suggested to investigate the best way to recover phenol from dark phases. The optimal condition for better separation should be investigated after this to get high yield of phenol from bio-oil. For example, investigate the effect of Ph or temperature to phase separation process.

CHAPTER 6 REFERENCE

- Abdullah, N., Gerhauser, H. and Bridwater, A.V. (2007). Bio-oil from Fast Pyrolysis of Oil Palm Empty Fruit Bunches. *J Phys Sci* 18(1), 57-54
- Abedi, J. Yeboah, Y.D., Realf, M., McGee, D., Howard, J. and Bota, K.B. (2001). An Integrated Approach to Hydrogen Production from Agricultural Residues for Use in Urban Transportation. Proceeding of the 2001 DOE Hydrogen Review. NREL/CP-570-30535
- Amen-Chen, C., Pakdel, H., Roy, C. (1997) *Biomass and Bioenergy*, 25-37.
- Azizan, M. T., Yusup, S., Mohd Laziz, F.D., Ahmad, M.M. (2009). Synthesis of Bio-Oil from Oil Palm's Empty Fruit Branch via Pyrolysis. 3rd WSEAS International Conference on Renewable Energy Sources, 24-26 February 2009, University of Cambridge, UK.
- Bridgewater, A.V., Peacocke G.V.C. (2000). Fast Pyrolysis Processes for Biomass. *Renew, Sustain, Energy Rev.*, 4, 1-73.
- Changyan, Y.; Zhang, B.; Moen, J.; Kevin, H.; (2010). Fractionation and Characterization of Bio-oil from Microwave-assisted Pyrolysis of Corn Stover. *Int J Agric & Biol Eng*, 2010; 3(3): 54–61.
- Chum, H.; Deibold, J.; Scanhill, J.; Johnson, D.; Black, S.; Schroeder, H.; R. E. (1989). Biomass pyrolysis oil feedstock for phenolic adhesive. In *Adhesive from*

Renewable Resources; Hemingway, R. W., Corner, A. H., Branham, S. J., Eds.; ACS Symposium Series No. 385; American Chemical Society; Washington, DC, 1989; pp 135-151.

Czernik, S.R., Bridgewater, A.V. (2004). Overview of Applications of Biomass Fast Pyrolysis oil. *Energy Fuels*, 18(2), 590-8.

Das, P., Sreelatha, T. and Ganesh, A. (2004). *Biomass Bioenergy* 27, 265-275

Joh, M.S., Mariyamni, A., Lim, X.Y., Farid, N.A. (2006). Production of Pyrolytic Oil for Enhanced Oil Recovery. 1st International Conference on Natural Resources Engineering & Technology 2006 24-25th July 2006; Putrajaya, Malaysia, 576-583.

Iuber, G.W., Iborra, S., and Corma, (2004). A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalyst, and Engineering. *Chemical Reviews*, 200, 106, 4044.

Islam, M.N., Zailani R. and Ani, F.N. (1999). Pyrolytic Oil from Fluidized bed Pyrolysis of Oil Palm Shell and its Characterization. *Renewable Energy*, 27 March.

Lawson, MD., Farid, N. (2000). Oil Palm Shell as a Source of Phenol. *Journal of Oil Palm Research* Vol. 12 No. I, June 2000, p. 86-94.

Wong, Y., Lee, K.T., Mohamed, A.R., Bhatia, S. (2007). Potential of Hydrogen from Oil Palm Biomass as a Source of Renewable Energy Worldwide. *Energy Policy*, 35, 5692-5701.

Mahfud, F.H. (2007), Exploratory Studies on Fast Pyrolysis Oil Upgrading, Doctoral Thesis, University of Gronigen.

Malaysia Palm Oil Board, 2009

Mohan, D., Pittman, Jr., C.U. Steele, P.H. (2006). Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels*, 20, 848-889.

Mourant, D.; Yang, D.-Q.; Lu, X.; Roy, C. (2005). *Wood Fiber Sci.* 2005, 37 (3), 542-548.

Murwanashyaka, J. N., Pakdel, H., Roy, C. (2001) Separation and Purification Technology, 24, 155-165.

Oasama, A. and Meier, D. (2005). *Anal. Appl. Pyrolysis* 73(2), 323-334

Oasama, A. and Peacocke, C. (2001) A Guide to Physical Property Characterization Biomass Derived Fast Pyrolysis Liquids. Technical Research Centre of Finland, Espoo, Finland 2001, VVT, Publication no. 450.

Oasama, A.; Kuoppala, E.; Gust, S.; Solantausa, Y. 2003 *Energy Fuels*, 17 (1), 1-12. 17(2), 433-443. 17(4), 1075-1084.

Rui, L.; Guo-Ping, S.; Yan-Yun, H.; Zheng, P.; Jiang, H.; Tang, Y.; Han-Qing, Y. 2011. Fractional Characterization of a Bio-oil Derived from Rice Husk. *Department of Chemistry, Biomass & Bioenergy*, , (671-678)

Qin, H. S., Jun, Q. N., Ming, G. R. and Qing, X. G. 2009. Effective phase separation of biomass pyrolysis oils by adding aqueous solution. *Energy and Fuels*,; 23:3307-3312.

Shirer, R. L.; CURTIN, D. Y. 1964. *The Synthetic Identification of Organic Compounds: A Laboratory Manual*, 4th Edition; Wiley, New York.

Vijaya, T.-R. 2001. *From Biomass to Fuels: Hydrotreating of Oxygen-Containing Feeds on a CoMo/AL₂O₃ Hydrodesulfurization Catalyst* Doctoral Thesis, Helsinki University of Technology, Finland.

Zhang H. G. 1990. In Department of Chemical Engineering; Universite Laval: Quebec, Canada.

SRI Consulting (SRIC), <http://www.sriconsulting.com/WP/Public/Reports/phenol/>

Biocoup, Separation of chemicals from pyrolysis oil, *Chemical and materials from biomass* 1-5 Nov 2010 Eindhoven University of Technology

<http://www.sriconsulting.com/CEH/Public/Reports/686.5000/> (as read on 25/9/2011)

Robert I. Baldwin, 1996, How Hofmeister Ion Interactions Affect Protein Stability, *Biophysical Journal*, October 1996, 2056-2063.

Seda Can and Taner Tanrisver (2007). The New Investigation With the salting-out effect on emulsifier-Free Emulsion Polymerization of Methyl Methacrylate, *Journal of Applied Polymer Science*, Vol. 103, 2494-2500 (2007)

Zhe, T., Qiang, L., Yin, Z., Xifeng, Z. and Qingxiang, G. (2009) One step bio oil upgrading through hydrotreatment esterification and cracking. *Ind Eng. Chem. Res.* 48: 6923-6929

CHAPTER 7 APPENDIX

7.1 Phenol Properties

Molecular formula	C ₆ H ₆ O
Molar mass	94.11 g mol ⁻¹
Appearance	Transparent crystalline solid
Density	1.07 g/cm ³
Melting point	40.5 °C, 314 K, 105 °F
Boiling point	181.7 °C, 455 K, 359 °F
Solubility in water	8.3 g/100 ml (20 °C)
Acidity (P _{K_a})	9.95 (in water)
Dipole moment	1.7 D

Table 6: Phenol properties

7.2 Fluidized Bed Reactor Calibration

Before producing pyrolysis oil, a calibration process was done to fluidized bed reactor machine to investigate the suitable flow rate of biomass to reactor.

7.2.1 Trial 1

Table 9 Feeder Speed: 0.7-0.8 rpm

Time (min)	Mass Out(kg)	Flowrate (kg/hr)
5	0.03	0.36
10	0.03	0.36
15	0.025	0.3
20	0.033	0.39
25	0.03	0.3

7.2.2 Trial 2

Table 10 Feeder Speed: 3.4 – 4.1 rpm

Time (min)	Mass Out(kg)	Flowrate (kg/hr)
5	0.105	1.26
10	0.125	1.5
15	0.125	1.56
20	0.13	1.5
25	0.125	1.5

7.2.3 Trial 3

Table 11 Feeder Speed: 6.1 – 6.7 rpm

Time (min)	Mass Out(kg)	Flowrate (kg/hr)
5	0.175	2.1
10	0.215	2.58
15	0.215	2.58
20	0.205	2.46
25	0.215	2.58

The desired flowrate for this process is set to be 1.5kg/hr. Based on the table above, it can be conclude that to achieve this flowrate, and the feeder speed must be set to 3.4 rpm to 4.1 rpm.

7.3 Gantt Charts of Research Activities

Activities	FINAL YEAR PROJECT 1													
	WEEK NUMBER													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Topic selection	█													
Research about topic		█	█	█	█	█								
Complete literature review				█	█	█	█	█	█	█	█	█		
Proposal Defence														
Identification of Extractant														
Development of Methodology														
Activities	FINAL YEAR PROJECT 2													
	WEEK NUMBER													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Characterization of Pyrolysis Oil	█	█												
Extraction of Phenol from Bio-Oil			█	█										
Characterization of Phenol				█	█	█	█							
Optimization of Extraction Method							█							
Data Analysis & Report								█	█					

Figure 15 Gantt Chart

7.4 Key Milestone

Activities	WEEK NUMBER									
	6	7	8	9	10	11	12	13	14	
Submission of Extended Proposal	#	#								
Submission of Interim Draft Report								#		
Submission Interim Report									#	
FINAL YEAR PROJECT 2										
WEEK NUMBER										
Submission of Progress Report			#							
Pre-EDX						#				
Submission of Draft Report							#			
Submission Of Dissertation & Technical Paper								#		
Oral Presentation									#	
Submission of Project Dissertation (Hard Bound)										#

Figure 16 Key Milestone